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I am submitting herewith a dissertation written by Gonzalo Córdoba Jr., entitled "The High Temperature Specific Heat Capacity of Gold, Lead and Zinc: Measurements and Analysis of Contributions." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Metallurgical Engineering.

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THE HIGH TEMPERATURE SPECIFIC HEAT CAPACITY OF GOLD, LEAD
AND ZINC: MEASUREMENTS AND ANALYSIS OF CONTRIBUTIONS

A Dissertation
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ABSTRACT

This dissertation deals with an analysis of contributions to the high temperature specific heat capacity of solid gold, lead, and zinc. The specific heat capacities have been measured with high accuracy from 300°K to 1200°K for gold, and into the liquid region for lead and zinc. These data then have been used as a basis for estimating the contribution of anharmonic lattice vibrations to the specific heat capacity.

The specific heat capacity at constant pressure C_p was converted to the constant volume condition by applying the dilation correction. Then the specific heat capacity at constant volume C_v was assumed to be formed by four independent contributions: $(C_{1v})_v$ and $(C_{2v})_v$, related to the formation of equilibrium monovacancies and divacancies, respectively, in lattice; $(C_L)_v$, related to the harmonic vibrations of the atoms in the lattice; $(C_E)_v$, related to changes in the energy distribution of the conduction electrons; and $(C_A)_v$, related to the anharmonic vibrations of the lattice. An analysis and summary of the expressions given in the literature for each of these independent contributions is presented.

The results of the rather extensive and careful measurements of the specific heat capacity of high purity (greater than 99.9 weight per cent pure) gold, lead and zinc are presented and compared to other data from the literature. The

measurements made in this research have a reproducibility of ± 1.0 per cent, and the absolute error is believed to lie within this range. The C_p results for gold are around four per cent higher than those obtained in other investigations. For solid lead and zinc, the C_p results are within ± 1.0 per cent of those of other investigations. The data of the present investigation has been treated statistically in order to represent C_p for each metal by a polynomial.

C_v was obtained by applying the dilation correction to the experimental C_p from this investigation. The dilation correction requires the coefficient of thermal expansion, the molar volume, and the isothermal compressibility, all as a function of temperature. A critical analysis was made of values of these quantities from the literature, and the data available were treated statistically and fitted by polynomials. Where sufficient data do not exist, extrapolations of existing data were used. From the uncertainties in the quantities in the dilation correction and in the experimental C_p , an estimate of the uncertainty in the C_v was obtained.

$(C_L)_v$ was calculated by using the Debye model of a harmonic lattice characterized by a single Debye temperature, obtained from the literature. $(C_E)_v$ was calculated from the Sommerfeld theory, assuming the contribution to be proportional to the absolute temperature; the proportionality constant was taken as the conventional electronic specific heat capacity coefficient, obtained from the literature. The contribution from the formation of equilibrium monovacancies

and divacancies was calculated from the temperature derivative of the energy of formation of each defect. Values of the molar energy and entropy of formation of each type of defect, which are required for the calculations, were obtained from the literature. The variation in the values of the quantities needed to calculate each of the contributions $(C_L)_v$, $(C_E)_v$ and $[(C_{1v}) + (C_{2v})]$, as obtained from the literature, was used to estimate the uncertainty in each contribution.

The excess specific heat capacity $(\Delta C_v)_A$ was obtained by subtracting the sum of $(C_L)_v$, $(C_E)_v$, and $(C_{1v}) + (C_{2v})$ from the experimental C_v . This excess specific heat capacity was assumed to be due to anharmonic vibrations of the lattice. The uncertainties in the various terms to calculate $(\Delta C_v)_A$ were used to establish the uncertainty in the calculated $(\Delta C_v)_A$. For gold and zinc, the anharmonic specific heat capacity is positive and amounts to about four and eight per cent of C_v near the melting point, both within the uncertainty of $(\Delta C_v)_A$; for both gold and zinc, this contribution could be zero or slightly negative. For lead, the anharmonic contribution is negative and is about 5.5 per cent of C_v near the melting point; even within the uncertainty in $(\Delta C_v)_A$, the contribution is quite negative.

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CHAPTER I

INTRODUCTION

Of prime importance in studying the crystalline (or solid) metallic state is the derivation of theoretical expressions for the temperature dependence of the internal energy of the crystal. The evaluation of the validity of a model which gives the energy, however, usually cannot depend on a direct measurement of the energy, but on the specific heat capacity, or temperature derivative of the energy, as this is an experimentally determinable quantity. Because of theoretical difficulties in developing a grand theory for the energy of a crystal, most developments have assumed independent contributions to the energy, each of which can be calculated separately and summed to give the total internal energy. An evaluation of the validity of these treatments, then, requires two things. One is accurate experimental heat capacities and the other is a careful evaluation of the significance of the difference between the experimental heat capacity and the calculated heat capacity based upon a given model. As will be shown in the following presentation, less attention has been given to calculations of the energy of crystals above 300°K than at much lower temperatures, and yet it will be shown that an analysis of theory and experimental data from 300°K to the melting point can yield valua-

ble information which will contribute to an understanding of the behavior of the metallic solid state.

This dissertation outlines research concerned with accurate measurements of the specific heat capacity of some pure metals, and an evaluation of simple models which can be used to calculate the specific heat capacity. Particular emphasis will be placed on an analysis of contributions to the high temperature specific heat capacity of pure metals as the melting temperature is approached. As the experimental techniques to be employed to determine the heat capacity have been well documented, they will be only briefly discussed; most of the attention will be given to a presentation of some of the theoretical expressions that have been advanced to calculate the specific heat capacity.

A. SPECIFIC HEAT CAPACITY

The increase in internal energy of a system is equal to the difference between the heat put into the system and the work done by the system on the surroundings. In terms of an infinitesimal amount of heat absorbed dQ and an infinitesimal amount of work done dW , the change in internal energy dE will be equal to

$$dE = dQ - dW^* \quad (1)$$

Unless otherwise stated, the work dW is usually a me-

* E alone is state dependent; Q and W depend on the path from one state to another.

chanical work of the type $PdV = dW$, where P is pressure and V is volume. Now the specific heat capacity refers to the amount of heat dQ absorbed by a system that undergoes a temperature increase dT , and is defined as

$$C \equiv \frac{dQ}{dT} \quad (2)$$

where T is the absolute temperature. Some publications refer to the specific heat capacity as the amount of heat or energy required to raise by one degree the temperature of one gram-atom of the substance, others refer to the specific heat capacity as the amount of heat required to raise by one degree the temperature of one gram of the substance. Sometimes the specific heat capacity is called specific heat, in other cases it is called heat capacity. In the present research the expression specific heat capacity is used whenever reference is made to the amount of heat required to raise by one degree the temperature of one gram-atom of the substance.

For a constant volume process, where

$$\left(\frac{\partial V}{\partial T} \right)_v = 0, \quad \left(\frac{\partial E}{\partial T} \right)_v = \left(\frac{dQ}{dT} \right)_v \equiv C_v \quad (3)$$

where C_v is the specific heat capacity at constant volume.

The enthalpy is defined as,

$$H \equiv E + PV \quad (4)$$

which leads to

$$dH = dE + PdV + VdP$$

or by using Equation (1)

$$dH = dQ + VdP \quad (5)$$

At constant pressure

$$\left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{dQ}{dT} \right)_p \equiv C_p \quad (6)$$

Where C_p is the specific heat capacity at constant pressure.

C_p and C_v are connected by the relation

$$C_p = C_v + \frac{T \alpha_v^2 V}{\beta_v} \quad (7)$$

where V = molar volume,

$$\alpha_v = \text{volume thermal expansivity} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p,$$

$$\text{and } \beta_v = \text{isothermal compressibility} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T.$$

The terms α_v , V and β_v are temperature dependent.

Consider for a moment how C_p might be measured. If an electrical heater is placed inside a sample of mass m , and the sample is located in an adiabatic, constant pressure chamber, then C_p can be determined by measuring the direct current power required to raise the temperature an increment ΔT during a time interval Δt . The average power $\bar{V}_t \bar{I}$ can be obtained by measuring the current I through the heater and the voltage drop V_t across the heater at the start of the temperature increment and at the end. Thus the average C_p , $\bar{C}_p$, assigned to a temperature inside the increment, is given by

$$\bar{C}_p = \frac{\bar{V}_t \bar{I} (\Delta t)}{m (\Delta T)} \quad (8)$$

The actual heat capacity can be approximated as closely as desired by making the temperature increment sufficiently small. It will be convenient in the following discussions to think of the magnitude of the specific heat as determined by the processes in the specimen that absorb the electrical energy as the temperature is increased.

B. SPECIFIC HEAT CAPACITY OF CRYSTALS

At any temperature above absolute zero, a crystal is a complicated structure consisting of vibrating interacting atom masses. For simple metals, the crystal can be looked upon as consisting of interacting point masses, and, independently, an electron cloud associated with the outer or valence electrons. On this basis, the question then is what analytical expression can be developed for the heat capacity to adequately explain the diverse temperature dependences of the heat capacity observed experimentally for different metals. Since the heat capacity is determined by the energy absorbing mechanisms, the question can be stated in terms of what are the mechanisms of energy absorption in the crystal.

There are two accepted principal mechanisms for the absorption of heat by a solid: one through increased kinetic energy of electrons and the other through increased atomic vibration. According to quantum mechanics the electronic heat capacity is directly proportional to the density of the electrons at the Fermi Level. Developed theoretical studies

have shown that the electronic contributions are proportional to the temperature as will be shown below in Section (B-b). A theoretical analysis (Section B-a-3) has shown that at very low temperatures the heat capacity contribution due to lattice vibration is proportional to T^3 and that at very high temperatures it approaches a value $3R^*$; between these extremes the dependency is more complicated.

Experimental studies have determined the following:

(a) there exists a shift of the heat capacity toward zero when the temperature approaches absolute zero (no vibration or electronic contribution); (b) from absolute zero up to intermediate temperatures, the heat capacity is proportional to T^3 ; and (c) at high temperature, the heat capacity approaches approximately a constant $3R$.

Theoretical expression for electronic and lattice contributions satisfy part (a) above of the experimental results since at sufficiently low temperatures the electronic contribution, due to its linear dependence on T , must dominate over the lattice heat capacity, which is proportionally to T^3 . Part (b) above is explained since with increasing temperature, the lattice contributions which are proportional to T^3 dominate over the electronic contributions which are only proportional to T . Part (c) is explained since as mentioned above the lattice contributions approach the constant $3R$.

* R is the gas constant.

a. Harmonic Lattice Specific Heat Capacity.

Since the above three experimental facts could not be explained by classical mechanics, Einstein postulated that a simple crystal could be regarded as an aggregate of atomic oscillators, each of which vibrates with the same natural frequency. He also assumed that the allowed energy states of these oscillators are integer multiples of $h\nu$, where ν is the frequency of oscillation and h is Planck's constant. The Einstein model, by using only one frequency of vibration for all atoms, represents a drastic simplification of the complicated vibrations of the atoms, which in fact are not independent of each other and so do not have the same restoring forces. Indeed the Einstein model predicts a specific heat capacity which is significantly lower than the experimental values below approximately 300°K.

A few years later, Debye showed that most of the quantitative discrepancy between Einstein's results and observations could be removed by the introduction of a more accurate analysis of the modes of vibration of a simple solid. Debye pointed out that the possible oscillation frequencies of a solid body range from very low values, corresponding to sound waves, to very high values, corresponding to infrared absorption peaks of solids. He suggested that a more accurate distribution might be found by treating the crystal as though it were a continuous elastic medium which has elastic constants that are independent of frequency. It was also

assumed that the medium was isotropic, and the distribution function of the frequencies of vibration of the atoms were proportional to the square of the frequency. The vibrational frequencies of a continuous medium range from zero to infinity, whereas, in an actual crystal, wave lengths shorter than interatomic distances are not independent of larger ones. The interdependence is shown by a simple example in Figure 1.

The transverse displacements of the atoms in this figure may be described equally well by the function a or b, or by any one of an infinite number of shorter waves that have the same amplitudes as a or b at the atomic positions. The same conclusions may be drawn from the fact that a system which contains N atoms has only 3N degrees of freedom, whereas a strictly continuous medium has an infinite number of degrees of freedom. Therefore it is necessary to introduce a condition that limits the number of modes used in determining the heat capacity. Because of this, all frequencies higher than the value ν_m , defined by the integral

$$\int_0^{\nu_m} f(\nu) d\nu = 3N, \quad (9)$$

are neglected by the Debye treatment. The term $f(\nu)$ is a distribution function dependent on the frequency of oscillation and will be described in part (B-a-3).

It should be emphasized that in the real crystal the 3N modes of frequency vibration are so close together that it is possible to define a continuous function $f(\nu)$ such that

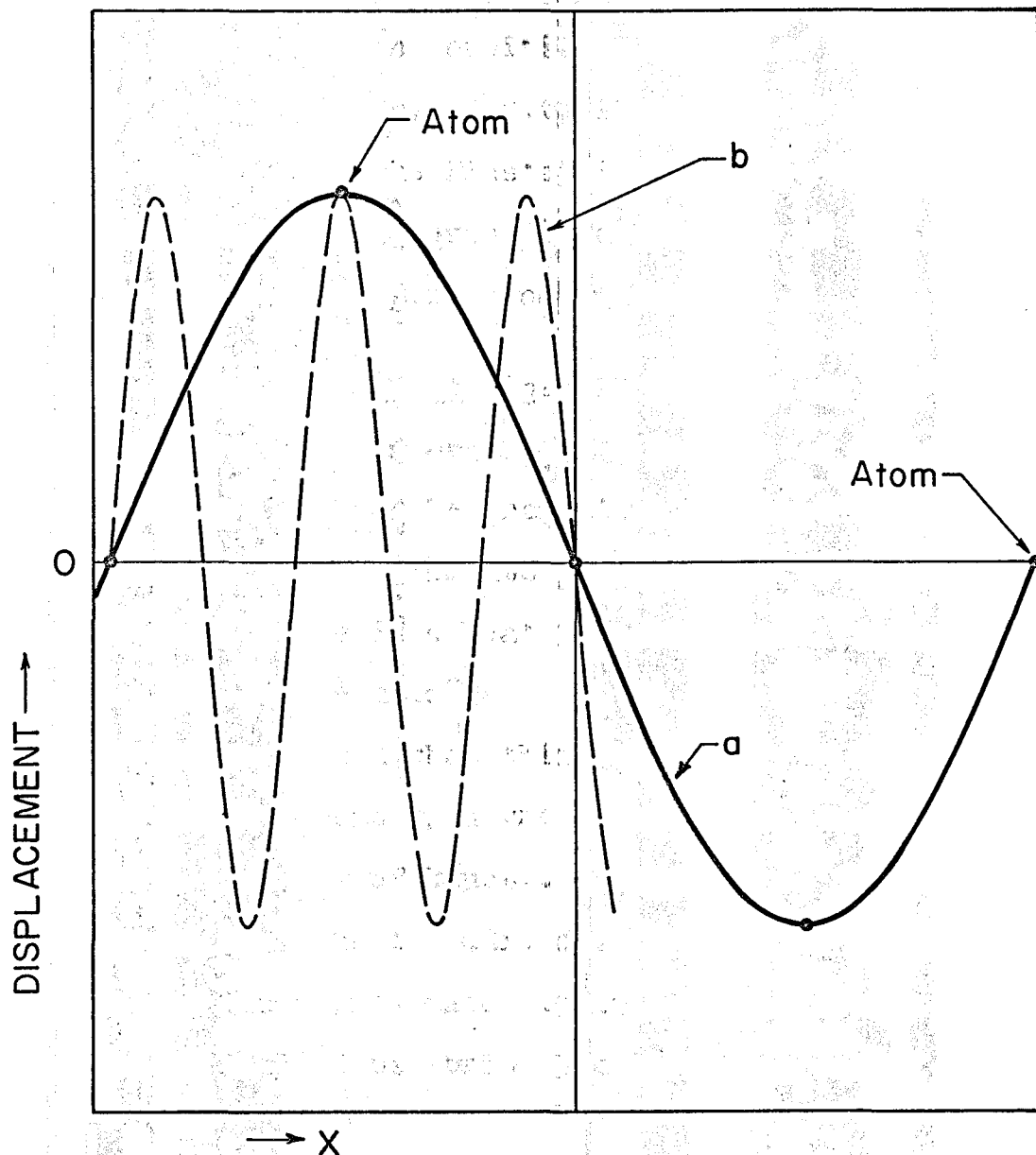


Figure 1. An example of the way in which a given periodic displacement of a lattice may be described by different harmonic functions a and b . The wave number σ_a and σ_b of the two functions bear the relation $\sigma_b = \sigma_a + n/l$, where l is the lattice distance, and $\sigma_a = 1/\lambda_a$, $\sigma_b = 1/\lambda_b$, λ_a and λ_b are the wavelength of the function a and b and n is an integer 1, 2, 3, 4, ... n .

$f(\nu)d\nu$ is the number of possible modes with frequencies between ν and $\nu + d\nu$. In the true crystal $f(\nu)$ is generally very complicated and exhibits a number of peaks. A comparison of the spectral density function $f(\nu)$ for NaCl as determined by using the Einstein's and Debye's models and the calculated real frequency distribution of the atoms is shown in Figure 2 as presented in Cusack¹.

1. Dulong and Petit Law. In 1819 Dulong and Petit found that at room temperature the product of the specific heat capacity (cal. deg⁻¹ gram⁻¹) at constant volume and the atomic weight of the elements (grams/mole) is approximately a constant C_v^* (specific heat capacity) equal to approximately 6.4 cal. deg⁻¹ mole⁻¹.

Boltzmann showed that this 6.4 value for C_v for an atomic solid is in accord with the expectations that the atoms would have $(3/2)RT$ of kinetic energy, as do the molecules of an ideal gas, and in addition, $(3/2)RT$ of potential energy, since the approximate simple harmonic motion of the atoms about their equilibrium has three degrees of freedom. So

$$C_v = \frac{d(\text{Energy})}{dT} = \frac{d}{dT} \left[\frac{3RT}{2} \text{ kinetic} + \frac{3RT}{2} \text{ potential} \right] = 3R \quad (10)$$

* $C_p = C_v + VT \frac{a_v^2}{\beta_v}$ as seen before, and at low temperatures $VT a_v/\beta_v$ becomes negligible so $C_p \cong C_v$.

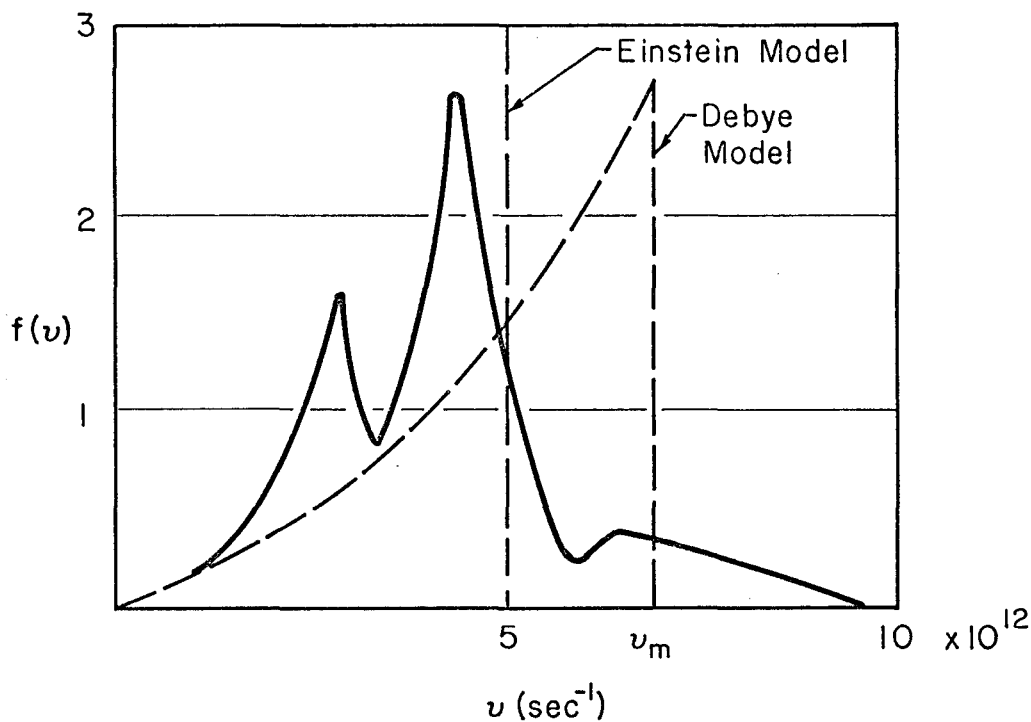


Figure 2. The spectral density function of lattice vibrations in NaCl.

Source: Cusack, N., The Electronic and Magnetic properties of Solids. Great Britain; Longmans, 1958.

Later measurements indicated that $3R$ was merely an approximate high temperature limiting value, approached by different elements at different temperatures. However, the heat capacity of all simple solids decreases with decreasing absolute temperature.

2. The Einstein Model. Consider a crystal of n molecules where each molecule has N_m atoms. In order to represent the instantaneous locations in space of N_m mass points for a given molecule, $3N_m$ coordinates are required which determine the number of degrees of freedom for that molecule. Thus the molecule has $3N_m$ degrees of freedom. The atoms comprising each molecule move through space as a connected entity; as do all the n molecules forming the crystal; therefore we can represent the translation of the crystal as a whole by the motion of the center of mass of its constituent atoms. Three coordinates are required to represent the instantaneous position of the center of mass and three to determine the rotation of the crystal as a whole around the three different axis so $3N_m \times n - 6^*$ coordinates represent the vibrational degrees of freedom. Since $3N \gg 6$ we can assume there are $3N$ degrees of vibrational freedom.

In 1906 Einstein proposed a model where the same frequency was assigned to all the oscillators each of which was a harmonic oscillator. One of the early successes of the

* $N_m \times n$ is equal to the total number N of atoms in the crystal.

quantum theory consisted in finding the reason for the decrease in heat capacity C_v with decreasing temperature. This decrease in C_v for crystals is quite unexplainable in classical theory (Dulong and Petit) where a constant value $3R$ was predicted for all temperatures. The explanation is due to the fact that the oscillators can only take up finite increments of energy. When a system of oscillators is at low temperature, most of them are in their lowest energy level, and a small rise of temperature is insufficient to excite them to the next higher level. Therefore C_v , which measures the intake of energy per unit increase of temperature, is smaller than at higher temperature.

The energy level of the i^{th} oscillators is given by

$$\epsilon_i = (v_i + 1/2) h\nu^* \quad (11a)$$

where ν = Frequency of oscillation, and

$$v_i = 0, 1, 2, 3, 4, \dots$$

According to statistical and quantum mechanics the summation over all the quantum states of the crystal gives the total vibrational energy of the system E_t . In this case, the energy of the j^{th} state is

$$E_j = E_0 + \sum_{3N} \epsilon_i \quad (11b)$$

where ϵ_i is the energy of the oscillators (atoms) analyzed over the $3N$ normal modes of vibration, and E_0 is equal to the

* $(1/2)h\nu$ corresponds to the zero point energy.

potential energy of the crystal when none of the oscillators are excited, and is computed relative to the same atoms at infinite separation.

The crystal can have Ω_0 different complexions due to different possibilities of orientations of the molecules in the lattice, which are quite distinct from the oscillators—the latter are not degenerate. Since in the case of metals each lattice point is occupied by only one atom, Ω_0 becomes equal to one.

From (11a) and (11b)

$$E = E_0 + \frac{1}{2} h \sum_{3N} \nu_i + h \sum_{3N} \frac{\nu_i}{(e^{h\nu_i/kT} - 1)} \quad (12)$$

Where E = internal energy of the crystal,

k = Boltzmann's constant,

h = Planck's constant,

ν_i = frequency of vibration of the i^{th} oscillator.

Using the Einstein assumption that ν is the same for all oscillators, Equation (12) becomes

$$E = E_0 + 3N \frac{1}{2} h\nu + 3Nh\nu \times \frac{1}{(e^{h\nu/kT} - 1)} \quad (13)$$

The second term in Equation (13) represents the zero point energy of all the oscillators (at absolute zero); the last term is due to the increase in excitation resulting from an increase in temperature. From Equation (13)

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad (14)$$

Upon expanding $e^{h\nu/kT}$ in Equation (13) to give

$$1 + \frac{h\nu}{kT} + \frac{1}{2!} \left(\frac{h\nu}{kT} \right)^2 + \frac{1}{3!} \left(\frac{h\nu}{kT} \right)^3 + \dots \frac{1}{n!} \left(\frac{h\nu}{kT} \right)^n \quad (15)$$

and noticing that at high temperatures, where $h\nu/kT \ll 1$, the third term in the expansion may be neglected, then

$$E = E_0 + \frac{3Nh\nu}{2} + 3Nh\nu \left[\frac{1}{\left(1 + \frac{h\nu}{kT} + \frac{1}{2!} \left(\frac{h\nu}{kT} \right)^2 - 1\right)^2} \right]$$

or

$$E = E_0 + \frac{3Nh\nu}{2} + 3NkT - \frac{3Nh\nu}{2}$$

or

$$E = E_0 + 3NkT \quad (16)$$

Thus at constant volume and high temperature

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = 3Nk = 3R \quad (17)$$

Thus, at high temperatures, Einstein's formulas agree with the Dulong and Petit theory. It is also clear from formula (14) that the higher the fundamental vibration frequency ν , the larger is the quantum of vibrational energy, and the higher the temperature at which C_v attains the classical value of $3R$. The elements that then follow Dulong and Petit's rule at room temperatures are those with relatively low vibration frequencies.

The parameter ν in Equation (14) is usually adjusted so as to obtain the best possible fit of theoretical and observed heat capacity curves. Although the parts of specific heat capacity temperature curves for which C_v is greater

than $3R/2$ usually can be fitted closely with an Einstein specific heat capacity function, the low-temperature portions usually can not. It was pointed out above that as the temperature approaches absolute zero, the heat capacity usually varies linearly as T^3 whereas Equation (14) varies as

$$3R \left(\frac{h\nu}{kT} \right)^2 e^{-h\nu/kT^*}$$

Figure 3 shows the Einstein heat capacity curve calculated for the case of silver (Denbigh²). It also shows the Debye curve, the origin of which will be explained below, and the experimental results. All these heat capacity values are plotted versus T/θ_D . The frequency ν for the Einstein equations can be determined from one experimental point at low temperatures and then the entire specific heat capacity curve can be drawn for the substance. The agreement with the experimental data is reasonable except at the lowest temperatures. It is clear that the higher fundamental vibration frequency ν , the larger is the quantum of vibrational energy, and the higher the temperature at which C_v attains the classical value of $3R$.

3. The Debye Model. The assumptions of the Debye theory are that the solid is isotropic, and that it is a continuous elastic medium which has elastic constants that are independent of frequency. In the isotropic case the fre-

* $Nk = R =$ gas constant

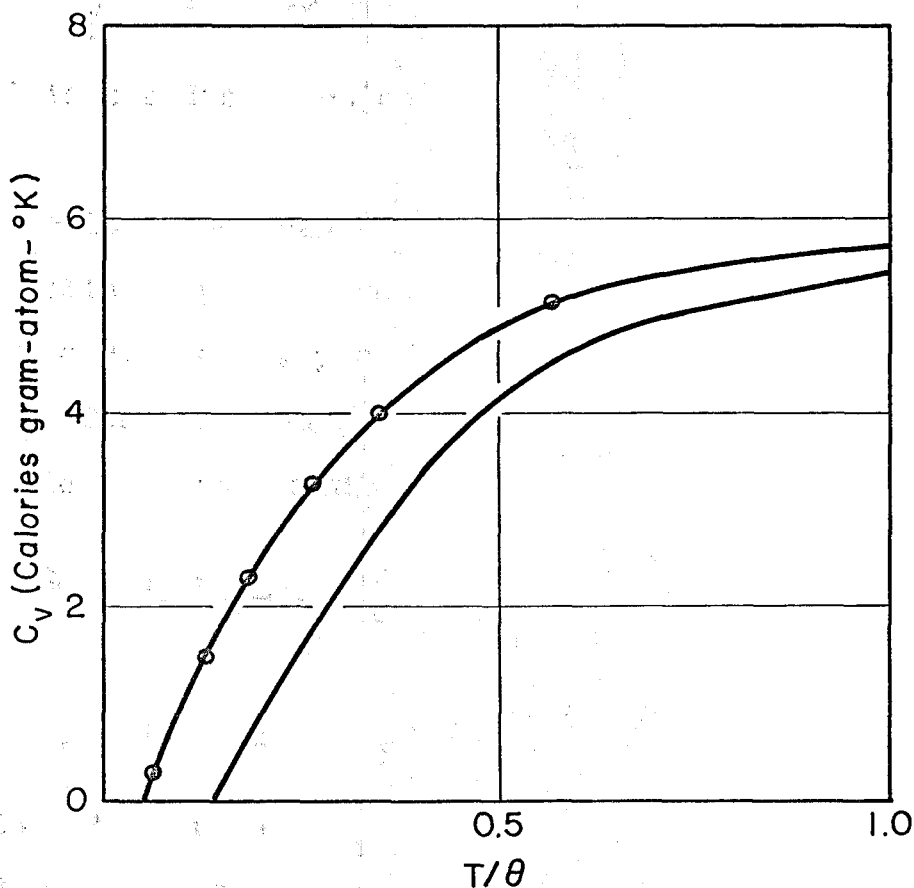


Figure 3. Upper curve, Debye approximation; lower curve, Einstein approximation. o, C_v for silver, by using experimental results and $\theta_D = 215^\circ\text{K}$. The experimental points have been worked out with the best value of θ to fit the Debye curve; corresponding points to show the best agreement which can be obtained with the Einstein curve have not been included.

Source: Denbigh, K., The Principles of Chemical Equilibrium. England: Cambridge University Press, 1961.

quency is independent of the direction of propagation, so that the distribution function may be expressed simply. The frequencies greater than a value ν_m were neglected, as mentioned above ν_m is defined by the equation

$$\int_0^{\nu_m} f(\nu) d\nu = 3N \quad (18)$$

where $f(\nu)$ is the distribution function for a continuous medium.

The function $f(\nu)$ can be determined by assuming a rectangular parallelepiped of isotropic medium,* bounded by the six planes $x = 0$, $x = L_x$, $y = 0$, $y = L_y$, $z = 0$, $z = L_z$ **. The equations for the propagation of longitudinal and transverse vibrations in this medium are

$$U_1 - u_1 = \Delta u_1 = \frac{1}{c_1^2} \frac{\partial^2 u_1}{\partial t^2} \quad (19)$$

$$U_t - u_t = \Delta u_t = \frac{1}{c_t^2} \frac{\partial^2 u_t}{\partial t^2} \quad (20)$$

respectively, where u_1 and u_t are the amplitudes of the vibrations at any time t , U_1 and U_t are the maximum amplitude of vibration and c_1 and c_t are their velocities in the longitudinal and transverse directions, respectively***.

*The choice of the geometric figure does not affect the results, as will be seen, since $f(\nu)$ will become a function of the volume of the chosen figure.

** L_x , L_y and L_z are the dimensions of the parallelepiped.

***The velocities may be related to the elastic constants for isotropic media.

Since the material is elastic and isotropic, the frequency distribution turns out to be insensitive to the choice of boundary conditions, so for simplicity it is assumed that the surface planes are rigidly held. In this case the boundary condition is that Δu_1 and Δu_t should be zero at these planes.

With this condition

$$\lambda_x = \frac{2L_x}{n_x}, \quad \lambda_y = \frac{2L_y}{n_y}, \quad \lambda_z = \frac{2L_z}{n_z} \quad (21)$$

where λ_x , λ_y , λ_z are the wave lengths of the modes of vibration whose amplitudes are obtained from Equations (19) and (20) and n_x , n_y and n_z are arbitrary integers (1, 2, 3, ...).

From Equation (21) and the equation $\lambda = c/\nu^*$

$$(22)$$

$$\nu_1^2 = \frac{c_1^2}{4} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad (23)$$

$$\nu_t^2 = \frac{c_t^2}{4} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad (24)$$

There are three independent modes of vibration associated with each set of intergers n_x , n_y , n_z , namely, two transverse waves of frequency ν_t and one longitudinal wave of frequency ν_1 . With all these conditions the amplitudes are

* $\lambda = (\lambda_x^2 + \lambda_y^2 + \lambda_z^2)^{1/2}$;
 λ_x , λ_y , and λ_z are measured along x, y and z axis, respectively.

$$u_1 = A_1 \sin \frac{\pi n_x X}{L_x} \sin \frac{\pi n_y Y}{L_y} \sin \frac{\pi n_z Z}{L_z} \sin \left(2 \pi \nu_1 t \right) \quad (25)$$

$$u_t = A_t \sin \frac{\pi n_x X}{L_x} \sin \frac{\pi n_y Y}{L_y} \sin \frac{\pi n_z Z}{L_z} \sin \left(2 \pi \nu_t t \right) \quad (26)$$

where A_1 and A_t are constants.

The number of waves per unit length (wave number components σ_x , σ_y , and σ_z) are

$$\sigma_x = \frac{n_x}{2L_x}, \quad \sigma_y = \frac{n_y}{2L_y}, \quad \sigma_z = \frac{n_z}{2L_z} \quad (27)$$

In terms of these quantities, Equations (23) and (24) become

$$\nu_1 = c_1 \sigma \quad (28a)$$

$$\nu_t = c_t \sigma \quad (28b)$$

where

$$\sigma = \sqrt{\sigma_x^2 + \sigma_y^2 + \sigma_z^2} \quad (29)$$

Equation (25) and (26) also can be written as a sum of exponential functions of the type

$$A e^{i2\pi (\vec{\sigma} \cdot \vec{r} - \nu t)} \quad (30)$$

where A is a constant, σ is a constant vector having components σ_x , σ_y , and σ_z , ν is the frequency of the wave, and $\vec{r}$ is the position vector.* For a fixed time t , Equation (30) is a constant at all points that satisfy the equation

* $\vec{\sigma}$ is a vector with cartesian coordinates of space x , y , and z .

$$\bar{\sigma} \cdot \bar{r} = \text{constant}^*$$

The case, $\sigma \cdot \bar{r} = \nu t = \text{constant}$, describes the motion of the wave front planes in the direction of σ with a velocity

$\nu/|\bar{\sigma}|$. The waves given by Equations (25) and (26) may now be obtained by adding together the sixteen functions that can be derived from Equation (30) by changing the signs of ν and of the three components of σ ***. The number of modes of vibrations having values of $\bar{\sigma}$ less than the value $\bar{\sigma}'$ will be computed in the following way:

(1) Represent the continuous variable σ_x , σ_y , and σ_z in a three dimensional coordinate system.

(2) All three points defined by Equation (27) are then distributed throughout the position's octant in the given reference system.

(3) The equation $\bar{\sigma} = \bar{\sigma}'$ defines a sphere in the same reference system, and the octant limited by this sphere will have a volume equal to $\left(1/6\right) \pi (\bar{\sigma}')^3$.

(4) The total number of points in the octant is

$$L_x L_y L_z \left(4/3\right) \pi (\sigma')^3^{***} \quad (32)$$

Equation (32) may be written

*That is, on planes orthogonal to the direction $\bar{\sigma}$. These planes are the wave fronts. The normal distance between planes that differ in phase by 2π clearly is $1/|\bar{\sigma}|$

$$^{***} \begin{pmatrix} +\nu \\ -\nu \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -\sigma_x & \sigma_x & -\sigma_x & \sigma_x & -\sigma_x & \sigma_x & \sigma_x & -\sigma_x \\ -\sigma_y & \sigma_y & \sigma_y & -\sigma_y & -\sigma_y & \sigma_y & -\sigma_y & \sigma_y \\ -\sigma_z & \sigma_z & -\sigma_z & -\sigma_z & \sigma_z & -\sigma_z & \sigma_z & \sigma_z \end{pmatrix}$$

***This value is obtained since the average volume oc-

$$V \left(\frac{4}{3} \right) \pi (\sigma')^3 \quad (33)$$

where V is the volume of the crystal.

Since there are three modes of vibration associated with each point in Equation (27), the total number of modes $N(\sigma')$ in which σ is less than σ' is

$$N(\sigma') = V(4\pi) \pi(\sigma')^3 \quad (34)$$

The equation $\nu = \nu'$ defines two spheres in $\bar{\sigma}$ space, one corresponding to longitudinal modes of vibration, and the other transverse to modes. The radii of these spheres are given by the equations

$$\bar{\sigma}'_1 = \frac{\nu'}{c_1}, \quad \bar{\sigma}'_t = \frac{\nu'}{c_t} \quad (35)$$

respectively.

The total number of modes having frequencies less than ν' is, from Equation (33) and (35),

$$N(\nu') = \frac{4}{3} V \pi \left(\frac{1}{c_1^3} + \frac{2}{c_t^3} \right) \nu'^3 \quad (36)$$

since one longitudinal mode and two transverse modes correspond to each value of $\bar{\sigma}$.

The mean velocity c has been defined by means of the equation

$$\frac{3}{c^3} = \frac{1}{c_1^3} + \frac{2}{c_t^3} \quad (37)$$

occupied by any one point, say $\sigma_{x_1} = \frac{1}{2L_x}$, $\sigma_{y_1} = \frac{1}{2L_y}$, $\sigma_{z_1} = \frac{1}{2L_z}$ is $\sigma_{x_1} \cdot \sigma_{y_1} \cdot \sigma_{z_1}$, which is equal to $\frac{1}{8L_x L_y L_z}$

Equation (36) becomes then

$$N(\nu') = V \frac{4\pi}{c^3} \nu'^3 \quad (38)$$

Debye determined the highest allowed frequency ν_m by setting (38) equal to $3N$, where N is the number of atoms in the solid. He also assumed that the number of modes of vibration in the frequency range from ν' to $\nu' + d\nu'$ and is given by the differential of Equation (38). Then

$$f(\nu) = 3V \frac{4\pi}{c^3} \nu^2 \quad (39)$$

In this formula ν has a maximum depending on the structure and dimensions of the lattice. Therefore

$$3N = \int_0^{\nu_m} dN = \frac{12V\pi}{c^3} \int_0^{\nu_m} \nu^2 d\nu = \frac{4\pi V}{c^3} \nu_m^3 \quad (40)$$

From Equation (40)

$$c^3 = \frac{4V\pi}{3N} \nu_m^3$$

Therefore Equation (39) becomes

$$\begin{aligned} f(\nu) &= \frac{3V \times 4\pi \nu^2}{4 V \pi \nu_m^3} \times 3N \\ f(\nu) &= \frac{9N}{\nu_m^3} \nu^2 \end{aligned} \quad (41)$$

From Equation (41)

$$dN = f(\nu) d\nu = \frac{9N}{\nu_m^3} \nu^2 d\nu \quad (42)$$

From Equation (13)

$$E = E_0 + \frac{h}{2} \sum_{3N} \nu_i + h \sum_{3N} \frac{\nu_i}{(e^{h \cdot \nu_i / kT} - 1)} \quad (13)$$

Replacing the summation by an integration and using Equation (42)

$$E = E_0 + \frac{h}{2} \int_0^{\nu_m} \frac{9N}{\nu_m^3} \nu^3 d\nu + h \int_0^{\nu_m} \frac{9N \nu^3 d\nu}{\nu_m^3 (e^{h \nu / kT} - 1)} \quad (43)$$

Defining

$$\theta_D = \frac{h \nu_m}{kT} \quad (44)$$

and

$$x = \frac{h \nu}{kT} \quad (45)$$

then Equation (43) becomes

$$E = E_0 + \frac{9Nk\theta_D}{8} + 9NkT \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \quad (46)$$

in which the second term is the total zero point energy of the crystal. The value of C_v is then

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = 3Lk \left(\frac{kT}{h \cdot \nu_m} \right)^3 \int_0^{h \cdot \nu_m / kT} \frac{e^x x^4 dx}{(e^x - 1)^2} \quad (47)$$

From Equation (45) and (47)

$$C_v = \frac{9Nh^2}{kT^2 \cdot \nu_m^3} \int_0^{\nu_m} \frac{\nu^4 e^{h \nu / kT} d\nu}{(e^{h \nu / kT} - 1)^2} \quad (48)$$

We shall define a characteristic temperature Θ_D by the equation

$$R\Theta_D = h \nu_m \quad (49)$$

and shall write Equation (48) in the form

$$C_v = 3Nk f_D \left(\frac{\Theta_D}{T} \right) \quad (50)$$

where

$$f_D \left(\frac{\Theta_D}{T} \right) = 3 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{e^x x^4 dx}{(e^x - 1)^2} \quad (51)$$

The mean velocity c and the characteristic temperature are related by means of the equation

$$\Theta_D = \frac{h \nu_m}{k} = \frac{h}{k} c \left(\frac{3N}{4\pi V} \right)^{1/3} \quad (52)$$

When the temperature becomes sufficiently low, the integral in Equation (51) may be expanded in a power series to show that

$$C_v = aT^3 \quad (T \ll \Theta_D) \quad (53)$$

where

$$a = \frac{12\pi^4}{5} Nk \left(\frac{1}{\Theta_D} \right)^3$$

For cases when the temperature becomes sufficiently large, $e^{h\nu/kT}$ becomes small, and Equation (48) may be reduced easily to $3R$. The Debye equation will become equal to the Einstein equation if ν in Equation (42) is assumed to be constant.

In Figure 3 the lower curve represents the value of C_V as a function of T/θ_D as calculated from Equation (16) of the Einstein theory, by substituting $h\nu/kT$ for θ_D/T . The upper curve represents C_V as a function of T/θ_D , according to Equation (50) of the Debye theory.

The limiting value of C_V is the same in both theories, namely, $3R$ at high temperatures, and in both theories C_V becomes zero at the zero absolute temperature. But at intermediate values of T/θ_D the Einstein theory predicts lower values of C_V , and, as mentioned above, these values approach zero too rapidly, when compared with experimental or Debye results.

Figure 3 also shows the value of C_V for silver (it is supposed that C_V was calculated from experimental C_p data). With θ_D chosen as 215°K , these results fall almost exactly on the Debye curve. Good agreement with the Einstein curve could also be obtained in the region above $T = 0.4\theta_E^*$ by appropriate choice of θ_E , but this choice results in very poor agreement in the low temperature region.

4. General Comments. The specific heat capacity at high temperature is not sensitive to the characteristics of the frequency distribution. This can be observed when the Einstein and Debye model, which are widely different, yield

* θ_E selected in order to make the calculated Einstein curve fit the experimental one.

specific heat capacity values not essentially different at high temperatures (the main difference occurs at low temperatures).

In many cases the Debye theory is correct at extremely low temperatures. At such temperatures the specific heat is contributed predominantly by the vibrations of the lowest frequency. Nevertheless there is a low temperature region, immediately above this extreme limit, where for some metals Debye theory shows considerable deviation from experimental data.

If the assumptions of Debye continuum theory (simple harmonic vibrations, elastic isotropy, no dispersion of wave propagation) were correct Θ_D would be independent of temperature; the fact that a variation of Θ_D with temperature has been obtained for some metals (when determined by a given technique) indicates that not all the assumptions made are applicable to these metals. Herbstein⁴ has presented some experimental results for several cubic crystals where a variation between the experimental and theoretical calculations by using Debye theory was observed. Nevertheless, analysis made of this specific heat capacity of metals at sufficiently high temperature⁵ indicated that the specific heat capacity above Θ_D is not sensitive to the characteristics of the frequency distribution.

The atomistic model of Born and Von Karman⁵ more frequently predicts specific heat capacity values in agree-

ment with experimental data in the critical temperature range where the Debye theory fails to do so, as was first shown by Blackman³. The essential point in the Born and Von Karman theory is the method used to calculate the frequencies of vibration of the lattice, based on a number of particles of given mass bound to each other by elastic forces acting between neighbors only. The elastic forces acting on the atoms are proportional to the elastic constant given by Hooks' Law.

By using Born and Von Karman's theory in the determination of the Debye temperature, Blackman³ showed the variation of the Debye temperature as a function of temperature. It is emphasized that this variation, obtained when relating Θ_D to Born and Von Karman's theory⁵, occurs at low temperatures. At sufficiently high temperatures, as shown by Blackman, the Θ_D calculated in this way tends to a constant value. This means that a fair representation of the specific heat capacity at relatively high temperatures can be achieved by using the Debye's formula with a suitable chosen value for the parameter Θ_D . This does not necessarily confirm the idea that the lattice vibrations can be suitably replaced by elastic waves.

For the temperatures used in the present research the Debye theory gives, then, a simple and excellent account of the specific heat capacity of solids in spite of the crude nature of the approximation made.

b. Anharmonic Lattice Heat Capacity

In a simple harmonic motion an atom starting from rest at any position x has a potential energy V , given by

$$V = \frac{1}{2} \xi x^2$$

where ξ is a proportional constant that depends on the structure, frequency of vibration etc., and a kinetic energy, given by

$$K_E = \frac{1}{2} m \frac{d^2 x}{dt^2}$$

where m is the mass of the atom.

The vibration of the atoms in a simple harmonic motion is based on the assumption that the displacement of the atoms is proportional to the force that produces such displacements. The harmonic theory was developed with the above assumption and with the application of the Schroedinger equation. According to wave mechanics, a system where the atoms have motion can be described by a wave function, ψ , which has the property of determining the probability that the various atoms have their coordinates in the range x_1 to $x_1 + dx_1 \dots z_n$ to $z_n + dz_n$. This probability is given by

$$\psi^2 dx_1 dy_1 \dots dz_n \quad (54)$$

where ψ^2 is the probability density. When a system of this type is in a time independent state and the particles of mass m_i move in a field of force which can be described by the

potential energy V , which is a function of the coordinates $x_1, y_1, \dots, z_n$, then ψ may be obtained by solving the equation

$$\sum_i \frac{1}{m_i} \left(\frac{\partial^2 \psi}{\partial x_i^2} + \frac{\partial^2 \psi}{\partial y_i^2} + \frac{\partial^2 \psi}{\partial z_i^2} \right) = - \frac{8\pi^2}{h^2} (E - V) \psi \quad (55)$$

together with any boundary condition appropriate for the particular problem. The summation is over all the particles (atoms) in the crystal. In this formula h is Planck's constant and E is the total internal energy. (This equation is concerned with $3N$ dimensions).

To fulfill the wave mechanical purpose, ψ shall describe a probability, in accordance with Equation (54). For this purpose it must be single valued, continuous and finite through the range of the coordinates. For the harmonic lattice $V = 1/2 \xi x^2$, and V the significant solutions are obtained only for particular values $\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3$ etc. of the energy of each particle. These are called eigen values. Therefore the formula

$$\epsilon_i = h(v_i + \frac{1}{2})\nu = \text{energy of the } i^{\text{th}} \text{ oscillator}$$

used and defined previously in the Einstein and Debye contributions to C_v results as a unique solution in the Schrodinger equation when the atoms are assumed to vibrate in harmonic oscillations.

When the potential energy in which the atoms move is not of the type $(1/2)\xi x^2$, the energy of each oscillator

resulting as a solution to Schroedinger equation is not equal to the one previously used. Such a case describes the anharmonic vibration where the restoring force is no longer directly proportional to the displacement.

The energy levels corresponding to an anharmonic potential energy curve can be expressed as a power series in

$$\epsilon_i = h\nu \left[\left(v_i + \frac{1}{2}\right) - x_e \left(v + \frac{1}{2}\right)^2 + y_e \left(v + \frac{1}{2}\right)^3 + \dots \right]$$

where x_e , y_e etc. are anharmonic constants.

Further theoretical analysis of anharmonic lattice contributions will not be presented because its complexity puts it beyond the purpose of the present research. However, some estimates of the anharmonic lattice contribution to the heat capacity have been made by other investigations. It is emphasized that an important purpose of the present research, as will be brought out, is to estimate contributions to the specific heat capacity which, when subtracted from the experimental heat capacity, will give a quantitative measure of the anharmonic contributions.

c. Electronic Contributions to Heat Capacity

A very important contribution, especially in metals which have conduction electrons, is the electronic heat capacity contribution. In many studies the primary interest in the measurement of the electronic specific heat in metals stems from the fact that it allows an evaluation to be made

of the density of states of the electrons at the Fermi energy in the energy band. In our case we will be primarily interested in using the density of states evaluation to calculate electronic heat capacities.

The basis of the theory of electronic heat capacity is founded on Drude's suggestion that the electrical and thermal properties of metals might be correlated by assuming that metals contain free electrons in thermal equilibrium with the atoms of the solid. The heat capacity was attempted to be explained by the free electron theory, but due to the fact that the results were extremely high, Sommerfeld's theory was developed and used with improved results.

1. Classical Free Electron Theory. The early theories of the conduction of electricity in metals introduced by Drude and others at the end of the nineteenth century used the notion of "free" electrons within the metal as a perfect gas. The application of methods which have been developed in connection with the kinetic theory of gases, in order to predict the resistivity of metals, led to the results which bore at least a qualitative resemblance to experimental results. The classical contribution of the electrons to the atomic heat capacity should be

$$(C_E)_V = \frac{3}{2} n_a R \quad (56)$$

where n_a is the number of free electrons per atom. Accordingly, the total $(C_E)_V$ for metals at room temperature should

be about $9/2R$, because n_a must be of the order of unity to account for the electrical properties. However, there is no tendency for the total atomic heat capacity of metals to be appreciably higher than that of insulators at room temperature, both being about $3R$. Since this is also the expected value of the lattice mode contribution $(C_L)_V^*$, the observed values of $(C_E)_V$ must be very small compared to the classical value given by Equation (56).

2. Sommerfeld Theory. The solution of the above difficulty is due to Sommerfeld. In the section dealing with the lattice contributions, we saw how Einstein accounted for the decrease in $(C_L)_V$ with decreasing temperature by replacing the classical equipartition value of the oscillator mean energy by the value calculated by Planck on the basis of his quantum hypothesis. This corresponds to replacing the Maxwell-Boltzmann distribution function, $f_{MB}(\epsilon)$,

$$f_{MB}(\epsilon) = \text{constant} \times e^{-\epsilon/kT} \quad (57)$$

from which the classical equipartition value, kT , of the mean

* $(C_L)_V$ is the lattice contribution to the heat capacity at constant volume.

**It is supposed that there are a set of energy levels available to the electrons such that the number lying between energies ϵ and $\epsilon + d\epsilon$ is $n(\epsilon) d\epsilon$. $n(\epsilon)$ is the density of states of the electrons.

oscillator energy is derived, by the Bose-Einstein distribution function

$$f_{BE}(\epsilon) = \frac{1}{e^{\epsilon/kT} - 1} \quad (58)$$

which is appropriate for particles with integral spin (in this case zero spin). Sommerfeld discussed the properties of electrons in metals using for them the Fermi-Dirac distribution function

$$f_{FD}(\epsilon) = \frac{1}{e^{[(\epsilon - \zeta)/kT]_+} + 1} \quad (59)$$

which is appropriate for particles with half integral spin (in this case spin equal to $\hbar/2$)*. The normalizing constant which appears in the Maxwell-Boltzmann and Fermi-Dirac distribution functions occurs in the latter as the energy ζ , which is the chemical potential of the electron. The energy ζ is often referred to as the Fermi level of electron distribution. It has the formal significance, evident from Equation (59), that

$$f_{FD}(\zeta) = \frac{1}{2} \quad (60)$$

It can also be seen from Equation (59) that $f_{FD}(\epsilon)$ decreases from nearly unity at $\epsilon = \zeta - \Delta\epsilon$ to nearly zero at $\epsilon = \zeta + \Delta\epsilon$, where $\Delta\epsilon \cong kT$.

Correspondingly, $|df_{FD}(\epsilon)/d\epsilon|$ is large only in this energy range.

* $\hbar = h/(2\pi)$, h = Planck's constant.

By the same argument as was used in connection with Equation (42), the density per unit volume of electron levels in momentum space can be written

$$g'(p)dp = 2(4\pi/h^3) p^2 dp \quad (61)$$

where p is momentum; the factor two occurs since there are two levels for each cell in momentum space, corresponding to the two directions for electron spin. For perfectly free electrons (electrons moving in a region of constant potential) the energy levels are given by

$$\epsilon = h\sigma \frac{2h\sigma}{m} = \frac{2h^2\sigma^2}{m} = \frac{p^2}{2m} \quad (62)$$

where σ is the wave-number, equal to the reciprocal of wavelength. This is the same as the classical expression, and Equation (61) can be transformed to

$$g(\epsilon)d\epsilon = 4\pi \left(\frac{2m}{h^2} \right)^{3/2} \sqrt{\epsilon} d\epsilon \quad (63)$$

The number of electrons per unit volume is then

$$n = 4 \left(\frac{2m}{h^2} \right)^{3/2} \int_0^{\infty} \pi f_{FD}(\epsilon) \sqrt{\epsilon} d\epsilon \quad (64)$$

At absolute zero the maximum energy level that an electron can occupy is defined by the Fermi energy level ζ_0 , $f_{FD} = 1$ for $\epsilon < \zeta_0$ and $f_{FD} = 0$ for $\epsilon > \zeta_0$. By substituting into Equation (64)

$$n = 4\pi \left(\frac{2m}{h^2} \right)^{3/2} \int_0^{\zeta_0} \sqrt{\epsilon} d\epsilon \quad (65)$$

Solving Equation (65) by ζ_0

$$\zeta_0 = \frac{h^2}{2m} \left(\frac{3n}{8\pi} \right)^{2/3} = 25.8 \left(\frac{n_a}{V_m} \right)^{2/3} \quad (66)$$

where ζ_0 is in electron volts, V_m is the molar volume in cubic centimeters and n_a is the number of electrons per atom. Since k is 0.863×10^{-4} electron volt per degree and ζ_0 in Equation (65) is of the order of few electron volts for metals, the transition energy range in which f_{FD} is appreciable different from zero or unity is small even at high temperatures. According to the Pauli exclusion principle an electron can be excited only to an unoccupied level, and since the thermal energy available for excitation at temperature T is about kT , only those electrons within about kT of the Fermi level can be thermally excited at temperature T . The number of electrons in this energy range will be roughly the fraction kT/ζ_0 of the total number, and each electron will have heat capacity equal to $3K/2$. So, the total electronic specific heat capacity will be of the order

$$(C_E)_v = \left(\frac{kT}{\zeta} \right) n_a R \quad (67)$$

Due to the very high value for $(C_E)_v$ obtained by calculations made with classical theory, Sommerfeld made a more accurate calculation, taking into account the small variation of the Fermi level with temperature. He considered the degeneracy of the energy levels and calculated the electronic C_v , and obtained a value lower than the value obtained by the classical method.

According to Sommerfeld's theory the value of the energy of the electron per unit volume is given by

$$n = c \int_0^{\infty} \frac{\eta^{1/2} d\eta}{e^{\eta - \eta'} + 1} \quad (68)$$

where

$$c = \frac{1}{2\pi^2} \left(\frac{2m}{h^2} \right)^{3/2} (kT)^{3/2}$$

$$\eta = \frac{\epsilon}{kT}$$

$$\eta' = \frac{\zeta}{kT}$$

and

ζ = Fermi energy at temperature T

The integration of Equation (68) gives

$$\int_0^{\infty} \frac{\eta^{1/2} d\eta}{e^{\eta - \eta'} + 1} \cong \frac{2}{3} (\eta')^{3/2} + \frac{\pi^2}{12} \frac{1}{\eta'^{1/2}} \quad (69)$$

Equation (68) becomes then

$$n = \frac{16\sqrt{2} \pi m^{3/2}}{3h^3} \left(\zeta^{3/2} + \frac{2k^2 T^2}{8 \zeta^{1/2}} + \dots \right) \quad (70)$$

In a first degree approximation the relation between ζ and ζ_0 is from Equations (65) and (70),

$$\zeta = \zeta_0 \left(1 - \frac{2k^2 T^2}{12 \zeta_0^2} \right) \quad (71)$$

The total internal energy U of the electrons per unit volume then will be given by

$$U = 2 \int_0^{\infty} \epsilon n(\epsilon) \cdot f_0(\epsilon) \cdot d\epsilon \quad (72)$$

By using a method similar to that used to find Equation (71), U as a function of temperature is found. This gives

$$U = \frac{16\sqrt{2}}{5h^3} m^{3/2} \pi \left(\zeta^{5/2} + \frac{5}{12} \pi^2 k^2 T^2 \zeta^{1/2} + \dots \right) \quad (73)$$

From Equations (71) and (73)

$$U = \frac{16\sqrt{2}}{5h^3} \pi m^{3/2} \left(\zeta_0^{5/2} + \frac{5}{12} \pi^2 k^2 T^2 \zeta_0^{1/2} + \dots \right) \quad (74)$$

Differentiating Equation (74) with respect to T gives, to a first degree approximation,

$$C_v = \frac{\partial U}{\partial T} = \frac{8\sqrt{2}}{3h^3} \pi m^{3/2} k^2 T \zeta_0^{1/2} = \frac{\pi^2}{2} \frac{k^2 T}{\zeta_0} n \quad (75)$$

When $n = N_0 Z$, where Z is the number of free electrons per atom,

$$\begin{aligned} C_v &= \frac{\pi^2}{2} \frac{ZkRT}{\zeta_0} \\ &= \gamma T \end{aligned} \quad (76)$$

where

$$\gamma = \frac{\pi^2}{2} \frac{ZkR^*}{\zeta_0} \quad (77)$$

The proportionality of C_v to T in Equation (76) only

* γ is usually referred to as the electronic specific heat capacity constant.

holds for low temperatures since it was obtained from the first degree approximation made after differentiation of Equation (74). At sufficiently high temperatures C_v must be determined by using a second order degree approximation since at this high temperatures C_v must tend asymptotically to the classical value $3/2nk$. The exact form of C_v as a function of T , however, depends upon the functional dependence of $n(\epsilon)$ on ϵ over the whole energy range. For most metals, nevertheless, terms of higher order than KT/ζ_0 in Equation (76) do not have any effect on the electronic specific heat capacity at temperatures where the solid metal exists.

The evaluation of Equation (72) to a second degree approximation gives

$$U = \frac{3}{5} n \zeta_0 \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{\zeta_0} \right)^2 - \frac{\pi^4}{16} \left(\frac{kT}{\zeta_0} \right)^4 \right], \quad (78)$$

$$C_v = \frac{1}{2} \pi^2 nk \frac{kT}{\zeta_0} \left[1 - \frac{3\pi^2}{10} \left(\frac{kT}{\zeta_0} \right)^2 \right] \quad (79)$$

Since $(C_L)_v$ is proportional to T^3 , at around $300^\circ K$ it should, as it actually occurs, be the main contribution in determining the specific heat capacity at this temperature. This is so, since at this temperature the effect of the electronic contribution (which as has been shown in this section is proportional to T) is small as compared to the contributions due to harmonic lattice vibration. Obviously, as the temperature approaches zero the opposite will occur and $(C_E)_v$ will dominate as compared to $(C_L)_v$. (The decrease

in $(C_E)_V$ is only proportional to T while the decrease in $(C_L)_V$ is proportional T^3 .)

d. Contributions from the Formation of Lattice Defects

All crystals contain a variety of imperfections, many of which, such as impurity atoms, dislocations, and grain boundaries, are produced during the heat treatment, mechanical preparation and handling of the crystal. A very important type of imperfection is structural point defects since they are present in the crystal at thermodynamic equilibrium. The basic structural point defect of interest to the present study is the vacancy, a vacant lattice site.

Point defects can be detected by measuring very carefully physical properties related to temperature. There is a great number of experimental measurements of these physical properties which strongly support the existence of vacancies in metals, although a clear quantitative interpretation of the data to give vacancy concentrations is frequently difficult. Due to the vacancy concentration increase with temperature, experimental methods involve either measurements at temperatures near the melting point or on samples quenched from these temperatures. Some of these measurements are (a) simultaneous measurements of the length and lattice parameter of a rod specimen as a function of temperature, (b) change in resistivity as a function of temperature or change in resistivity as a function of quenching temperature (sam-

ples quenched from high temperature are assumed to retain the equilibrium vacancy concentration that they have at that temperature.), and (c) heat capacity measurements (Vacancies increase the internal energy of a crystal, and because an increase in temperature results in an increase in vacancy concentration, the heat capacity is also altered with respect to temperature.).

When a crystal is at a given temperature, it has an equilibrium concentration of lattice defects. Upon raising the temperature infinitely slowly, the defect concentration increases to the new equilibrium value and in so doing the crystal absorbs energy. This energy absorption causes a rise in the heat capacity. Thus contributions to the heat capacity from the formation of equilibrium lattice defects must be considered along with those contributions previously presented. For the purposes of this research, attention will be centered only on the formation of monovacancies and divacancies, as these seem to be the most important defects present in simple metal crystals.

Point defects are characterized by the disturbance around a single atomic site. The mechanisms for the formation of a vacancy can be visualized as follows. Assuming that the lattice vibrations within the crystal have sufficient energy to displace an atom to the surface of the crystal, a vacant lattice site will be produced, and with further cooperative motion, atoms in deeper lattice sites within the crystal will move toward the surface by using the va-

cant sites already produced in previous or simultaneous migrations. For each atom to move or jump from its lattice site to a vacant lattice site, it needs to have the necessary activation energy.

The crystal under equilibrium conditions at a given temperature has reached thermodynamic stability between vacancies and atoms. Spontaneous changes have to occur in the crystal in order to achieve equilibrium at this new temperature until a minimum Gibbs free energy value is obtained which is characteristic of that temperature, pressure and crystal structure.

The Gibbs free energy is defined as

$$G \equiv H - TS \quad (80)$$

or
$$G = E + PV - TS \quad (81)$$

where H , E , P , V , and T have been previously defined, and S is the entropy of the system. For the formation of vacancies, the volume change is small, so that PV can be assumed to be constant.

For the case of N atoms and N_v monovacancies at a given temperature, the free energy change due to addition of monovacancies to the crystal is

$$(\Delta G)_{1v} = (\Delta H)_{1v} - T(\Delta S)_{1v} \quad (82)$$

where

$(\Delta G)_{1v}$ = Gibbs free energy change due to the formation of N_{1v} monovacancies

$(\Delta H)_{1v}$ = Enthalpy change due to the formation of N_{1v} monovacancies

Let Δh_{1v} be the enthalpy change for the formation of one monovacancy; then

$$(\Delta H)_{1v} = N_{1v} \cdot \Delta h_{1v} \quad (83)$$

Within the crystal there is a change in entropy for two main reasons. The first entropy change ΔS_{1v} is due to the fact that the atoms adjacent to each hole are less restrained than those surrounded by other atoms and can therefore vibrate in a more irregular fashion as compared to the atoms removed from the hole. Each vacancy contributes to the total entropy of the system so $\Delta S_1 = N_{1v} \Delta s_{1v}$, where Δs_{1v} is the entropy change due to one monovacancy. The second entropy change ΔS_m arises from the entropy of mixing and is expressed by the equation

$$\Delta S_m = -N_T k \left[X_v \log_e X_v + (1 - X_v) \log_e (1 - X_v) \right] \quad (84)$$

where N_T = Total number of lattice sites ($N + N_v$)

k = Boltzmann's constant

X_v = Concentration of vacancies = N_{1v}/N_T

$(1 - X_v)$ = Concentration of atoms = $N/N_T = C_0$

Equation (84) becomes after simplification

$$\Delta S_m = k \left[N_T \log_e N_T - N_{1v} \log_e N_{1v} - N \log_e N \right] \quad (85)$$

The free energy equation (82) can be written also as

$$\Delta G_{1v} = N_{1v} \Delta h_{1v} - (\Delta S_m + \Delta S'_{1v})T \quad (86)$$

Usually ΔS_{1v} is neglected due to the argument that its effect on the number of vacancies is of secondary importance.

Under equilibrium conditions, ΔG_{1v} should be minimum at a given temperature; therefore,

$$\frac{d(\Delta G_{1v})}{dN_{1v}} = 0 = \Delta h_{1v} - \Delta S_{1v} T + kT \log_e \frac{N_{1v}}{N + N_{1v}}^* \quad (87)$$

Rearranging Equation (87) in an exponential way

$$\frac{N_{1v}}{N + N_{1v}} = \left(e^{\Delta S_{1v}/k} \right) \left(e^{-\Delta h_{1v}/kT} \right) \quad (88)$$

Usually $N_{1v} \ll N$, so Equation (62) becomes:

$$\frac{N_{1v}}{N} = x_{1v} = \left(e^{\Delta S_{1v}/k} \right) \left(e^{-\Delta h_{1v}/kT} \right) \quad (89)$$

For the case of divacancies, if the coordination number is z , then there are $zN/2$ adjacent pairs of lattice sites in the crystal. Therefore the divacancies can be distributed in the following number of ways, W , given by

$$W = \frac{(zN/2)!}{[(zN/2) - n_2]! n_2!} \quad (90)$$

where n_2 is the number of divacancies which can be distributed in the N lattice sites.

By using the same procedure as above, and with

$$\Delta S_m = k(\log_e W) \quad (91)$$

the concentration of divacancies at a given temperature is given by

$$\frac{N_{2v}}{N} = x_{2v} = \frac{1}{2} z \left(e^{\Delta S_{2v}/k} \right) \left(e^{-\Delta h_{2v}/kT} \right) \quad (92)$$

where Δh_{2v} is the energy of formation of a divacancy and

* ΔS_{1v} is the change in the entropy of the crystal due to the relaxation of atoms around the monovacancy.

ΔS_{2v} is the entropy of formation of the divacancy. Let us define B as the energy of formation of divacancy from two vacancies. This is called the binding energy. Since Δh_{1v} is the formation energy of a single vacancy, then

$$\Delta h_{2v} = 2\Delta h_{1v} - B \quad (93)$$

Therefore Equation (92) may be written as

$$X_{2v} = \frac{1}{2} z \left(X_{1v} \right)^2 e^{B/kT} e^{\Delta S_{2v}/k} \quad (94)$$

The binding energy can be determined by assuming that the relaxation energy around a monovacancy and a divacancy is equal, so that B becomes proportional to the lattice cohesive energy⁶, E_c^* , being on the average $E_c/6$ for the cases of face center cubic or hexagonal close packed crystals and $E_c/4$ for body center cubic crystals. Bartlett and Dienes⁵⁵ point out that when the relaxation energy of monovacancies and divacancies is not nearly the same, but is assumed to be distributed among the bonds in the same way as the cohesive energy, B for face center cubic and hexagonal close packed systems is equal to $\Delta h_{1v}/6$ and for body center cubic $\Delta h_{1v}/4$.

A more sophisticated approach by Girifalco and Weiser^{7,8} and Weiser and Girifalco⁹ considers the relaxation of the atoms around the vacancies by employing the Morse crystal.

* E_c is also equal to the average energy necessary to remove an atom from the surface (the sublimation energy) and is assumed to be one half the energy needed to remove an atom from the interior to infinity.

Their analysis is based upon the energy of interaction ϕ_{ij} between two isolated atoms, i and j as a function of their separation r_{ij} . This energy ϕ_{ij} is given by

$$\phi_{ij} = D \quad e^{-2T(r_{ij} - r_0)} - 2 e^{-T(r_{ij} - r_0)} \quad (95)$$

Where D = Dissociation energy

T = Constant

r_0 = is the equilibrium separation between the two atoms.

The constants D, T , and r_0 can be determined from the energy of sublimation at zero pressure and temperature, the compressibility at zero pressure and temperature and the lattice constant at zero temperature, The contributions to C_v of the monovacancies and the divacancies can then be determined by calculating at a given temperature the total energy of formation of the equilibrium concentration of vacancies.

From Equation (89) and (92), for monovacancies

$$\begin{aligned} (\Delta H_{1v})_{\text{equilibrium}} &= \Delta h_{1v}(N_{1v}) \\ &= \Delta h_{1v} N \left[e^{\Delta S_{1v}/k} \right] \left[e^{-\Delta h_{1v}/kT} \right] \quad (96) \end{aligned}$$

and for divacancies

$$\begin{aligned} (\Delta H_{2v})_{\text{equilibrium}} &= \Delta h_{2v}(n_2) \\ &= N \Delta h_{2v} \frac{z}{2} \left[e^{\Delta S_{2v}/k} \right] \left[e^{-\Delta h_{2v}/kT} \right] \quad (97) \end{aligned}$$

Therefore the contribution to C_v^* at a given temperature, due

*The experimental measurements on Δh_{1v} are made at

to the monovacancies and divacancies can be determined by

$$\frac{d(\Delta H_{1v})}{dT} \quad \text{and} \quad \frac{d(\Delta H_{2v})}{dT}, \quad \text{so}$$

$$(C_{1v})_v \cong \left(N e^{\Delta S_{1v}/k} \right) \times \left(\frac{\Delta h_{1v}^2}{kT^2} \right) \left(e^{-\Delta h_{1v}/kT} \right) \quad (98)$$

and

$$(C_{2v})_v \cong \left(\frac{N}{2} e^{\Delta S_{2v}/k} \right) \times \left(\frac{\Delta h_{2v}^2}{kT^2} \right) \left(e^{-\Delta h_{2v}/kT} \right) \quad (99)$$

The divacancies play a significant role only at higher temperatures since their formation requires higher energy.

e. Summary of Contributions to the Specific Heat Capacity of Solids.

In the above sections a brief analysis has been made of the different contributions to the heat capacity at constant volume. Specially, (a) Equation (48) uses the Debye model in order to calculate the harmonic lattice contribution, (b) Equation (76) uses the Sommerfeld theory in order to calculate the electronic contribution, and (c) Equations (98) and (99) give the monovacancy and divacancy contributions, respectively. Then assuming independent contribution to the specific heat capacity

$$(C_v)_{\text{experimental}} = (C_L)_v + (C_E)_v + (C_{1v})_v + (C_{2v})_v + (C_{\text{anharmonic}})_v \quad (100a)$$

constant pressure, so it is assumed that the change in volume due to the formation of a vacancy at a given pressure, is zero. Thus $(C_{1v})_v \cong (C_{1v})_p$

or

$$(C_{\text{anharmonic}})_v = (C_v)_{\text{experimental}} - (C_L)_v - (C_E)_v - (C_{1v})_v - (C_{2v})_v \quad (100b)$$

where

$(C_v)_{\text{experimental}}$ = heat capacity at constant volume obtained from the experimental heat capacity data at constant pressure (see next section),

$(C_L)_v$ = harmonic lattice vibration contribution to the heat capacity at constant volume,

$(C_{1v})_v$ = contribution to the heat capacity at constant volume from the formation of monovacancies,

$(C_{2v})_v$ = contribution to the heat capacity at constant volume from the formation of divacancies,

and

$(C_{\text{anharmonic}})_v$ = anaharmonic contribution to the heat capacity at constant volume.

For the purpose of the present research only contributions given by Equations (100a) or (100b) are assumed to have a noticeable effect on the final result of the specific heat capacity.

One of the purposes of this research was to determine from experimental specific heat capacity data the anharmonic contributions to the specific heat capacity in solids, which involved the use of Equation (100b). Since this equation uses the experimental specific heat capacity at constant volume and since experimentally the specific heat capacity

at constant pressure was obtained, a conversion from C_p to C_v was needed. The method used for this conversion is explained in the following section.

C. CONVERSION OF C_p TO C_v

The heat capacity ordinarily measured is C_p , the heat capacity at constant pressure. However, the theories discussed above are based on the assumption that the volume is kept constant as the temperature changes; hence they refer to C_v , the heat capacity at constant volume.

The heat capacity at constant volume, C_v , is related to the heat capacity at constant pressure, C_p , by the following expression

$$C_p = C_v + C^d \quad (101)$$

where the dilation term, C^d , is given by

$$C^d = \frac{\alpha_v^2}{\beta_v} TV \quad (102)$$

where α_v is the coefficient of volume thermal expansion, V is the atomic volume, and β_v is the isothermal compressibility. The difficulty in using Equation (102) to determine the dilation term is that the coefficient of expansion, the volume, and the compressibility must be known for each temperature at which one wishes to calculate C_v , and these quantities, especially the compressibility, usually are known over a small temperature range, and usually only at low temperature. Fortunately, this limitation sometimes can be overcome by one of the following three possibilities.

a) Rewriting Equation (102) as

$$C^d = \alpha_v^2 T V \frac{C_p^2}{\beta_v C_p^2}$$

and letting

$$A = \frac{\alpha_v^2 V}{\beta_v C_p^2}$$

we have

$$C^d = A C_p^2 T \quad (103)$$

It has been found experimentally for some metals that A is almost constant over a wide range of temperatures. Thus, for such metals, one needs to calculate A at a given temperature to determine C_v from C_p over a wide range of temperatures. This approach is referred to as the Nernst-Lindemann approximation, obtained by rewriting Equation (101) as

$$C_v = C_p (1 - A C_p T) \quad (104)$$

b) From Equations (101) and (102)

$$C_p - C_v = \frac{\alpha_v^2}{\beta_v T V} \quad (105)$$

Equation (105) is rewritten as

$$C_p = C_v (1 + \Gamma \alpha_v T) \quad (106)$$

where Γ is Gruneisen's constant

$$\Gamma = \frac{V/\beta_v}{C_v/\alpha_v} \quad (107)$$

The other terms are the same as defined previously.

It is sometimes assumed that Γ is independent of tem-

perature. However, the work by Brooks and Bingham¹⁰ and Brooks¹¹ has shown that both of the possibilities (a) and (b) were not very accurate for pure aluminum and copper, respectively.

c) The existing data of coefficient of expansion, volume and the compressibility as a function of temperature can be extrapolated into the range in which they do not exist.

The determination of the dilation term involved the need of α_v , V and β_v as a function of temperature. For the metals used in this research there are no data of these terms over all temperature ranges, so an analysis was made in order to see which of the three different ways to accomplish the calculation term would be more advantageous.

D. SUMMARY

The discussions presented in the Introduction have attempted to illustrate the importance of knowledge of the heat capacity-temperature relation in contributing to the understanding of the crystalline metallic state. The postulation of contributions to the heat capacity by various mechanisms and a comparison of the sum of these contributions to the experimentally determined values clearly are necessary to evaluate theories of the metallic state. The present research is an attempt to contribute to such an evaluation. This has been done by the experimental determination of the heat capacity of gold from about 300°K to about 1300°K and

of lead and zinc from 300°K to 800°K (which will be into the liquid state). The contributions to the heat capacity then have been calculated utilizing the expressions presented in this Introduction, and an evaluation of the significance of the difference between the experimental heat capacity and the sum of these contributions has been made.

It was necessary to transform the experimental C_p to C_v , as discussed in Section C. The status of available data of the coefficient of volume expansion, volume, and isothermal compressibility as a function of temperature was determined to see where the dilation term could be calculated directly. Otherwise the use of approximations such as the Gruneissen's or the Nernst-Lindemann constants were used.

To calculate the theoretical contributions to the heat capacity, it was necessary to locate from the literature and evaluate the parameters that were needed, such as the Debye temperature, the electronic heat capacity coefficient, and the energy and entropy of formation of vacancies.

After the experimental specific heat capacity C_p was converted to C_v , the sum of the Debye heat capacity, electronic heat capacity, and the contribution from the formation of lattice defects were subtracted from this C_v . The difference obtained has been evaluated in terms of the temperature dependence and magnitude to see if it can be accounted for by an anharmonic contribution.

This approach is illustrated by the work of Brooks and

Bingham¹⁰ on aluminum, as by Brooks¹¹ on copper. In Figure 4 is shown for the case of aluminum the experimental C_p as a function of temperature, from about 100°K to close to the melting point. For aluminum sufficient data are available so that the dilation correction could be made directly. The solid C_v curve represents C_p minus the dilation term. In Figure 4 the calculated C_v curve is the sum of the Debye heat capacity and the electronic heat capacity. In Figure 5 is plotted the difference between the "experimental" C_v and the calculated C_v ; this difference being called the excess heat capacity. The contribution to the heat capacity from the formation of monovacancies was subtracted from the excess heat capacity, and the lower curve in Figure 5 was obtained. It is seen that the remaining excess heat capacity is about 10 per cent of C_v close to the melting point. Brooks and Bingham¹⁰ argued that the magnitude of this excess heat capacity is too large to be caused by uncertainties in any of the experimental measurements (i.e. C_p , α_v , V , β_v), or uncertainties in the parameters (i.e. Debye temperature) used to obtain the calculated heat capacity. Thus they assumed that this difference could be assigned to the anharmonic heat capacity.

Few quantitative theories exist to predict the temperature dependence of the anharmonic heat capacity, much less the magnitude for a specific metal. However, in the case of aluminum, Stedman et al.¹², have predicted that the anharmonic heat capacity should vary linearly with $(C_v)^2 T$, and

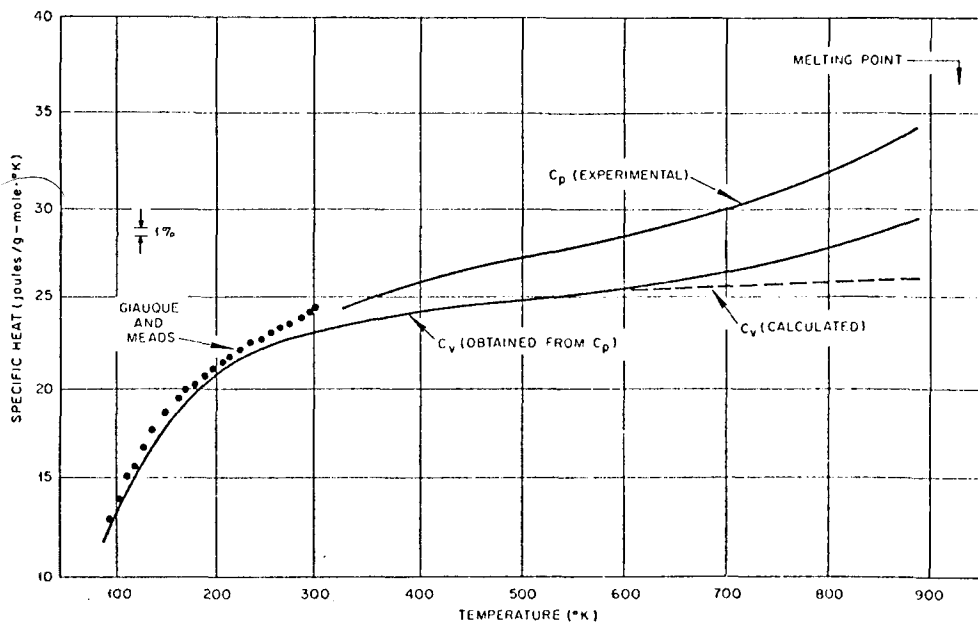


Figure 4. The experimental and calculated specific heat capacity for aluminum. The calculated values include the harmonic lattice contributions and electronic contributions.

Source: Brooks, C. R. and Bingham, R. E., The Specific Heat of Aluminum from 330 to 890°K and Contributions from the Formation of Vacancies and Anharmonic Effects, Journal of Physics and Chemistry of Solids, 29: 1553-1560, 1968.

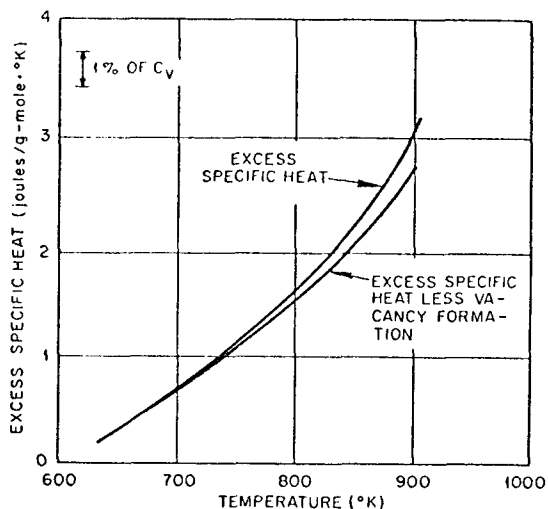


Figure 5. The excess specific heat capacity of aluminum as a function of temperature.

Source: Brooks, C. R. and Bingham, R. E., The Specific Heat of Aluminum from 330 to 890°K and Contributions from the Formation of Vacancies and Anharmonic Effects, Journal of Physics and Chemistry of Solids, 29: 1553-1560, 1968.

Brooks and Bingham⁵, found this to be approximately followed, as shown in Figure 6.

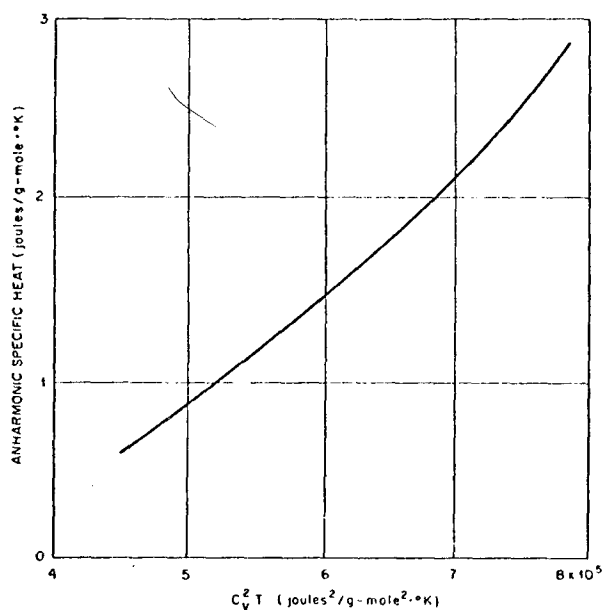


Figure 6. The anharmonic heat capacity of aluminum as a function of $C_V^2 T$.

Source: Brooks, C. R. and Bingham, R. E., The Specific Heat of aluminum from 330 to 890°K and Contributions from the formation of Vacancies and Anharmonic Effects, Journal of Physics and Chemistry of Solids, 29: 1553-1560, 1968.

CHAPTER II

EXPERIMENTAL PROCEDURES

A. EQUIPMENT

The specific heat capacity data for this research were determined by using the vertical adiabatic calorimeters designed and in operation in the Chemical and Metallurgical Engineering Department of The University of Tennessee. Their operating characteristics have been outlined in previous publications by Stansbury, et al.¹³, Pawel and Stansbury¹⁴, Brooks, et al.¹⁵ and Stansbury and Brooks¹⁶ and thus the method will only be described briefly here.

Basically the general procedure to obtain the specific heat capacity is to calculate the average specific heat capacity $\bar{C}_{pt}$ over a measured temperature interval ΔT , from determination of the time Δt required for a known power input P to raise the sample temperature by the amount ΔT . Keeping the system adiabatic (that is to say, keeping the sample and the surroundings at the same temperature), the power input to the sample's heater will be used only to heat the sample. Since measurements are made upon continuous heating the technique is referred to as dynamic adiabatic calorimetry¹⁶.

In general the vertical calorimeters consist of a polished sample of known mass m_s suspended concentrically inside

a metal cylinder, which serves as the main shield to achieve adiabatic conditions. Also above and below the sample are shields, so that the sample is centered in a region which approaches an adiabatic chamber. The shields are generally heated by radiation from heaters located close to each individual shield. Platinum-platinum 13 weight per cent rhodium thermocouples are welded at a point on each shield and also on the sample. The temperature of the sample or the temperature of any shield is measured with a potentiometer.

The temperature control of the system is obtained by the use of a circuit where the voltage of a thermocouple on the sample is applied to a low leakage capacitor. This voltage is then transferred to a central capacitor by a vibrating switch and its value compared to that of a thermocouple and one of the shields. The voltage difference of the two thermocouples is amplified and its output goes to a recording potentiometer which activates a DAT controller that pulses power to the heater of the shield. This procedure is used for each different control thermocouple located on the different shields of the calorimeter. Basically they are all compared to the temperature of the sample so that when the sample heats, the control points on the shields surrounding the sample follow the sample temperature by application of the necessary power to the different heaters. The sensitivity of the temperature control is indicated by the fact that, during operation, a deviation of $\pm 0.05^{\circ}\text{C}$ is at-

tained between the main shield and the sample.

The average specific heat capacity $\bar{C}_{pt}$ of the combined sample (mass m_s) and heater (mass m_h) is determined by measuring the voltage across the heater V_t and the current I through the heater at the beginning and end of the temperature change ΔT , and measuring simultaneously the time Δt required to increase the temperature by the amount ΔT . This apparent specific heat capacity is given by

$$\bar{C}_{pt} = \frac{\bar{V}_t \bar{I} \Delta t}{M \Delta T} \quad (1)$$

where $\bar{V}_t$ and $\bar{I}$ are the average voltage and current over the temperature interval ΔT , and M is the sum of sample and heater mass ($m_s + m_h$). The quantity $(\bar{V}_t \bar{I}/M)$ is the energy input rate and is essentially constant for a given current.

Although close temperature control between the sample and the shields is attained, temperature gradients do exist along the shields¹⁸, which means that the chamber in which the sample is located is not adiabatic. The non-adiabatic condition can be easily detected by turning off the power to the sample (at a given temperature), and allowing the system to come to steady state (static operation). Although the temperature controllers indicate that the points on the shields and on the sample at which the thermocouples are located are at the same temperature (within, for example, $\pm 0.05^\circ\text{C}$), the temperature of the sample is observed to change with time. This change in the sample's temperature

with time is called the drift rate $R(T)$, which may be positive or negative, depending on which absorbs heat, the sample or the surrounding; it is found to be essentially constant with time.

It is clear that a method must be devised to correct for the heat loss (or gain), and a relation to do so was derived by Pawel¹⁷. At any temperature, it is assumed that an indication of the heat loss attained during dynamic operation is correctly given by the static drift rate obtained at the temperature of interest. Using this assumption, the expression derived by Pawel is:

$$C_{pd} = \frac{\bar{C}_{pt}}{1 - [\bar{C}_{pt} R \cdot (T)/(K)]} \quad (2)$$

where

C_{pd} = apparent specific heat capacity corrected for non-adiabatic conditions,

$\bar{C}_{pt}$ = apparent specific heat capacity as given by Equation (1),

K = Energy input rate = $(\bar{V}_t \bar{I}/M)$,

and $R(T)$ = Drift rate.

A correction must be made to the apparent specific heat capacity C_{pd} since the heater absorbs part of the energy supplied to raise the temperature of the sample in order to raise its own temperature. This correction was derived by Pawel¹⁷, and when C_{pd} is given in Joules per gram it becomes:

$$C_p = C_{pd} + \frac{m_h}{m_s} (C_{pd} - 0.4729) \quad (3)$$

where

C_p = true specific heat capacity of the sample,

m_h = heater weight,

and m_s = sample weight.

Brooks¹⁸ has shown that by using the basic design and dimensions of the adiabatic calorimeters in the Chemical and Metallurgical Engineering Department at The University of Tennessee, error due to other heat losses are negligible.

The specific heat capacity determinations using the calorimeters at The University of Tennessee have a reproducibility of ± 1.0 per cent from 300 to 1300°K. This value was established by extensive measurements on copper¹⁵, using all three calorimeters, each employing a wide range of energy input rates (which is related to the heating rate), sample mass, and shield and sample thermocouple locations. The results of these extensive measurements, coupled with a detailed analysis of sources of errors^{16, 18} led to the conclusion that the experimental method gives specific heat capacity values having an absolute error within the reproducibility.

In the present investigation, in order to insure attainment of the most accurate specific heat capacity values of gold, lead, and zinc, two calorimeters were employed, data were taken in numerous operations each using a different energy input rate, and in the case of lead, three different samples were used. Also, before making measurements for each metal, the specific heat capacity of copper was deter-

mined in order to compare the result to that obtained previously in the extensive measurements on copper¹⁵. For each metal, all data reflected a reproducibility of ± 1.0 per cent, after applying the corrections given by Equations (2) and (3); the measurements made on copper agreed with those obtained previously within the reproducibility of ± 1.0 per cent.

B. SAMPLES

The specific heat capacity of three pure metals were determined in the calorimeters described above. One gold, one zinc and three lead samples were used.

a. Gold

The sample used was a cylinder three inches long by one inch in diameter with a weight of 659.7159 grams. The gold stock, from which the sample originated, had, according to the supplier*, a purity equal to or greater than 99.999 weight per cent.

The average chemical analysis of the gold stock used to make the sample is given in Table I.

A residual resistivity ratio analysis on the sample, made at the Cryogenics Division of the Institute for Basic Standards of the National Bureau of Standards, showed an approximate purity of 99.9998 weight per cent. This analysis

*Degussa (Zweingniederlassung Hanau), Germany.

TABLE I
SPECTROGRAPHIC RESULTS FOR GOLD SAMPLE

Impurities	Average Content (ppm)*		
Iron	0.4	to	2.5
Silver	0.2	to	3.3
Copper	0.1	to	---
Aluminum	0.1	to	0.35
Nickel	0.1	to	0.3
Paladium	0.1	to	2
Platinum	3	to	8
Bismuth	2	to	---

*(ppm) = parts per million assumed to be by weight.
No detail was given by the supplier.

was based on the increasing resistivity observed in metals by increasing impurities. The ratio of the residual resistivity at 4°K to the residual resistivity at 273°K is determined for a sample of known purity and impurities concentration. The ratio for a sample of known purity is related to the sample of unknown purity, assuming that at 4°K the only contribution to the residual resistivity is due to the impurity concentration (see Appendix A).

b. Lead

Three samples were used for this metal. One sample was prepared by melting lead bars obtained from United Mineral and Chemical Corporation* into a high purity stabilized zirconia crucible. A high frequency furnace was used to melt the lead. The sample was then cast into a low carbon steel can (around 0.2 weight per cent carbon). The can was around 0.035 inch in thickness t , 1.0 inch in diameter D , and 2.75 inches in length L . The weight of the can was 48.5199 grams (this includes the seal ring). The weight of the can plus lead was 420.0500 grams. Figure 7 shows the general diagram of the can used. Prior to casting, the can was very carefully cleaned with nitric acid.

During the melting and casting the molten lead was flushed with helium to minimize oxidation of the lead. The

*United Mineral and Chemical Corporation, 129 Hudson Street, New York, New York, 10013

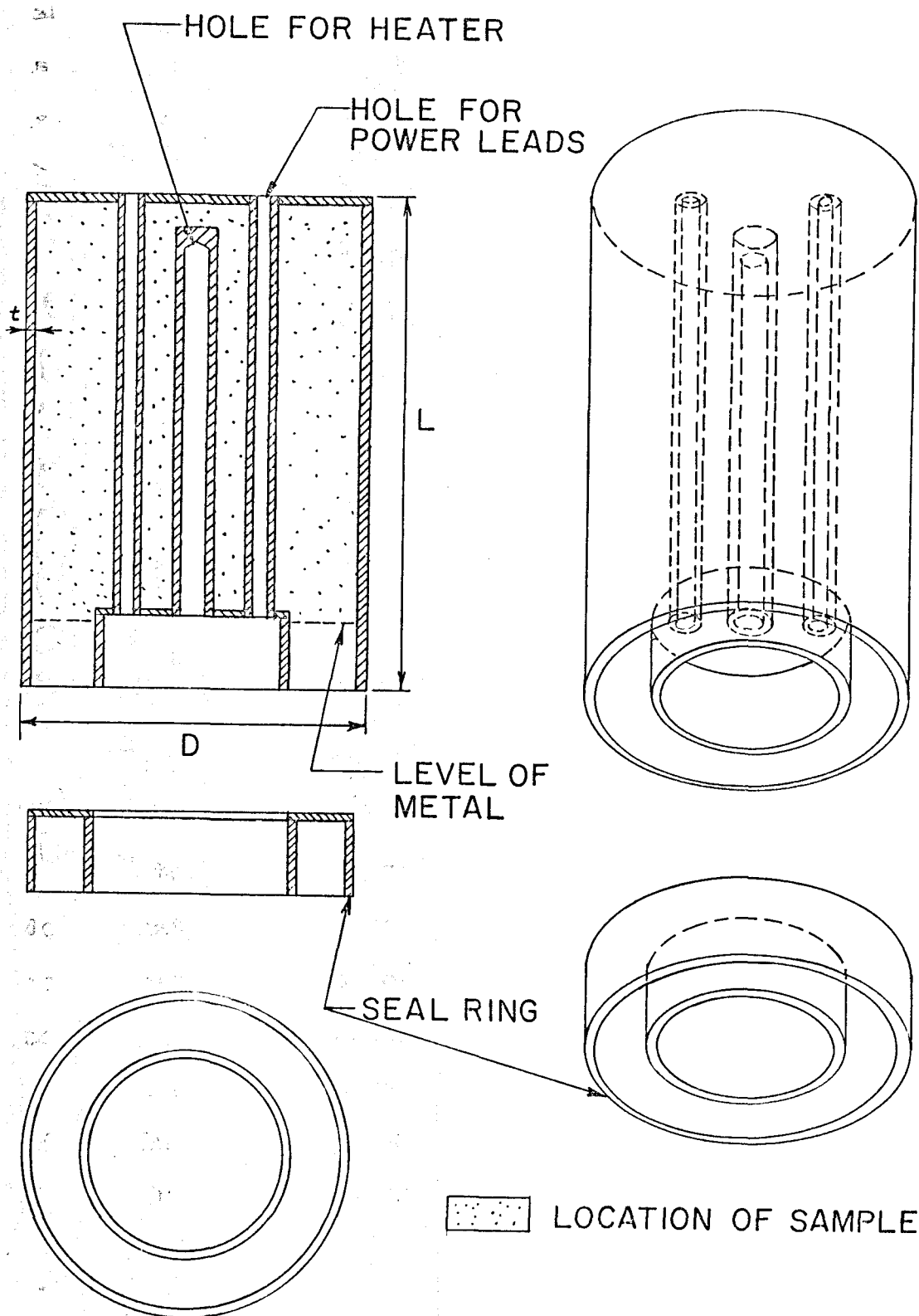


Figure 7. General diagram of the low carbon steel can used to cast lead and zinc.

can was sealed by welding on it a ring of the same material as the rest of the can (Figure 7). The seal ring was placed as close as possible to the cast lead in order to minimize the empty space inside the can.

According to the producer the average purity of the lead used to make the sample was 99.9999 per cent. A spectrographic analysis made on a piece of the sample before it was cast in the can is given in Table II. No composition analysis was made on the sample after the experiments were finished.

The second sample was a single crystal obtained from Material Research Corporation*. The single crystal was prepared by zone refining. The sample was one inch in diameter and three inches long, and its weight was of 394,1880 grams.

The holes for the heater and the leads for the single crystal were machined at liquid nitrogen temperature in an attempt to avoid recrystallization of the sample prior to the determination of the specific heat capacity. The result was not completely satisfactory; small grains, about one millimeter in diameter, were subsequently observed around the machined holes. Basically most of the sample was mainly a big grain after being machined, so the sample will be referred in any future comment as a single crystal.

* Material Research Corporation, Orangeburg, New York
10962

TABLE II

SPECTROGRAPHIC RESULTS FOR THE CANNED LEAD SAMPLE

Impurities	Average Content (ppm)*	Impurities	Average Content (ppm)*
Silver	1	Gold	2
Berlium	1	Calsium	10
Hafnium	10	Iron	6
Magnesium	2	Iridium	100
Antimony	6	Sodium	20
Tantalum	40	Rhodium	20
Vanadium	1	Silicon	50
Thulium	4	Titanium	150
Aluminum	4	Zinc	20
Bismuth	1	Boron	2
Cesium	40	Cadmium	6
Magnese	1	Gallium	1
Rubidium	10	Potassium	4
Scandium	2	Niobium	4
Tungsten	20	Tin	1
Lutetium	10	Thallium	4
Arsenic	20	Zirconium	4
Copper	2	Barium	10
Indium	20	Cobalt	4
Molybdenum	1	Lithium	1
Phosphorus	100	Nickel	4
Thrium	20	Strontium	40

*(ppm) = parts per million by weight.

The third sample was polycrystalline, also from Material Research Corporation. Its weight was 360.2710 grams. The average purity of the type of lead used to make the second and third samples is 99.999 weight per cent, as given by the producer. The average mass spectrographic analysis of the lead stock used to make the sample is shown in Table III.

c. Zinc

The zinc sample was cast into a can in a similar way as the lead sample. The can was of similar material as that used with lead. The can was three inches long, one inch in diameter and approximately 0.06 inch in thickness. The average purity given by the producer of the zinc used to make the sample is 99.9999 weight per cent. No analysis of the sample was made after it had been used in the calorimeter. The weight of the can was 89.7318 grams and the weight of can plus zinc was 375.6745 grams.

C. GENERAL COMMENTS

The specific heat capacity of the lead and zinc samples cast into the low carbon steel can was determined at different heating rates in the solid region prior to the determination of the specific heat capacity in the liquid region. This was done in order to obtain sufficient data in the solid region before any high degree of contamination or reaction could occur between the liquid lead or zinc and the can.

TABLE III

SPECTROGRAPHIC ANALYSIS FOR THE UNCANNED LEAD SAMPLES

Impurities	Average Content (ppm)*	Impurities	Average Content (ppm)*
Lithium	0.01	Silver	0.1
Beryllium	0.005	Cadmium	0.04
Boron	0.03	Indium	0.05
Fluorine	0.01	Tin	2.
Sodium	0.3	Antimony	0.4
Magnesium	0.1	Tellurium	0.02
Aluminum	0.15	Iodine	0.005
Silicon	1.0	Cesium	0.01
Phosphorus	0.15	Barium	0.01
Sulfur	1.0	Lanthanum	0.007
Potassium	2.0	Cerium	0.007
Calcium	2.0	Praseodymium	0.007
Scandium	0.01	Neodymium	0.03
Titanium	0.15	Samarium	0.03
Vanadium	0.25	Eurpium	0.04
Chromium	0.03	Gadolinium	0.04
Manganese	0.025	Terbium	0.01
Iron	0.1	Dysprosium	0.03
Cobalt	0.03	Holmium	0.01
Nickel	0.15	Erbium	0.02
Copper	0.4	Thulium	0.01
Zinc	0.3	Ytterbium	0.03
Gallium	0.003	Lutetium	0.01
Germanium	0.04	Hafnium	0.03
Arsenic	0.01	Tantalum	1.0
Selenium	0.004	Tungsten	0.03
Bromine	0.1	Rhenium	0.02
Rubidium	0.03	Osmium	0.02
Strontium	0.002	Iridium	0.02
Yttrium	0.002	Platinum	0.03
Zirconium	0.004	Gold	0.03
Niobium	0.005	Mercury	0.3
Molybdenum	0.02	Thallium	3.0
Ruthenium	0.03	Bismuth	1.0
Rhodium	5.0	Thorium	0.1
Palladium	0.02	Uranium	0.1

*(ppm) = Parts per million by weight.

Whenever an operation involved the determination of the specific heat capacity in the liquid phase, measurements were also made in the solid phase upon heating. This allowed comparison of results on the solid state, before the lead or zinc were ever melted, with those solid phase results obtained after melting the sample. The fact that all of the results, in both the liquid and solid regions, were within the ± 1 per cent reproducibility is used as an indication that no appreciable contamination or reaction did occur between the can and the lead.

The specific heat capacity for the gold sample was determined on twenty different occasions, sixteen of them made in calorimeter number one and four in calorimeter number two. The energy input rates used for the gold sample were between 69.8 Joules per gram per hour (approximately 500°C per hour at around 1200°K) and 11.6 Joules per gram per hour (approximately 83°C per hour at around 1200°C).

For the case of lead, ten operations were made for the uncanned samples, two of them on the single crystal. The specific heat capacity of the canned sample was determined in seventeen different occasions; seven of them included the determination of the specific heat capacity within the liquid region. The energy input rates were between 15.1 Joules per gram per hour (approximately 113°C per hour at around 590°K) and 61.7 Joules per gram per hour (approximately 460°C per hour at around 590°K).

Finally, the specific heat capacity for the zinc sample was made only on six different occasions, two of which involved the liquid region. Data above 810°K were not obtained for this sample since a leak was formed along the weld of the can and the seal ring. The energy input rates for this sample were between 96.1 Joules per gram per hour (approximately 240°C per hour at 690°K) and 37.6 Joules per gram per hour (approximately 94°C per hour at 690°K).

CHAPTER III

EXPERIMENTAL RESULTS

The present chapter will involve a presentation of the specific heat capacity data obtained for gold, lead and zinc. The results of the gold and lead uncanned samples are based on the use of Equations (1), (2) and (3) in Chapter II. Those results for the canned lead and zinc samples involved a further correction since the heat absorbed by the can had to be subtracted in order to obtain the specific heat capacity of the metal.

Because for each metal a considerable number of data points were obtained, the specific heat capacity dependence on temperature is represented by a functional relationship obtained by using the least squares curve fitting method. The resulting fitted curve is used for the comparison of the specific heat capacity results of this and other investigations and in any further calculation involving the use of the experimental C_p .

The measured melting point and heat of fusion for lead and zinc will also be presented and compared to other results given by the literature.

A. GOLD

The specific heat capacity data for gold, shown in Figure 8, was determined in twenty different operations with

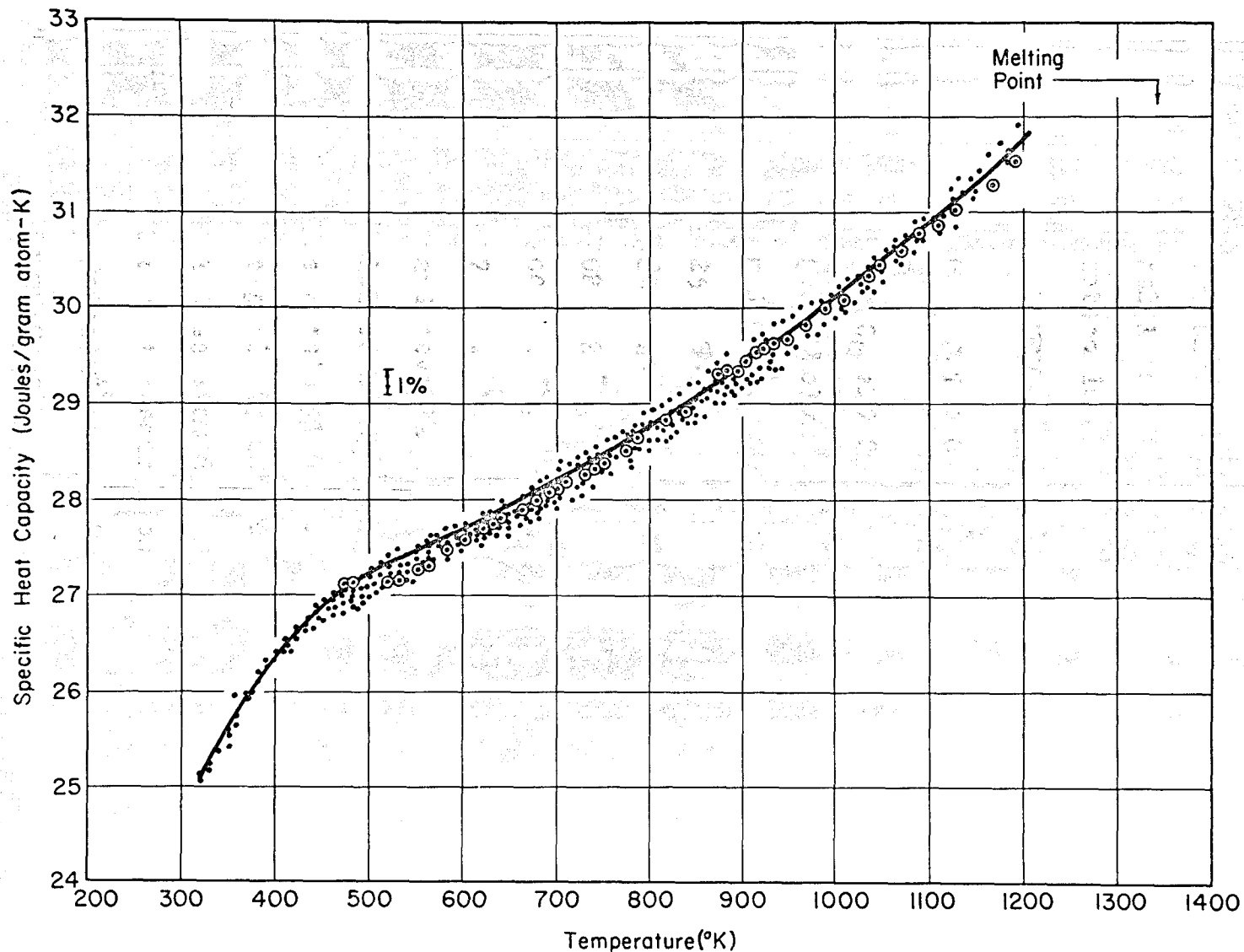


Figure 8. The specific heat capacity C_p for gold as obtained in the present research. The solid curve is the fitted polynomial. The circles represent a single operation.

energy input rates ranging from 11.6 to 69.8 Joules per gram per hour. A total of 514 data points were obtained during all twenty operations.

The polynomial as obtained by using the least square curve fitting method is also shown as a solid line in Figure 8. The fitted polynomial is of the form

$$C_p = C_1T + C_2 + \frac{C_3}{T} + \frac{C_4}{T^2} + \frac{C_5}{T^3} \quad (1)$$

where C_1 , C_2 , C_3 , C_4 and C_5 are constants and T is the temperature in degrees Kelvin.

With C_p in Joules per gram-atom per degree Kelvin,

$$C_1 = +1.425 \times 10^{-2},$$

$$C_2 = -6.763 \times 10^{+0},$$

$$C_3 = +1.208 \times 10^{+4},$$

$$C_4 = -3.200 \times 10^{+6},$$

$$C_5 = +2.376 \times 10^{+8}.$$

The standard deviation of the data as related to the fitted polynomial is 0.1239. Further, 99.4 per cent of the data points lie within ± 1.0 per cent of the curve. This corroborates the capability of the calorimeters to produce the data within ± 1.0 as stated by Brooks et al.¹⁵

The most recent research on gold had been made by Jaeger, Rosenbohn and Bottema¹⁹ in 1932 and Vollmer and Kohlhaas²⁰ in 1968. Their results are shown in Figure 9 together with the polynomial fit as determined in the present research.

The results of Jaeger, Rosenbohn and Bottema¹⁹ were based on the use of a dropping calorimeter where the enthalpy

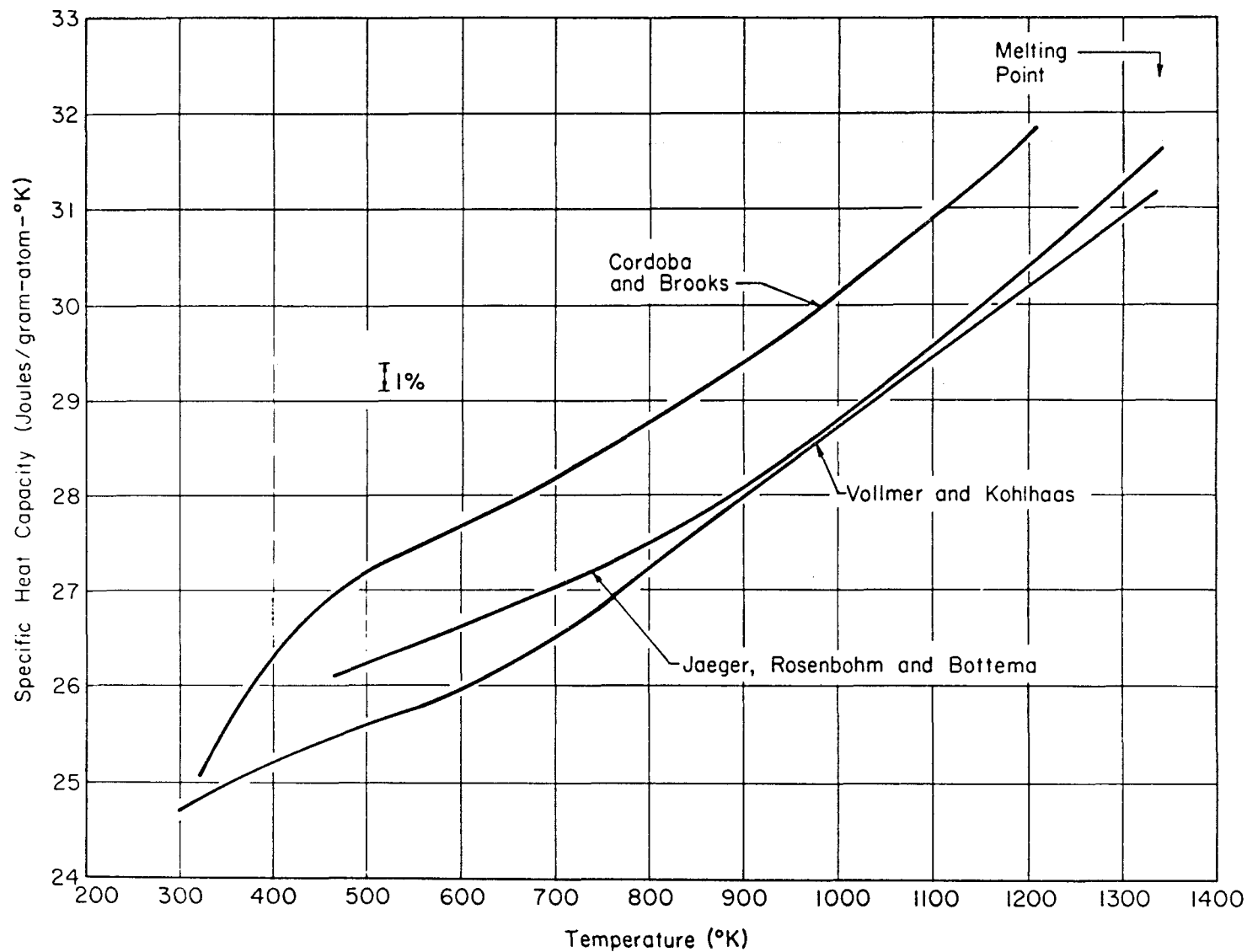


Figure 9. The specific heat capacity C_p for gold as obtained by different investigations.

change was measured with respect to a reference temperature. The slope of the data was then obtained in order to determine the specific heat capacity of gold. Their C_p calculation lies three per cent below the polynomial curve at around 475°K and four per cent at around 1220°K. However, Oriani²¹ noted that the data obtained by Jaeger, Rosenbohn and Bottema¹⁹ are in question since their method to determine the heat effect due to the platinum capsule did not take into account the heat lost by radiation and convection during the descent of the capsule from the furnace to the calorimeter.

Figure 9 also shows a difference in the C_p obtained in the present research with respect to the data of Vollmer and Kohlhaas²⁰. The C_p difference between 600 and 1200°K is around five per cent and decreases to about one per cent at 320°K. Vollmer and Kohlhaas²⁰ stated that their derivations of formulas, where some assumptions are made, form the basis for errors in the calculation of the specific heat capacity which finally leads to an uncertainty of ± 2.0 per cent in the C_p results. No variation in the reproducibility of their data was given in their report.

B. LEAD

The determination of the specific heat capacity for lead involved twenty-seven different operations. The energy input rates used ranged from 15.1 to 61.7 Joules per gram per hour. Nine operations were made using the uncanned poly-

crystalline sample and two were made using the single crystal. The use of the canned sample involved seven operations into the liquid phase. A total of 478 data points were obtained for the solid phase and 136 for the liquid phase.

The results of the different calculations involving the use of Equations (2) and (3) in Chapter II in order to calculate C_p are shown in Appendix D from Table XXXI to Table LVII.

The specific heat capacity as obtained from Equation (3) in Chapter II gave in the case of the canned specimen the total specific heat of can plus lead. Thus, a final correction had to be made in order to obtain the specific heat capacity of lead. The correction is based on a heat balance and yields the formula

$$C_{p\text{Lead}} = \frac{C_{p\text{S}}m_{\text{S}} - C_{p\text{Iron}}m_{\text{C}}}{m_{\text{Lead}}} \quad (2)$$

where

$C_{p\text{Lead}}$ = specific heat capacity of lead,

C_p = specific heat capacity of lead plus can as obtained in Equation (3) in Chapter II,

m_{S} = mass of lead (m_{S}) plus the mass of the can (m_{C}),

and $C_{p\text{Iron}}$ = specific heat capacity of iron.

No chemical analysis was made on the steel can used, but microstructural observation indicated that the can was a low carbon steel around 0.2 weight per cent carbon in iron. The specific heat capacity used for the low carbon steel can was obtained from the measurements made on pure iron by Kollie

et al.²². The data of McElroy²³ has shown that the difference in the specific heat capacity for pure iron and a 0.8 weight per cent low carbon steel (eutectoid composition) is within the ± 1.0 per cent reproducibility of his measurements. Furthermore, the specific heat capacity data of iron of McElroy²³ and of Kollie et al.²² agree within the ± 1 per cent reproducibility, so the tabulated iron data given by Kollie et al.²² were used in Equation (2) for the specific heat capacity of the steel can in order to determine the final specific heat capacity of lead. In Equation (2) the product $C_{p\text{Iron}} m_c$ was approximately 34 per cent of the product $C_{p\text{mS}}$. This means that a variation of one per cent in the specific heat capacity of iron will produce an error of ± 0.7 per cent in the specific heat capacity of lead.

The final results of the specific heat capacity obtained by using Equation (2) in the present chapter are shown in Figure 10 and are also tabulated for each operation in Appendix D from Table XXXI to Table LVII.

The reproducibility of the results as obtained from Equation (3) in Chapter II was within ± 1 per cent; the use of Equation (2) in the present chapter increased that difference, as will be demonstrated. If the maximum absolute error in two different results of C_p (Equation(2)) obtained at a given temperature is 2.0 per cent (that is, $\pm 1\%$) as obtained from Equation (3) in Chapter II, the error after using Equation (2) in this chapter would be determined

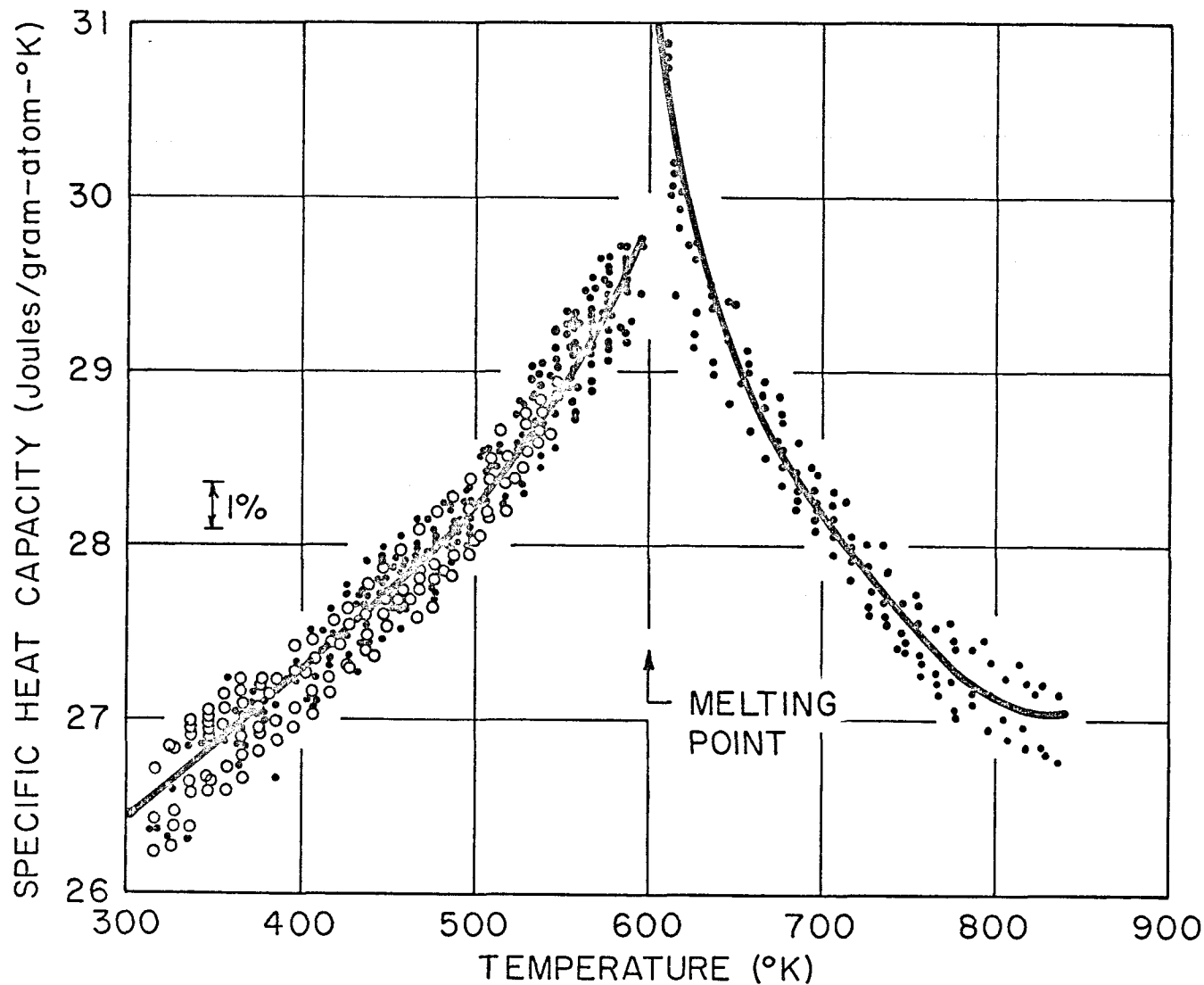


Figure 10. The specific heat capacity C_p for lead as obtained in the present research. The solid curve represents the fitted polynomial. o represents the data of the uncanned specimens.

as follows. Let case number one be given by

$$(C_{p\text{Lead}})_1 = \frac{C_{p1} m_s - C_{p\text{Iron}} m_c}{m_{\text{Lead}}} \quad (3a)$$

where C_{p1} is one of the results obtained from Equation (3) in Chapter II. Let case number two be given by

$$(C_{p\text{Lead}})_2 = \frac{C_{p2} m_s - C_{p\text{Iron}} m_c}{m_{\text{Lead}}} \quad (3b)$$

where C_{p2} is another result obtained by using Equation (3) in Chapter II, and differs from C_{p1} by 2.0 per cent; that is

$$C_{p2} = (1 + 0.02) C_{p1} \quad (4)$$

The difference in the specific heat capacity for lead as obtained from the two different results is given by

$$C_{p\text{Lead}} = (C_{p\text{Lead}})_1 - (C_{p\text{Lead}})_2 \quad (5)$$

Substituting Equations (3a), (3b) and (4) in Equation (5)

$$C_{p\text{Lead}} = 0.02 C_p \frac{m_s}{m_{\text{Lead}}} \quad (6)$$

The average value of the results obtained from Equation (3a) and (3b) is given by

$$(C_{p\text{Lead}})_{\text{average}} = \frac{1.01 C_p m_s - C_{p\text{Iron}} m_c}{m_{\text{Lead}}} \quad (7)$$

The percent difference E_M for these cases obtained by using Equations (6) and (7), is

$$\begin{aligned} E_M &= \frac{100(0.02 C_p m_s / m_{\text{Lead}})}{1.01 C_p m_s / m_{\text{Lead}} - C_{p\text{Iron}} m_c / m_{\text{Lead}}} \\ &= \frac{2.0 C_p m_s}{1.01 C_p m_s - C_{p\text{Iron}} m_c} \end{aligned} \quad (8)$$

As can be observed in Appendix D from Tables XXXI to LVII the $C_{p\text{Iron } m_c}$ is around 34 per cent of $C_{p m_s}$. Thus, Equation (8) becomes

$$E_M = \frac{2.0 C_{p m_s}}{(1.01 - 0.34) C_{p m_s}} = 2.9\% \quad (9)$$

Equation (9) indicates that if a reproducibility in the calorimeter data of ± 1 per cent is obtained, a reproducibility in the specific heat capacity of lead of around ± 1.5 per cent would be obtained. The reproducibility obtained in Equation (9) will be changed only by ± 0.01 per cent if an error of ± 1.0 per cent exist in the specific heat capacity of iron.

a. Solid Phase

The least square curve fitting method was used to determine two different polynomials, one to fit the data of the solid phase and the other to fit the data of the liquid phase. The polynomial for the solid phase is also given by Equation (1), where, for the specific heat capacity in Joules per gram-atom per degree Kelvin, the constants are

$$\begin{aligned} C_1 &= +0.6843185385 \times 10^{-1}, \\ C_2 &= -0.6172149452 \times 10^{+2}, \\ C_3 &= +0.4532106482 \times 10^{+5}, \\ C_4 &= -0.1054424630 \times 10^{+8}, \\ C_5 &= +0.9096087375 \times 10^{+9}. \end{aligned}$$

The standard deviation of the 478 data points with respect to the fitted polynomial is 0.1726. This low value for the standard deviation indicates that a great amount of

the data is located close to the fitting curve; 92.05 per cent of the data points are within ± 1.0 per cent of the polynomial curve. (This ± 1.0 per cent variation on the solid lead specific heat capacity indicates that the reproducibility of 92.05 per cent of the lead data as obtained from Equation (3) in Chapter II is ± 0.7 per cent from 300 to 600°K.) Any future calculation involving C_p will be made by using the polynomial curve described above.

A comparison of the results obtained in this research with other investigations is shown in Figure 11. The most recent investigations are those by Pochapsky²³ in 1953, Douglas and Dever²⁴ in 1954 and Leadbetter²⁵ in 1968.

The investigation of Pochapsky²³ on the specific heat capacity was made by using a fine wire which was included in one arm of a balanced Wheatstone bridge. A pulse of current was introduced in the battery circuit, which heated the wire and unbalanced the bridge. The specific heat capacity of the wire was calculated from the deflection of a ballistic galvanometer detector. Pochapsky²³ estimated a maximum absolute error for the specific heat capacity of less than five per cent.

Figure 11 shows that Pochapsky's data are around one per cent below the present data for temperatures below 450°K, and the difference increases to around four per cent at 600°K. The difference is well within his estimated error.

The data obtained by Douglas and Dever²⁴ were obtained

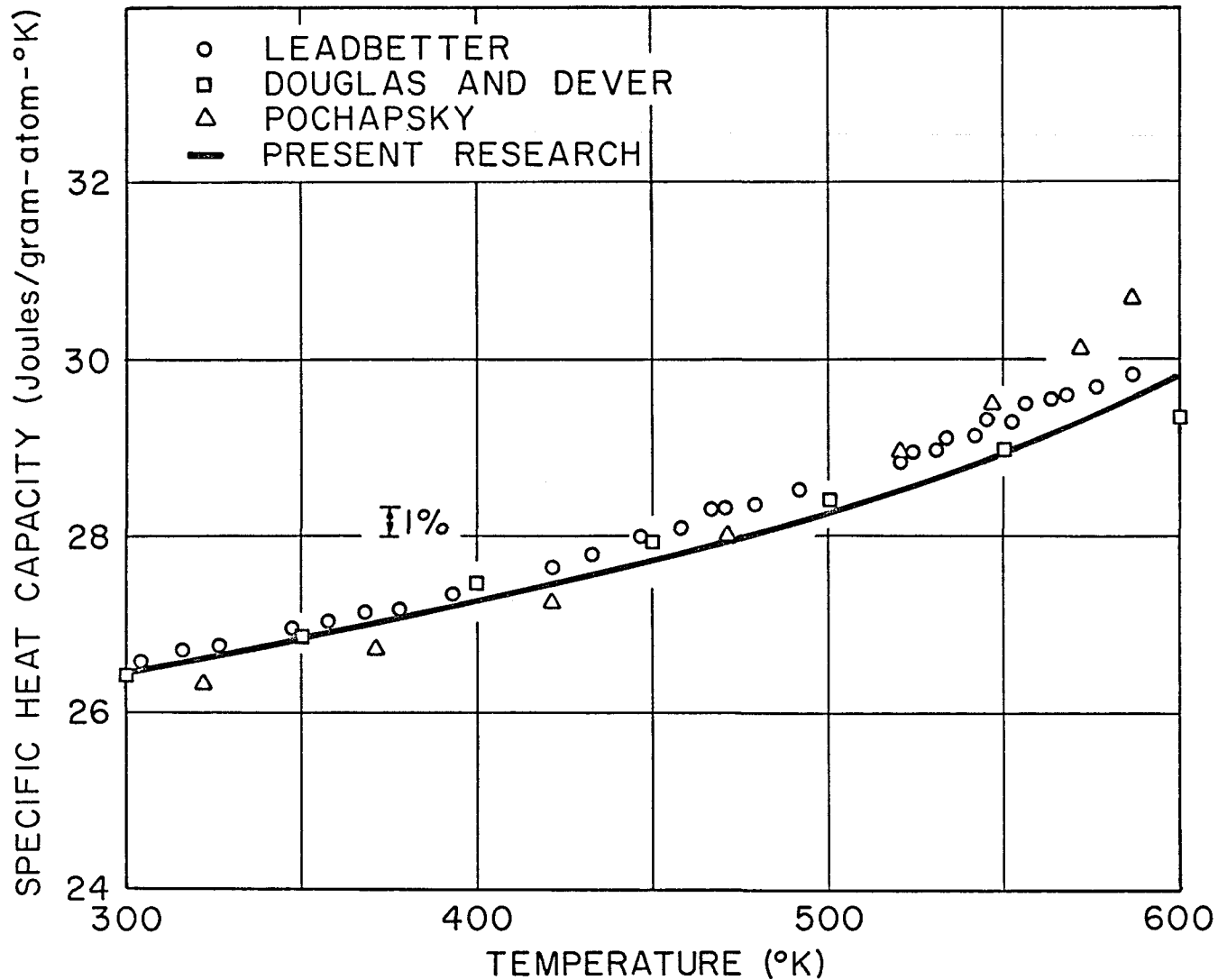


Figure 11. The specific heat capacity for solid lead as obtained by different investigations.

by using a "dropping calorimeter" where the enthalpy change of lead with respect to temperature was measured by using 0°C as reference temperature. The specific heat capacity was determined by differentiating a polynomial fitting the enthalpy change data. Below 550°K their tabulated data are within one per cent of the present results; at 600°K their data are about one per cent below the present results. It is clear that very good agreement in the solid phase has been obtained between Douglas and Dever²⁴ and the present research.

The most recent research, by Leadbetter²⁵, who used an adiabatic calorimeter, produced data points which are around 0.4 per cent higher than the result of the present research, for temperatures below 400°K ; above 400°K his data are one per cent higher. The C_p data obtained by Leadbetter is then within the reproducibility of the data of the present research.

b. Liquid Phase

The polynomial obtained for the liquid phase by using the least square fitting method is given by

$$C_p = \frac{C_1}{T^4} + \frac{C_2}{T^3} + \frac{C_3}{T^2} + \frac{C_4}{T} + C_5 \quad (10)$$

where, for C_p in Joules per gram-atom per degree,

$$C_1 = +29345.14 \times 10^{+1},$$

$$C_2 = -16348.52 \times 10^{+8},$$

$$C_3 = +34140.33 \times 10^{+5},$$

$$C_4 = -31605.27 \times 10^{+2},$$

$$C_5 = +11199.68 \times 10^{-1},$$

and T = absolute temperature in degrees Kelvin.

The standard deviation of the 136 data points with respect to the fitted polynomial is 0.2391; and above 610°K 97.7 per cent of the data points are within ± 1.0 per cent from the polynomial.

Figure 12 shows data points obtained for temperatures very close to the melting point. Most data points were obtained by heating the sample continuously from the solid phase; nevertheless, some operations involved heating the sample to temperatures around 840°K and then allowing it to cool to temperatures close to the melting point, but still in the liquid region. Power was reapplied and data were taken after the system was under control. It was impossible to obtain proper control below 610°K so with this procedure it was impossible to check the data points between the melting point and 610°K . The data points between 600°K and 610°K (obtained by continuously heating the sample from the solid phase) could be high due to pieces of solid metal not completely melted, or it could be a normal behavior of the specific heat capacity of the liquid at temperatures close to the melting point. The latter possibility would mean that there is a very sharp increase of the enthalpy within this ten degrees temperature interval.

Figure 13 shows the specific heat capacity in the liquid region obtained by different investigations. It can be observed that a great discrepancy exists between the dif-

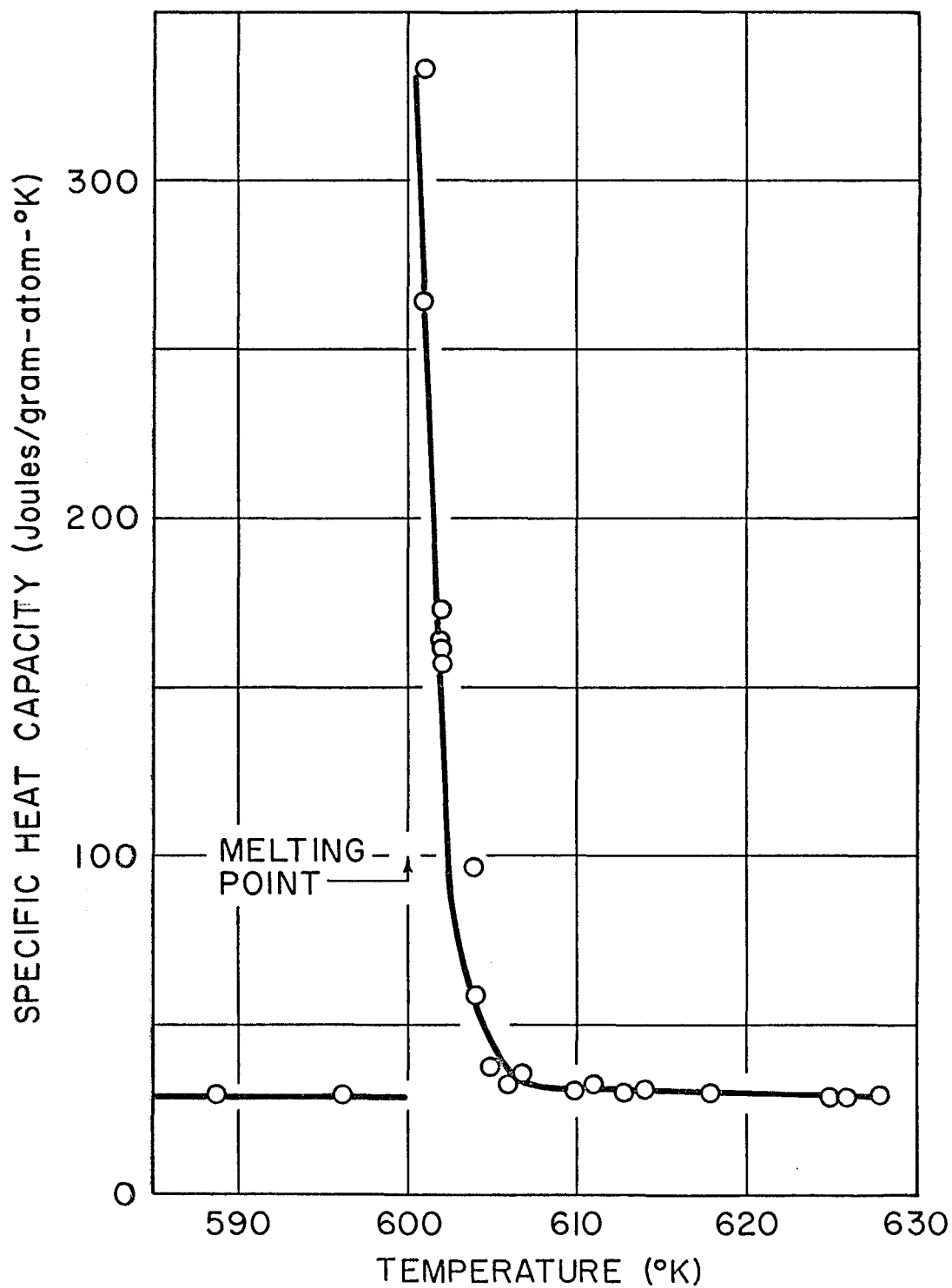


Figure 12. Specific heat capacity for lead at temperatures close to the melting point.

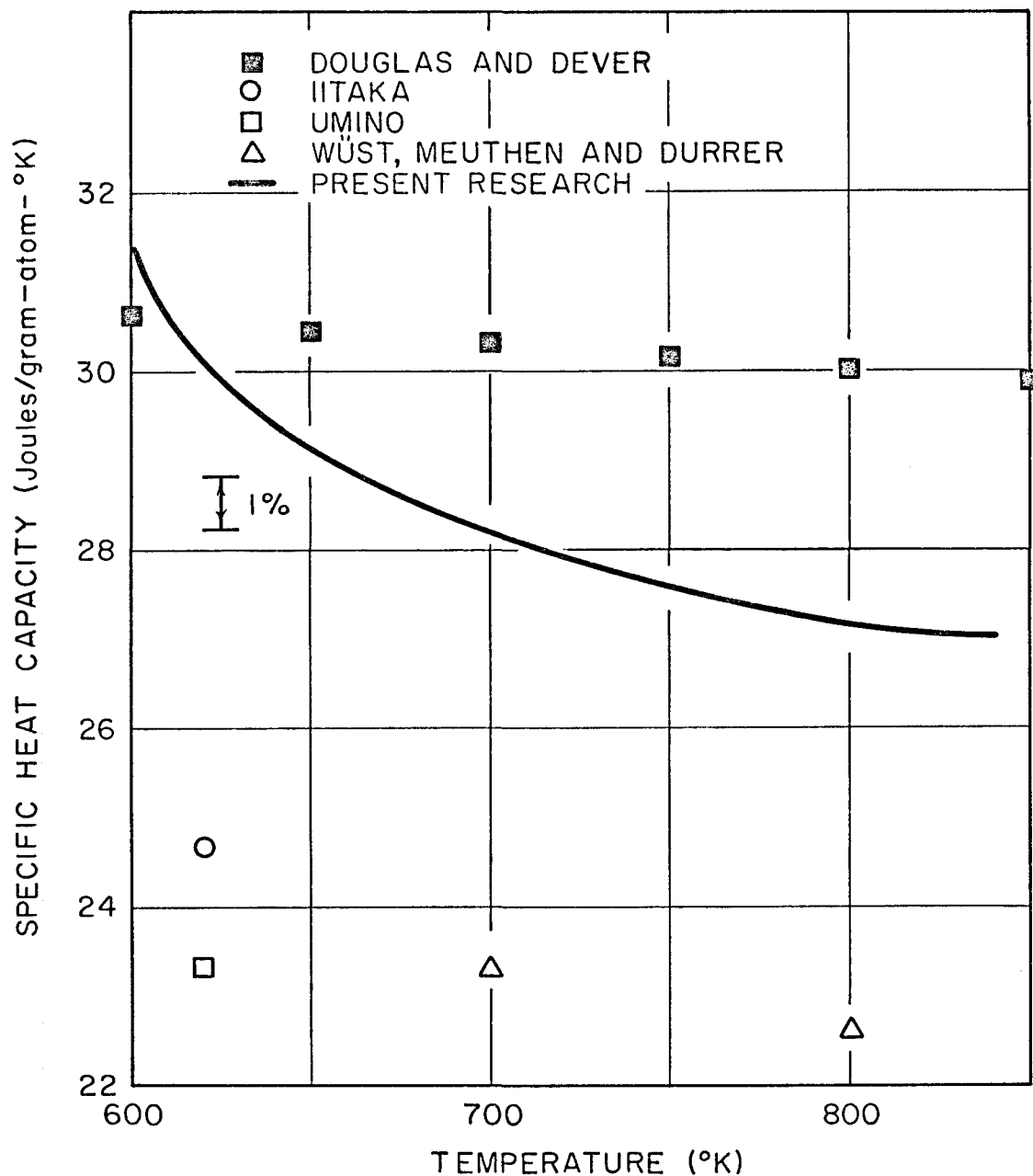


Figure 13. The specific heat capacity for liquid lead as obtained by different investigations.

ferent results. Douglas and Dever²⁴ made calculations on the specific heat capacity by measuring the enthalpy change with respect to zero degree centigrade. At temperatures close to the melting point their data agree within ± 1.0 per cent with the polynomial obtained in this research, but above 650°K , the difference in the results increases up to five per cent at 840°K .

Iitaka²⁶ and Umino²⁷, by using a dropping calorimeter, determined each only one data point in the liquid, it being close to the melting point (Figure 13). These points from Iitaka²⁶ and Umino²⁷ are nine and eleven per cent, respectively, below the present research polynomial.

Wüst, Menthen and Durrer²⁸, by using a dropping calorimeter, obtained data points in the liquid (Figure 13) which are ten per cent below the curve obtained in the present research.

In the present research, the melting point of lead was found to be $600.6 \pm 0.2^{\circ}\text{K}$. The melting point for lead, reported by Mellor²⁹ and Kelley³⁰, both based on compilations of data from different investigations, is 600.6°K ; this value is in very good agreement with the result obtained in the present research. Since the temperature of the sample is measured by using a thermocouple located on the outside of the steel can, the result obtained for the melting point indicates that a very negligible temperature gradient exist across the sample. The measured heat of fusion was 22.85

± 1.0 Joules per gram-atom, which is one per cent below the heat of fusion reported by Douglas and Dever²³. The uncertainty is due to the lack of exact knowledge of the initiation and end of melting. The time was measured by observing the upset that occurred in the temperature controllers during the phase transformation. The calculation of the heat of fusion by measuring the time that the sample remained at 600.6°K gave a considerable error, since a small increase of temperature occurred always prior to the complete melting of the lead, which gives an erroneous appreciation of the time used for melting.

An empty space of around 0.1 cubic centimeters (6.1×10^{-3} cubic inches) was left between the lead in the can and the seal ring. If we assume this space to be empty at room temperature and the lead vapor formed at high temperature to be ideal, the 2.0×10^{-13} moles of vapor formed at 840°K would require an energy of 3.7×10^{-8} Joules*. This power is obviously very negligible so no effect due to vaporization was produced in the C_p results. The amount of energy for vaporization is actually smaller than the calculated 3.7×10^{-8} Joules since the expansion of lead is greater than that of iron, and since the air trapped during the welding of the

*The calculations of the heat of vaporization and amount of moles at 840°K were calculated from vapor pressure versus temperature data obtained from: American Society for Metals. "Heat Treating, Cleaning and Finishing," Metals Handbook, 2: 269, 1967.

seal ring decreases the amount of vaporization.

C. ZINC

The determination of the heat capacity for zinc was made in six different operations with energy input rates ranging from 37.6 to 96.1 Joules per gram per hour. 212 data points were obtained, 20 of them in the liquid region. The resulting data points are shown in Figure 14 together with the polynomials fitted into the solid and liquid data.

The calculations of the data points made by using Equations (2) and (3) in Chapter II and Equation (3) in the present chapter are shown in Appendix E, from Table LVIII to Table LXIII.

a. Solid Phase

The polynomial obtained for solid zinc was of the same type as that obtained for gold and given by Equation (1) in the present chapter. For the C_p in Joules per gram-atom per degree, the constants of the equation are

$$C_1 = +162.07 \times 10^{-3},$$

$$C_2 = +236.14 \times 10^{+0}$$

$$C_3 = +161.54 \times 10^{+3},$$

$$C_4 = -438.84 \times 10^{+5},$$

$$C_5 = +436.57 \times 10^{+7}.$$

A standard deviation of 0.1591 was obtained, with 92.6 per cent of the data points located within ± 1.0 per cent of the fitted polynomials. A further analysis made on the

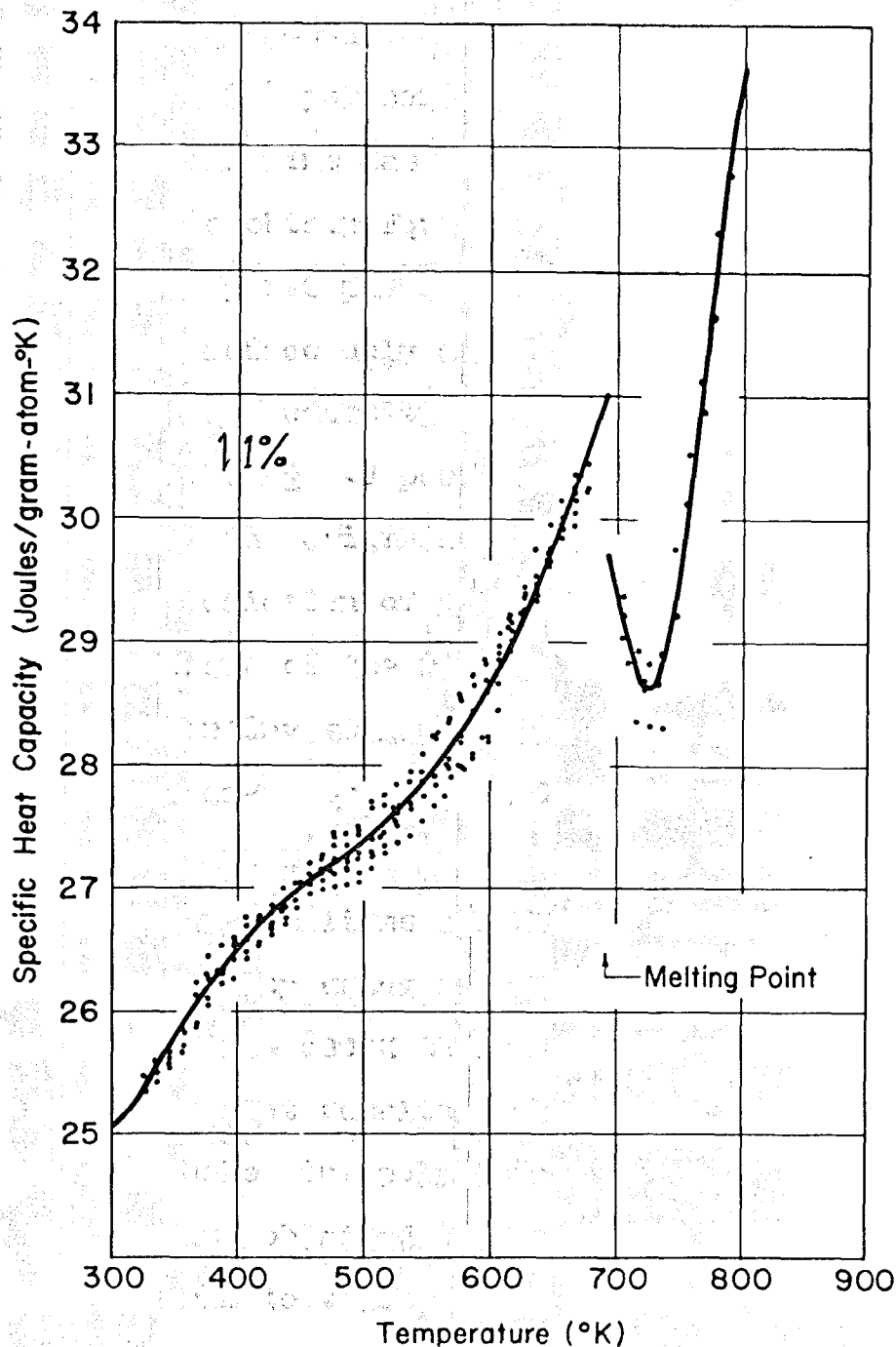


Figure 14. The specific heat capacity for zinc as obtained in the present research. The solid curve is the fitted polynomial.

C_{pZinc} data as obtained from Equation (3) in the present chapter shows that a variation of ± 1.0 per cent in the C_p data as obtained in Equation (3), Chapter II, will produce a variation of ± 1.4 per cent. This variation in the specific heat capacity of zinc was obtained by using a method similar to that used to obtain Equation (9) in the present Chapter. A variation of ± 1.0 per cent in the specific heat capacity of iron will produce only a variation of ± 0.4 per cent in the specific heat capacity of zinc. Since most of the data points are within ± 1.0 per cent of the polynomial curve, it indicates that the original data was obtained from the calorimeter at a variation of ± 0.7 per cent.

A comparison of the results of the present investigation with other investigations is shown in Figure 15. Behrens and Drucker³¹, by using a dropping calorimeter, obtained data which are within ± 1.0 per cent of the present results. Eastman, Williams and Young³² determined the specific heat capacity by using a dropping calorimeter also. For temperatures below 600°K their data are within ± 1.0 per cent of the present results. Their data point at 673°K is two per cent below the polynomial.

The results obtained by Jaeger and Poppema³³, using a dropping calorimeter, are within ± 1.0 per cent of the present research polynomial for temperatures below 600°K . The data point given at 673°K is two per cent above the curve. Figure 15 also shows the data points obtained with a drop-

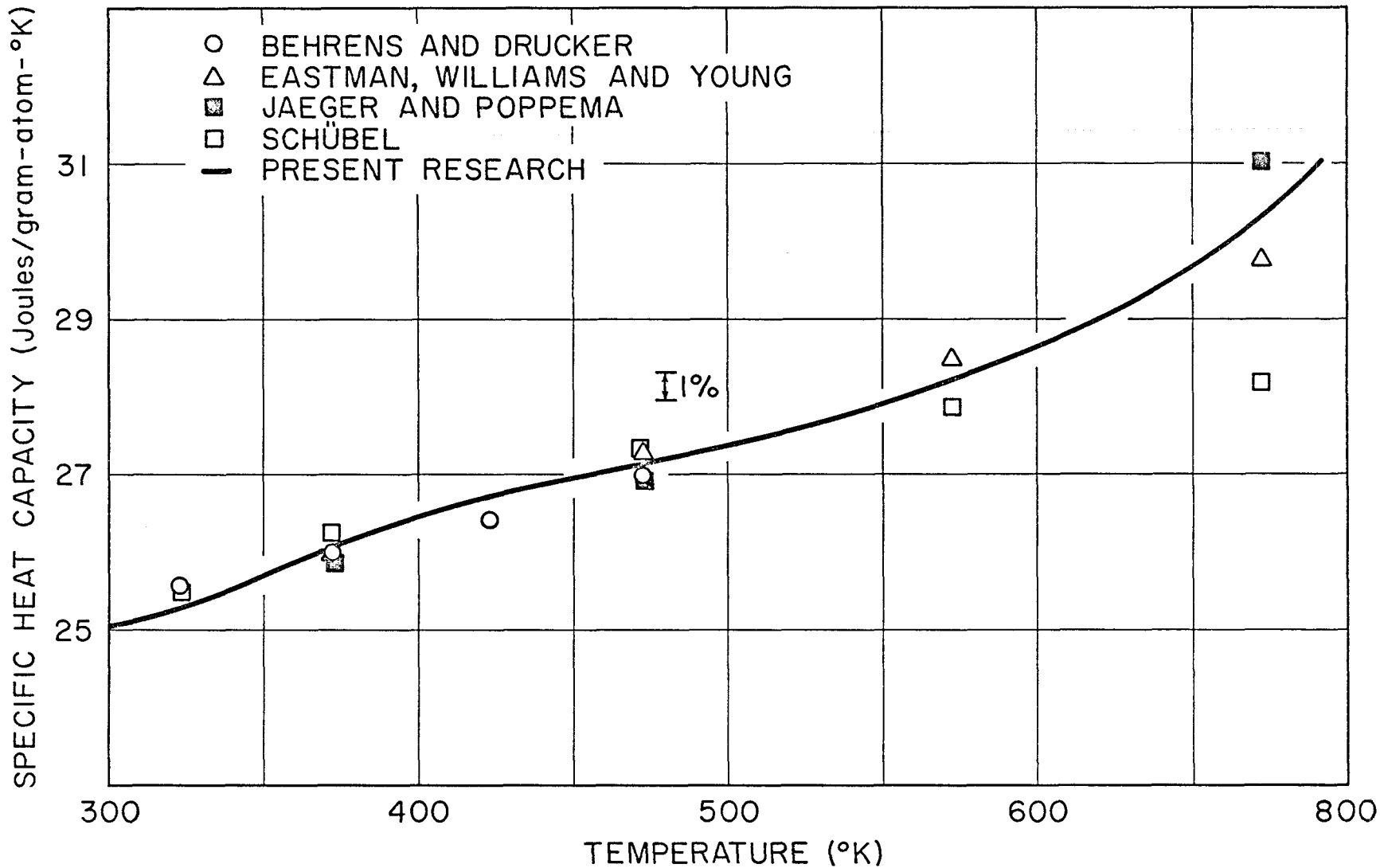


Figure 15. The specific heat capacity for solid zinc as obtained by different investigations.

ping calorimeter by Schübel³⁴ which for temperatures below 600°K are at ± 1.0 per cent from the polynomial, and at 673°K are 6.8 per cent below the present research's polynomial. In general, it is observed that good agreement exists for temperatures below 600°K, and that the greatest discrepancy exist at temperatures close to the melting point.

Most investigations had problems with the evaporation of zinc. In the present research, the container was sealed so that a very small space, (around 0.02 cubic centimeters) could be left inside the can. An analysis, similar to that described for lead, showed that at temperatures above the melting point the estimated 0.02 cubic centimeters in free space could not affect the data of the liquid phase, and much less the solid data (see next Section).

b. Liquid Phase

The polynomial obtained by fitting the data points of the liquid phase is given by

$$C_p = C_1 + C_i T^{i-1} \quad (i = 2, \dots, 7) \quad (10)$$

where, for C_p in Joules per gram-atom per degree,

$$C_1 = -243.64 \times 10^{+3},$$

$$C_2 = +111.91 \times 10^{+1},$$

$$C_3 = -974.25 \times 10^{-3},$$

$$C_4 = -312.35 \times 10^{-5},$$

$$C_5 = +791.32 \times 10^{-8},$$

$$C_6 = -672.87 \times 10^{-11},$$

$$C_7 = +204.02 \times 10^{-13}.$$

The standard deviation of the data points with respect to the above polynomial is 0.2578; the data points were all within ± 1.0 per cent from the polynomial.

It was mentioned in Chapter II that a leak in the can prevented measurements above 800°K.

A comparison of the fitted polynomial with the values chosen by Hultgren et al.³⁵ from the heat content data obtained from different investigations is shown in Figure 16. The different heat content values used by Hultgren et al.³⁵ have a range of about ± 418.4 Joules per gram-atom, which probably causes considerable error in the slope of heat content data versus temperature. Thus, the discrepancy in C_p values of Hultgren et al.³⁵ and those of this research is probably due to errors in the enthalpy. The maximum difference as observed in Figure 16 was of five per cent at around 725°K.

The melting point of the zinc was determined at 693.0°K ± 0.1 which is 0.04 per cent higher than the value given by Hultgren et al.³⁵. The heat of fusion was 99.0 ± 4 Joules per gram-atom. Hultgren et al.³¹ lists data for heat of fusion for zinc ranging from 92.6 Joules per gram-atom to 125.0 Joules per gram-atom, all obtained from different investigations. The results obtained in the present research were not affected by the vapor (which is assumed behaves as an ideal gas) formed at high temperature in the estimated free space inside the container. For the zinc sample a much

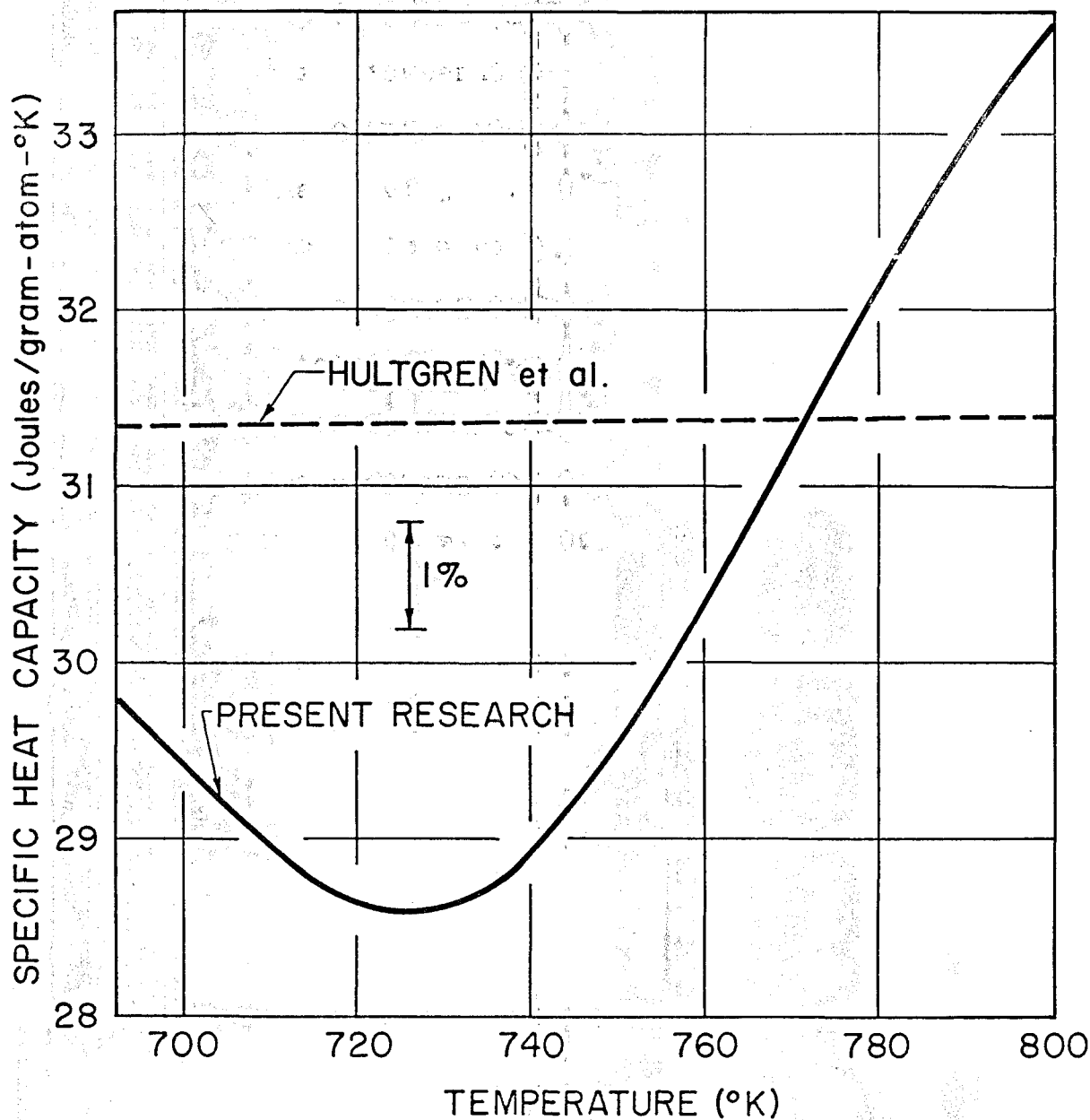


Figure 16. The specific heat capacity for liquid zinc as obtained by different investigations.

better fit was obtained between the seal ring and the zinc inside the can.

By assuming that the empty space is filled completely with vapor at high temperature, and that the vapor behaves as an ideal gas, the 4×10^{-9} moles of vapor formed at 840° required an energy of 3.6×10^{-4} Joules. This energy is obviously too small to have any effect in the C_p results. This effect is even going to be smaller due to the higher expansion coefficient of zinc with respect to iron, which eventually reduces the empty space. Also, any air trapped in the empty space during the welding of the seal ring will diminish the amount of vapor formed.

CHAPTER IV

ANALYTICAL DETERMINATION OF THE SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME

The experimental results of the specific heat capacity at constant pressure C_p were presented in Chapter II for the three different metals used in the present research. The calculation of the specific heat capacity at constant volume C_v from the C_p values obtained experimentally requires the determination of the dilation term C^d , since

$$C_v = C_p - C^d \quad (1)$$

where

$$C^d = \frac{a_v^2}{\beta_v} TV \quad (2)$$

and a_v = coefficient of volume thermal expansion,

β_v = isothermal compressibility,

V = atomic volume,

and T = absolute temperature.

Since the existing literature does not contain sufficient data on the temperature dependence of the coefficient of volume thermal expansion, the isothermal compressibility and the atomic volume, it was required to make an analysis of the error involved in the different approximations which can be used to determine C^d . The approximations, which were explained in Section C, Chapter I, are as follows:

a) The use of the Gruneisen's constant Γ which is related to C^d by

$$C^d = \Gamma \alpha_v C_v T, \quad (3)$$

where

$$\Gamma = \frac{V/\beta_v}{C_v/\alpha_v} \quad (4)$$

To use this expression for C^d Gruneisen's constant can be determined from existing data at a given temperature and then assumed to be constant over a temperature range; then, only values of α_v , (which are much more plentiful than β_v) are needed to calculate C^d .

b) The use of the Nernst-Lindemann approximation, where C^d is related to a constant A by the equation

$$C^d = A C_p^2 T \quad (5)$$

where

$$A = \frac{\alpha_v^2 V}{\beta_v C_p^2} \quad (6)$$

The constant A can be determined from existing data at a given temperature, and then assumed to be constant over a temperature range.

c) Extrapolation of the existing low temperature data for α_v , V and β_v . The usual experimental quantity is not β_v but the adiabatic compressibility β_A ; β_v is obtained from the relation³⁶

$$\beta_v = \beta_A + \frac{T V \alpha_v^2}{C_p} \quad (7)$$

The uncertainty in the dilation term due to any possible error in α_v , β_v and V can be determined by assuming that each of them is independent from the others. Differentiating Equation (2) and assuming small errors in α_v , β_v and V , the error in C^d at a given temperature will be given by

$$\Delta C^d = \frac{2\alpha_v}{\beta_v} T V (\Delta \alpha_v) + \frac{\alpha_v^2}{\beta_v} T (\Delta V) - \frac{\alpha_v^2}{\beta_v^2} T V (\Delta \beta_v) \quad (8)$$

Equation (8) will give the maximum variation in C^d by using the maximum positive values of α_v and V , and the maximum negative value of β_v . That is, Equation (8) can then be written as

$$\Delta C^d = \frac{2\alpha_v}{\beta_v} T V \cdot |\Delta \alpha_v| + \frac{\alpha_v^2}{\beta_v} T \cdot |\Delta V| + \frac{\alpha_v^2}{\beta_v^2} T V |\Delta \beta_v| \quad (9)$$

A. GOLD

a. Coefficient of Volume Thermal Expansion

The least square curve fitting method was used to fit a polynomial to the $\Delta l/l_0^*$ data points given by Nix and MacNair³⁷ from 86 to 1003°K. The polynomial used is

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 \quad (10)$$

where

*The length change $\Delta l = l - l_0$ at any temperature T was measured with respect to the length of the bar l_0 measured at 0°C.

$$C_1 = -34.75 \times 10^{-4},$$

$$C_2 = +11.70 \times 10^{-6},$$

$$C_3 = +34.40 \times 10^{-10},$$

and T = temperature in degree Kelvin.

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.20×10^{-4} which represents a three per cent deviation at 300°K and 0.7 per cent at 700°K .

$\Delta l/l_0$ measurements were also made in 1941 by Esser and Eusterbrock³⁸ from 323°K to 1223°K . Their data were fitted to the least square curve fitting method to obtain the polynomial

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5 \quad (11)$$

where

$$C_1 = -93.33 \times 10^{-5},$$

$$C_2 = +61.54 \times 10^{-7},$$

$$C_3 = -15.03 \times 10^{-9},$$

$$C_4 = +21.68 \times 10^{-12},$$

$$C_5 = -14.49 \times 10^{-15},$$

$$C_6 = +37.08 \times 10^{-19},$$

and T = temperature in degrees Kelvin

The standard deviation of the $\Delta l/l_0$ data point with respect to the above polynomial is 0.21×10^{-4} which represent a four per cent deviation at 300°K and 0.4 per cent at 723°K .

In a more recent investigation made in 1961 by Simmons and Balluffi³⁹, measurements of $\Delta l/l_0$ were made from 323°K

to 1333°K. The polynomial obtained by using their data is

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 \quad (12)$$

where

$$C_1 = -31.91 \times 10^{-4},$$

$$C_2 = +10.35 \times 10^{-6},$$

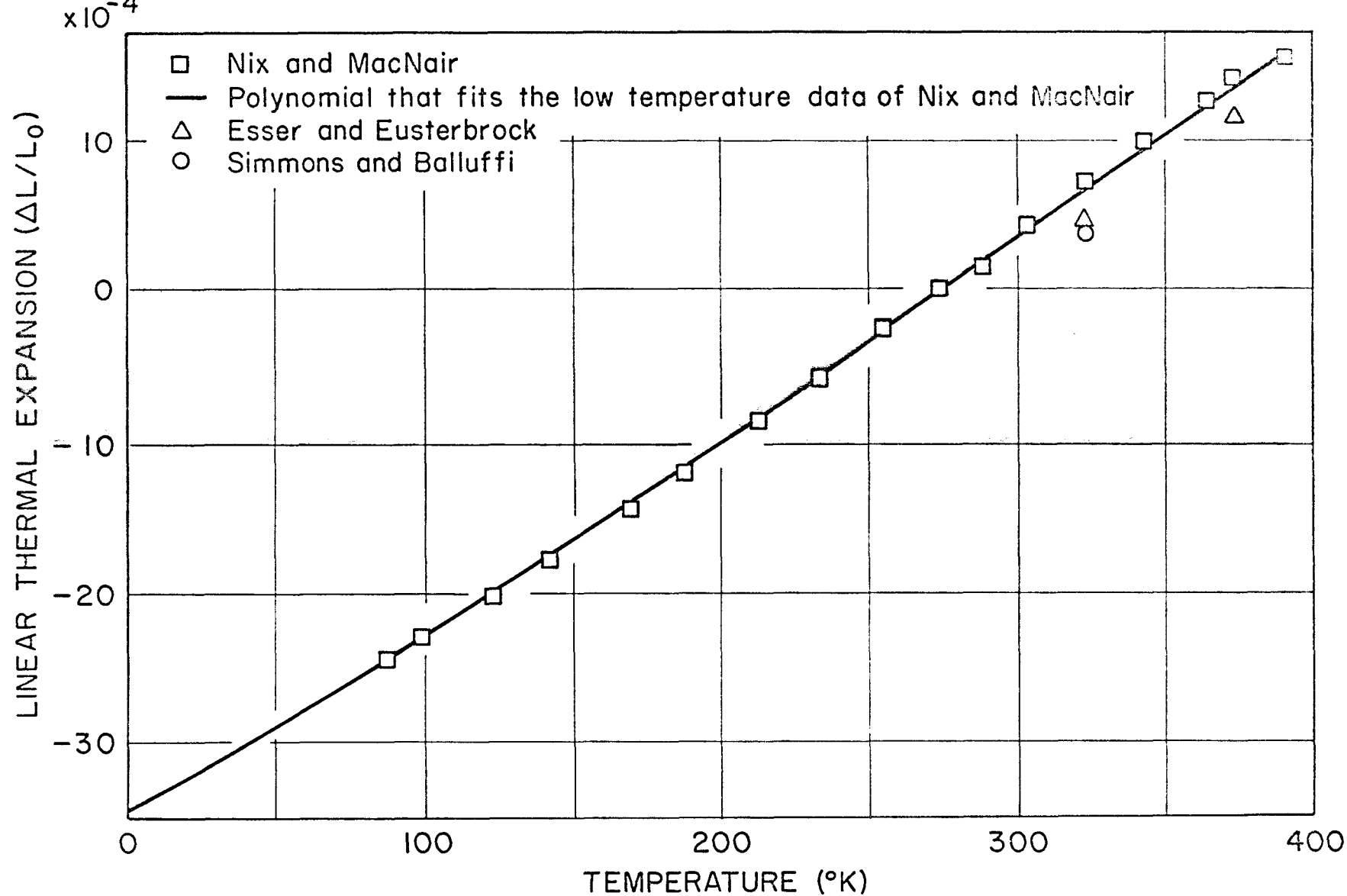
$$C_3 = +43.25 \times 10^{-10},$$

and T = temperature in degrees Kelvin

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.50×10^{-4} which represents an eleven per cent deviation at 300°K and 0.7 per cent at 723°K.

Figure 17 shows the low temperature $\Delta l/l_0$ values obtained by Nix and MacNair³⁷ and the polynomial determined from their data. At 323°K a difference of 2.3×10^{-4} (30 per cent) exists between the values of Esser and Eusterbrock³⁸ and Simmons and Balluffi³⁹. It is emphasized that the difference is high due to the very low values of Δl near 300°K, and it will be seen later that this difference produces only a very small error in the α_v calculation.

Figure 18 shows the high temperature linear thermal expansion $\Delta l/l_0$ where it is observed that a reasonable agreement exists between the data of Nix and MacNair³⁷ and those of Simmons and Balluffi³⁹ for temperatures above 400°K. The difference between the polynomial that fits the data of Nix and MacNair³⁷ and the polynomial that fits those of Simmons and Balluffi³⁹ remains constant at four per cent for temperatures above 500°K.



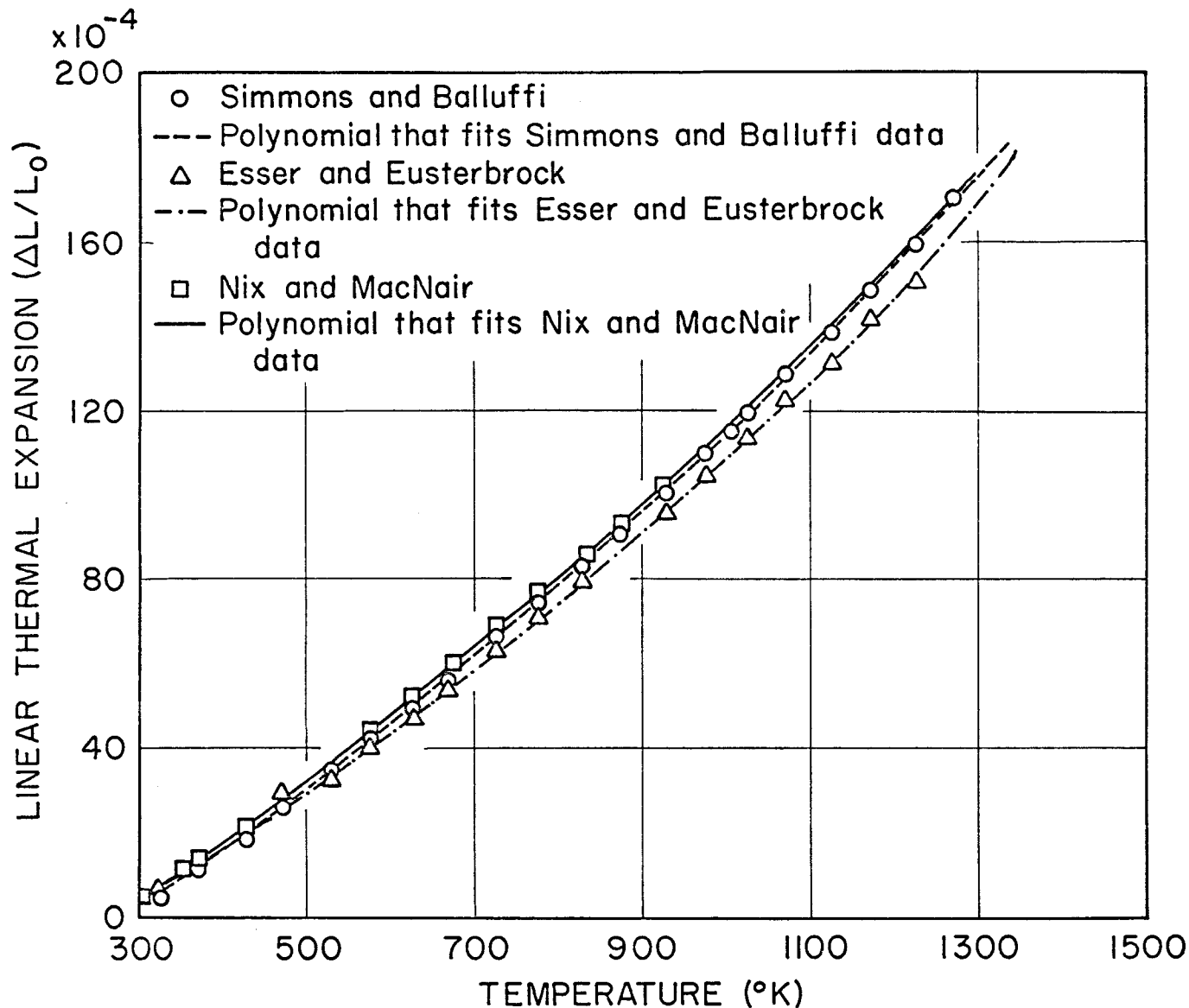


Figure 18. High temperature linear thermal expansion for gold.

The polynomial that fits the data of Esser and Eusterbrock³⁸ deviates farther from those data points of Nix and MacNair with increasing temperature. The polynomial calculated in this research to represent Esser and Eusterbrock³⁸ data gives results that are 0.1×10^{-6} per cent away from the polynomial calculated by them, which they used to calculate the linear coefficient thermal expansion α , so, no further use of Equation (11) will be made in the calculation of α and α_v ($\alpha_v = 3\alpha$).

The coefficient of linear thermal expansion α as a function of temperature is shown in Figure 19, where the results of Nix and MacNair³⁹ and Esser and Eusterbrock³⁸ are shown. Nix and MacNair determined the coefficients of linear thermal expansion at a given temperature by graphically measuring the slopes of the curve given by $\Delta l/l_0$ versus temperature. The α values given by Esser and Eusterbrock³⁸ were determined from a polynomial they fitted to their $\Delta l/l_0$ data. The results of Nix and MacNair³⁷ and those of Esser and Eusterbrock³⁸ differ by around one per cent from 300°K to around 900°K. Above 900°K, the difference increases to be four per cent at 1100°K. The polynomials that fit both Nix and MacNair³⁷ and Esser and Eusterbrock α data are shown in Figure 19. The polynomial that fits the α data of Nix and MacNair is given by

$$\alpha = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 + c_6 T^5 \quad (13)$$

where for, α in $^{\circ}\text{K}^{-1}$,

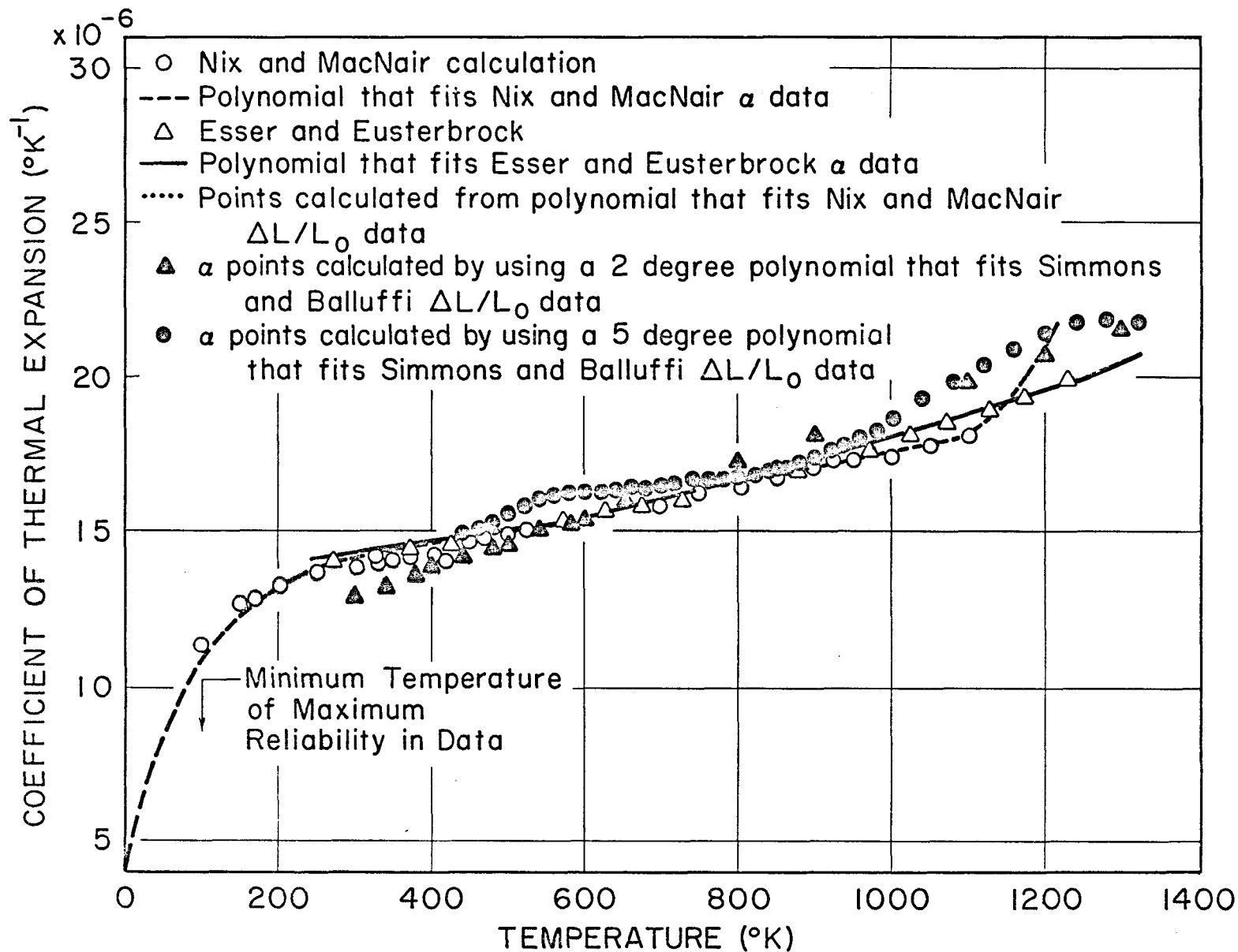


Figure 19. Coefficient of linear thermal expansion for gold.

$$C_1 = +43.97 \times 10^{-7},$$

$$C_2 = +94.20 \times 10^{-9},$$

$$C_3 = -35.33 \times 10^{-11},$$

$$C_4 = +63.31 \times 10^{-14},$$

$$C_5 = -52.25 \times 10^{-17},$$

$$C_6 = +16.14 \times 10^{-20},$$

and T = temperature in degrees Kelvin.

The polynomial that fits the α data obtained by Esser and Eusterbrock is given by

$$\alpha = C_1 + C_2 T + C_3 T^2 \quad (14)$$

where for, α in $^{\circ}\text{K}^{-1}$,

$$C_1 = +13.54 \times 10^{-6},$$

$$C_2 = +13.25 \times 10^{-10},$$

$$C_3 = +31.00 \times 10^{-13},$$

and T = temperature in degrees Kelvin.

The standard deviation of the polynomial used to fit the α data of Nix and MacNair³⁷ was 0.23, which would give a variation of around two per cent at 300 $^{\circ}\text{K}$. It was impossible to obtain a better fit to the α data of Nix and MacNair due to the irregularity of the α values which they determined by using a graphical method. The standard deviation of the polynomial used to fit the data of Esser and Eusterbrock³⁸ was 0.004 which gives a variation of 0.06 per cent at 300 $^{\circ}\text{K}$. It is clear that the method used by Esser and Eusterbrock³⁸ is more precise since a more exact slope is determined from the polynomial used to fit the greater amount of $\Delta l/l_0$ data points obtained experimentally, than by reading approximately

the values of the tangents at a given temperature from a curve drawn through a lesser number of data point.

The polynomials used in the present research to fit the $\Delta l/l_0$ data of Nix and MacNair³⁷ and Simmons and Balluffi (Equations (10) and (12)) were used to determine α as follows.

In general, let $\Delta l/l_0$ be given by

$$\frac{\Delta l}{l_0} = c_1 + c_2 T + c_3 T^2 + \dots c_n T^{n-1} \quad (15)$$

then

$$\Delta l = l_0 (c_1 + c_2 T + c_3 T^2 + \dots c_n T^{n-1}) \quad (16)$$

From Equation (16), the length l at a temperature T is given by

$$l = l_0 (1 + c_1 + c_2 T + c_3 T^2 + \dots c_n T^{n-1}) \quad (17)$$

Differentiating Equation (17) with respect to T

$$\frac{dl}{dT} = l_0 (c_2 + 2c_3 T + \dots (n-1) c_n T^{n-2}) \quad (18)$$

The linear coefficient of thermal expansion α is given by

$$\alpha = \frac{1}{l} \frac{dl}{dT} + (c_2 + 2c_3 T + \dots (n-1) c_n T^{n-2}) / (1 + c_1 + c_2 T + c_3 T^2 + \dots c_n T^{n-1}) \quad (19)$$

The α calculated from the polynomial used to fit the $\Delta l/l_0$ data of Nix and MacNair³⁷ (Equation (10)), by using Equation (19), is also shown in Figure 19, where it is observed that a difference of six per cent was obtained with respect to the graphical measurements of α made by Nix and MacNair³⁷ at 300°K. This difference decreases to zero per

cent at around 500°K and increases again to four per cent at 1100°K . The α calculated from the polynomial (Equation 10) maintains a difference of one per cent with respect to the values calculated by Esser and Eusterbrock³⁸ over the entire temperature range (300°K to 1330°K).

Since the α calculated from Equation (10) by using the procedure summarized in Equation (19) was used for comparison and for future calculations, it was decided to represent the calculated α^* by a simpler polynomial, given by

$$\alpha = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 \quad (20)$$

where, for α in $^{\circ}\text{K}^{-1}$,

$$c_1 = +11.74 \times 10^{-6},$$

$$c_2 = +67.67 \times 10^{-10},$$

$$c_3 = -11.99 \times 10^{-14},$$

$$c_4 = -21.97 \times 10^{-18},$$

$$c_5 = +72.21 \times 10^{-23},$$

and T = temperature in degrees Kelvin.

The standard deviation of the α values calculated from the polynomial used to represent the $\Delta l/l_0$ data of Nix and MacNair, by using Equation (19), with respect to those obtained by using the above polynomial (Equation (20)), is $0.2 \times 10^{-19} ^{\circ}\text{K}^{-1}$ which represents a variation of 0.1×10^{-12} per cent at 300°K ; this difference shows that the use of the polynomial instead of the calculated α did not produce any appreciable

*All calculations involving the use of Equation (19) were made for a temperature interval of ten degrees.

deviation in the α results.

The α calculated from the polynomial that fits Simmons and Balluffi³⁹ $\Delta l/l_0$ data (Equation (12)) by using Equation (19) is also shown in Figure 19 (Page 107).

A deviation of six per cent exists at 300°K between the values defined by Equation (20) and those calculated from the $\Delta l/l_0$ data of Simmons and Balluffi³⁹. The difference decreases to zero at around 750°K and increases again to four per cent at 1200°K. It is observed that except for the ends of the temperature range used in the present research (300°K to 1330°K) the agreement is reasonably good and the difference is mainly due to:

- 1) Errors near 300°K in the shape of the polynomial curve fitted to Simmons and Balluffi³⁹ $\Delta l/l_0$ data points. The fact that the $\Delta l/l_0$ data by Nix and MacNair³⁷ are given for temperatures as low as 80°K gives a much more reasonable polynomial fit for their data for temperatures around 300°K. Simmons and Balluffi³⁹ data start at 323°K so a great amount of different curves with different slopes can fit this first set of data points.
- 2) Error in the polynomial used to fit the highly separated Simmons and Balluffi³⁷ $\Delta l/l_0$ data points. The more separated the data points, usually the higher the standard deviation of the polynomial of a given order used to represent the data. A polynomial of very high order used to lower the standard deviation

tion of the very separated set of data points results in a wavy curve that give erroneous slopes. To observe this effect, a five degree polynomial was used to fit the $\Delta l/l_0$ data of Simmons and Balluffi; α was then calculated, and the result (Figure 19) showed that, even with a lower standard deviation, the irregularity in the α with respect to temperature, and the difference in these values with respect to the other calculations, increased considerably. At 1200°K, the difference in the α obtained from the second and fifth degree polynomial fit to Simmons and Balluffi³⁷ $\Delta l/l_0$ data is four per cent ($0.8 \times 10^{-6} \text{ } ^\circ\text{K}^{-1}$). The same analysis made on Nix and MacNair $\Delta l/l_0$ data give a difference of 0.4 per cent ($0.09 \times 10^{-6} \text{ } ^\circ\text{K}^{-1}$).

The above analysis indicates that the larger the number of data points, and the smaller the ΔT intervals, the higher the probability of finding the right α values.

The coefficient of linear expansion given by Equation (20) and obtained from the polynomial that fits Nix and MacNair $\Delta l/l_0$ data was used in the determination of the dilation term ($\alpha_v = 3\alpha$). Since basically most α results given in Figure 19 (Page 107) agree within one per cent, except for the end points (300°K and 1300°K) calculated from Simmons and Balluffi³⁸ $\Delta l/l_0$ data, an estimated maximum variation ± 2.0 per cent was given to the values obtained by Equation (20) in order to see the effect that this variation has on the

specific heat capacity at constant volume (Section A-e).

b. Molar Volume

The molar volume at 25°C was calculated from the lattice parameters data given by Pearson⁴⁰, and was used as a reference to calculate the molar volume as a function of temperature. For gold, the calculation was based on the use of Equation (17) as follows:

$$C = V_{298} \frac{1 + C_1 + \dots + C_n T^{n-1}}{1 + C_1 + \dots + C_n T_R^{n-1}} \quad (21)$$

where

V = molar volume at a temperature T ,

V_{298} = reference molar volume at 298°K (25°C),

T_R = reference temperature (298°K)

Using Equation (21) values of molar volume were calculated at ten degrees intervals, and the values were fitted to a polynomial curve. The resulting polynomial, shown in Figure 20, is given by

$$V = C_1 + C_2 T + C_3 T^2 + C_4 T^3 \quad (22)$$

where, for V in cubic centimeters per gram atom,

$$C_1 = +10.101 \times 10^{+0},$$

$$C_2 = +35.567 \times 10^{-5},$$

$$C_3 = +10.874 \times 10^{-8},$$

$$C_4 = +26.961 \times 10^{-13},$$

and T = temperature in degree Kelvin.

The standard deviation of the data points obtained by using Equation (21) with respect to the above polynomial is

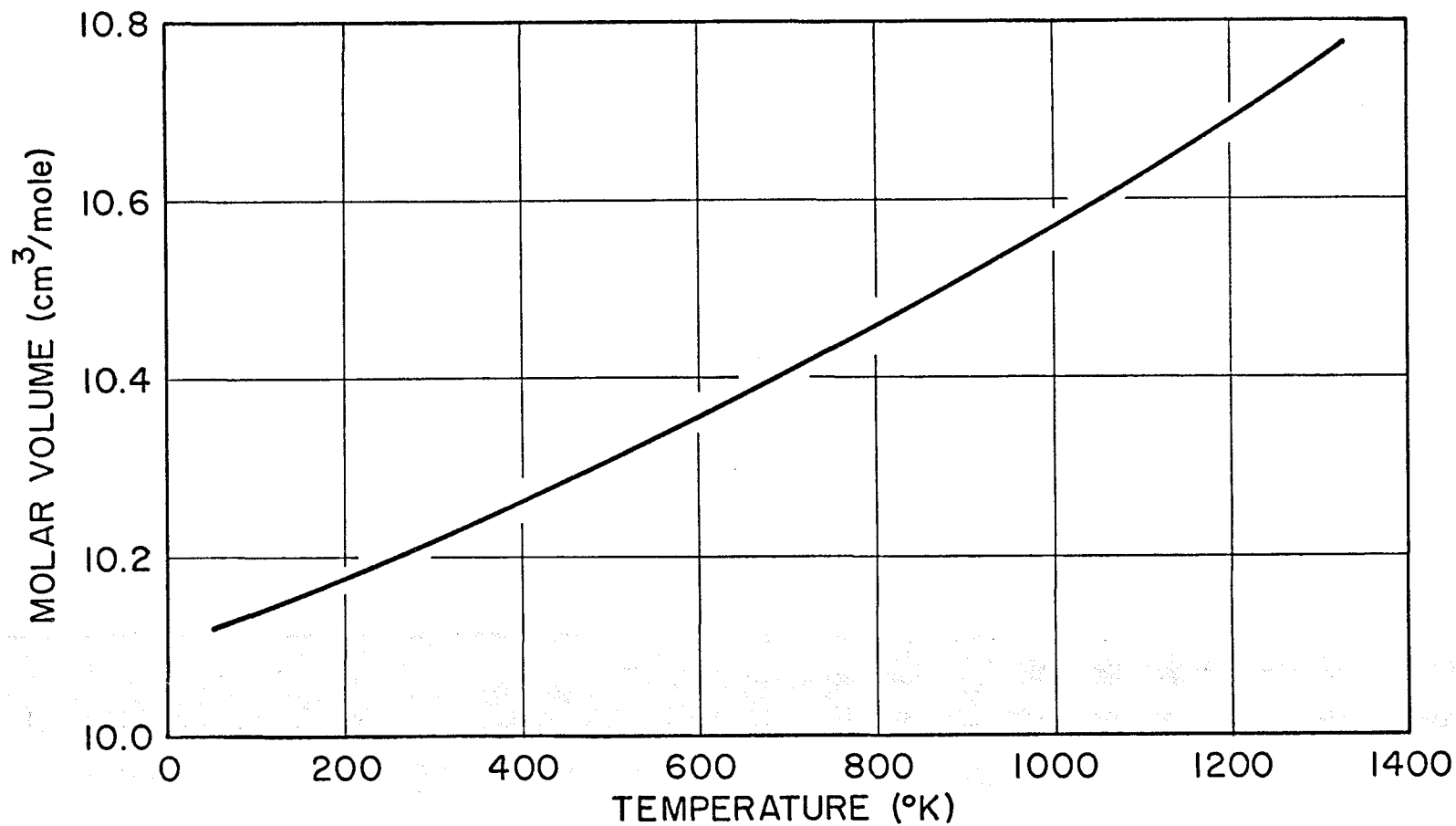


Figure 20. Molar volume for gold.

0.2×10^{-7} which represents a variation of 0.2×10^{-6} per cent at 300°K .

The good agreement between the $\Delta l/l_0$ data of Nix and MacNair³⁷ and those of Esser and Eusterbrock³⁸, where for high temperatures the maximum variation is of one per cent, indicates that the maximum uncertainty in the molar volume is no greater than one per cent. This uncertainty was used to calculate the variation of the calculated C_v (Section A-e).

c. Isothermal Compressibility

The adiabatic bulk modulus K for gold was determined by Chang and Himmel⁴¹ from the elastic constant measurements for temperatures between 300°K and 800°K . Their data were fitted by the polynomial.

$$K = C_1 + C_2T + C_3T^2 \quad (23)$$

where, for K in dynes per square centimeters,

$$C_1 = +17.83 \times 10^{+11},$$

$$C_2 = -17.89 \times 10^{+7},$$

$$C_3 = -88.58 \times 10^{+3},$$

and T = temperature in degree Kelvin.

The standard deviation of the data points with respect to the polynomial is 0.003×10^{-12} dynes per square centimeters (around 0.2 per cent). The polynomial was used for a temperature range of 200°K to 1330°K and is shown in Figure 21.

The maximum deviation of the extrapolated bulk modulus is assumed not to be greater than one per cent at 1330°K . The adiabatic compressibility β_A is the reciprocal of K .

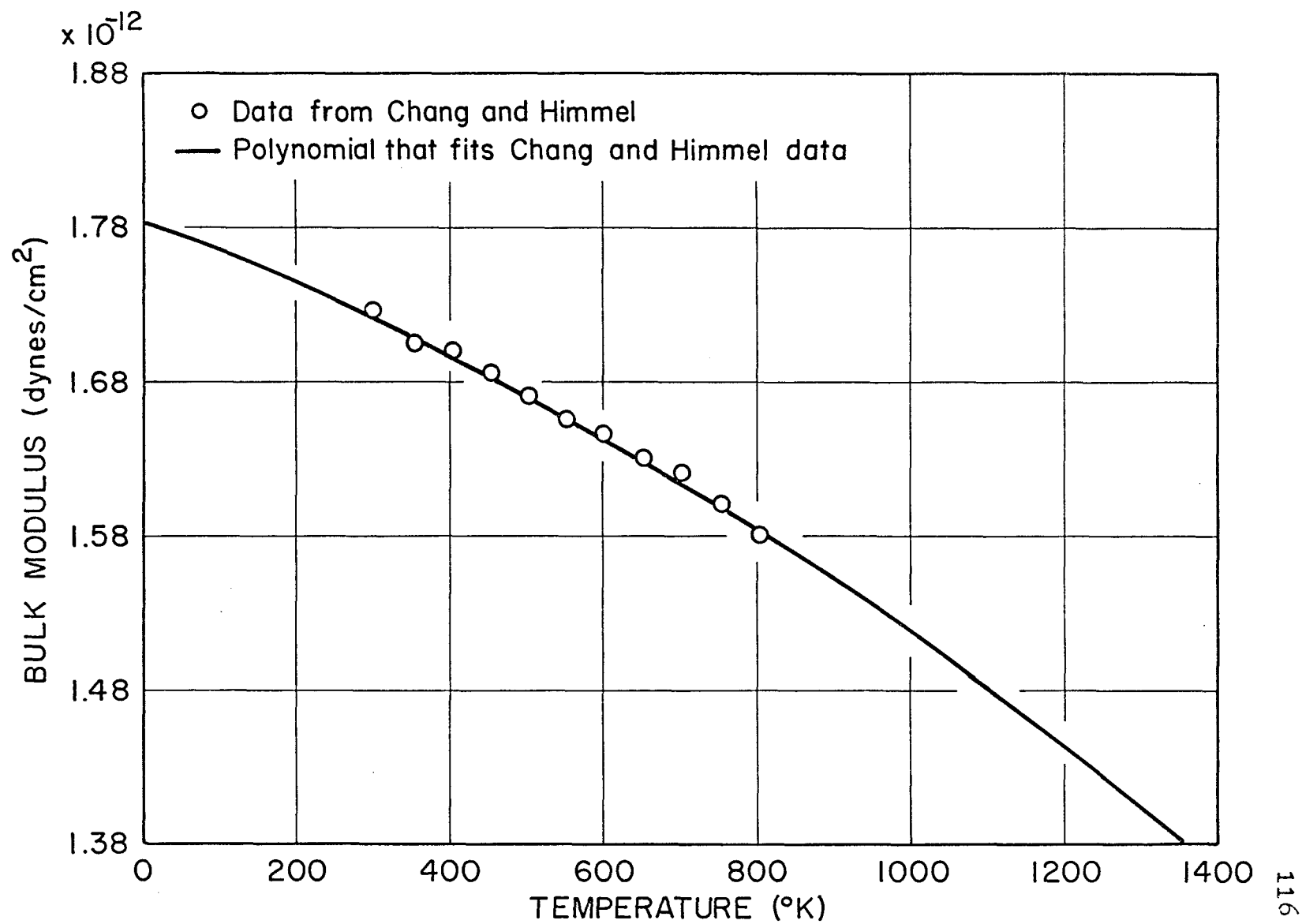


Figure 21. Bulk modulus for gold.

The high temperature ($T > 300^\circ\text{K}$) calculation of the isothermal compressibility β_v was made by using Equation (7), (20) and (22) and the C_p data given by Equation (1) in Chapter III. The low temperature range (200°K to 300°K) β_v was obtained by using Equations (7), (19), and (22) and the low temperature C_p data by Geballe and Giauque⁴².

Polynomials were determined for the calculated β_v values for the low and high temperature data. The polynomial for the low temperature data is given by

$$\beta_v = C_1 + C_2T + C_3T^2 \quad (200 \leq T \leq 300^\circ\text{K}) \quad (24)$$

where, for β_v in square centimeters per degree, the constants are

$$C_1 = +5.610 \times 10^{-13},$$

$$C_2 = +1.092 \times 10^{-16},$$

$$C_3 = +8.443 \times 10^{-20},$$

and T = absolute temperature in degree Kelvin.

The standard deviation of the calculated β_v points with respect to the above polynomial is 0.2×10^{-18} square centimeters per dyne which represents a variation of 0.3×10^{-4} per cent.

The polynomial for the high temperature data is given by

$$\beta_v = C_1 + C_2T + CT^2 \quad (300^\circ \leq T \leq 1333^\circ\text{K}) \quad (25)$$

where, for β_v in square centimeters per dyne, the constants are given by

$$C_1 = 5.660 \times 10^{-13},$$

$$C_2 = 8.463 \times 10^{-16},$$

$$C_3 = 11.567 \times 10^{-20},$$

and T = absolute temperature in degree Kelvin.

The standard deviation of the calculated data points at high temperature with respect to the polynomial representing the data points is 0.1×10^{-15} square centimeters per dyne which represents a variation of 0.1 per cent at 300°K .

Figure 22 shows the polynomial for the low and high temperature β_v data.

The difference in the isothermal compressibility at 300°K calculated by using the low and high temperature polynomials representing the β_v value is 0.2 per cent.

At 1330°K , a one per cent variation in the bulk modulus, molar volume and C_p , and a two per cent variation in α_v , produces a maximum uncertainty of two per cent in β_v . This two per cent variation in β_v was used to calculate the uncertainty in the dilation term C^d and the specific heat capacity at constant volume (Section A-e).

d. Specific Heat Capacity at Constant Volume

The calculation of the dilation term was made by using Equations (2), (20), (22) and (24) for $200^\circ \leq T \leq 300^\circ\text{K}$ and Equations (2), (20), (22) and (25) for $300^\circ \leq T \leq 1333^\circ\text{K}$. The specific heat at constant volume was obtained for the low temperature region ($200^\circ \leq T \leq 300^\circ\text{K}$) by using Equation (1), the C_p values obtained by Geballe and Giauque⁴² and the C^d

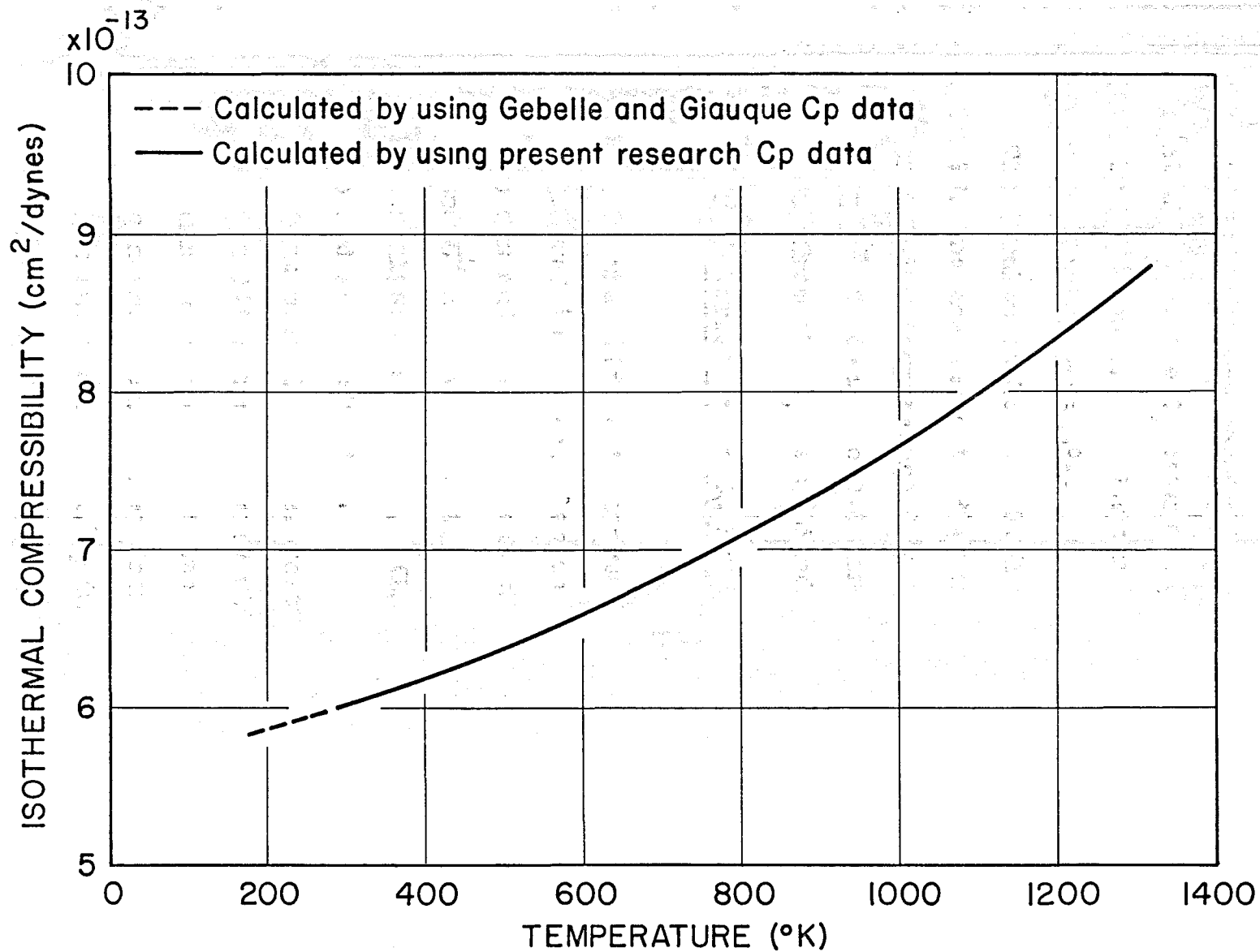


Figure 22. Isothermal compressibility for gold.

value obtained for $200^{\circ} \leq T \leq 300^{\circ}\text{K}$. The high temperature C_v ($300^{\circ} \leq T \leq 1333^{\circ}\text{K}$) was obtained by using Equation (1) in the present chapter, the C_p obtained in the present research and given by Equation (1) in Chapter III and the C^d values obtained for $300^{\circ} \leq T \leq 1333^{\circ}\text{K}$.

The results at low and high temperature are given in Table IV, and are shown in Figure 23. At 320°K the difference between the low temperature C_v results obtained from Geballe and Giauque⁴² C_p data are 2.0 per cent higher than the value calculated from the C_p determined in the present research.

e. Probable Variation in C_v Due to Error in the α_v , β_v and v

Due to the different uncertainties in the different terms involved in the calculation of the dilation term, an analysis was made on the effect of this uncertainties in the calculated C^d and the final C_v .

The analysis made on α_v ($\alpha_v = 3\alpha$), v and β_v (Section A-a, A-b and A-c) indicated:

- 1) that most α values, calculated and obtained from the literature, agreed within one per cent so the maximum variation of the α_v used in the present research (calculated from the polynomial that fits Nix and MacNair $\Delta l/l_0$ data) was no greater than two per cent;
- 2) that a variation no greater than one per cent in the values of the molar volume is expected since Simmons

TABLE IV

SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME: GOLD

Low Temperature Data		High Temperature Data			
Temperature	C_v	Temperature	C_v	Temperature	C_v
(degree Kelvin)	(Joules/gram-atom/degree Kelvin)	(degree Kelvin)	(Joules/gram-atom/degree Kelvin)	(degree Kelvin)	(Joules/gram-atom/degree Kelvin)
200	23.8995	320	24.1253	570	25.5363
210	23.9811	330	24.3132	580	25.5391
220	24.0330	340	24.4789	590	25.5414
230	24.0887	350	24.6247	600	25.5432
240	24.1606	360	24.7528	610	25.5448
250	24.2279	370	24.8651	620	25.5462
260	24.2948	380	24.9633	630	25.5475
270	24.3612	390	25.0491	640	25.5489
280	24.4232	400	25.1238	650	25.5504
290	24.4762	410	25.1887	660	25.5521
300	24.5288	420	25.2449	670	25.5540
310	24.5771	430	25.2935	680	25.5563
320	24.6175	440	25.3353	690	25.5590
		450	25.3711	700	25.5620
		460	25.4417	710	25.5656
		470	25.4277	720	25.5696
		480	25.4497	730	25.5742
		490	25.4682	740	25.5793
		500	25.4836	750	25.5850
		510	25.4965	760	25.5912
		520	25.5070	770	25.5982
		530	25.5157	780	25.6057
		540	25.5226	790	25.6139
		550	25.5283	800	25.6227
		560	25.5328	810	25.6322

TABLE IV (continued)

Low Temperature Data		High Temperature Data			
Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)	Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)	Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)
		820	25.6423	1090	26.1620
		830	25.6531	1100	26.1897
		840	25.6646	1110	26.2179
		850	25.6767	1120	26.2466
		860	25.6896	1130	26.2759
		870	25.7031	1140	26.3057
		880	25.7172	1150	26.3360
		890	25.7321	1160	26.3668
		900	25.7476	1170	26.3981
		910	25.7637	1180	26.4299
		920	25.7806	1190	26.4622
		930	25.7980	1200	26.4949
		940	25.8162	1210	26.5281
		950	25.8350	1220	26.5618
		960	25.8544	1230	26.5960
		970	25.8744	1240	26.6306
		980	25.8951	1250	26.6657
		990	25.9164	1260	26.7012
		1000	25.9383	1270	26.7371
		1010	25.9608	1280	26.7735
		1020	25.9839	1290	26.8103
		1030	26.0076	1300	26.8475
		1040	26.0319	1310	26.8851
		1050	26.0568	1320	26.9232
		1060	26.0823	1330	26.9616
		1070	26.1083		
		1080	26.1349		

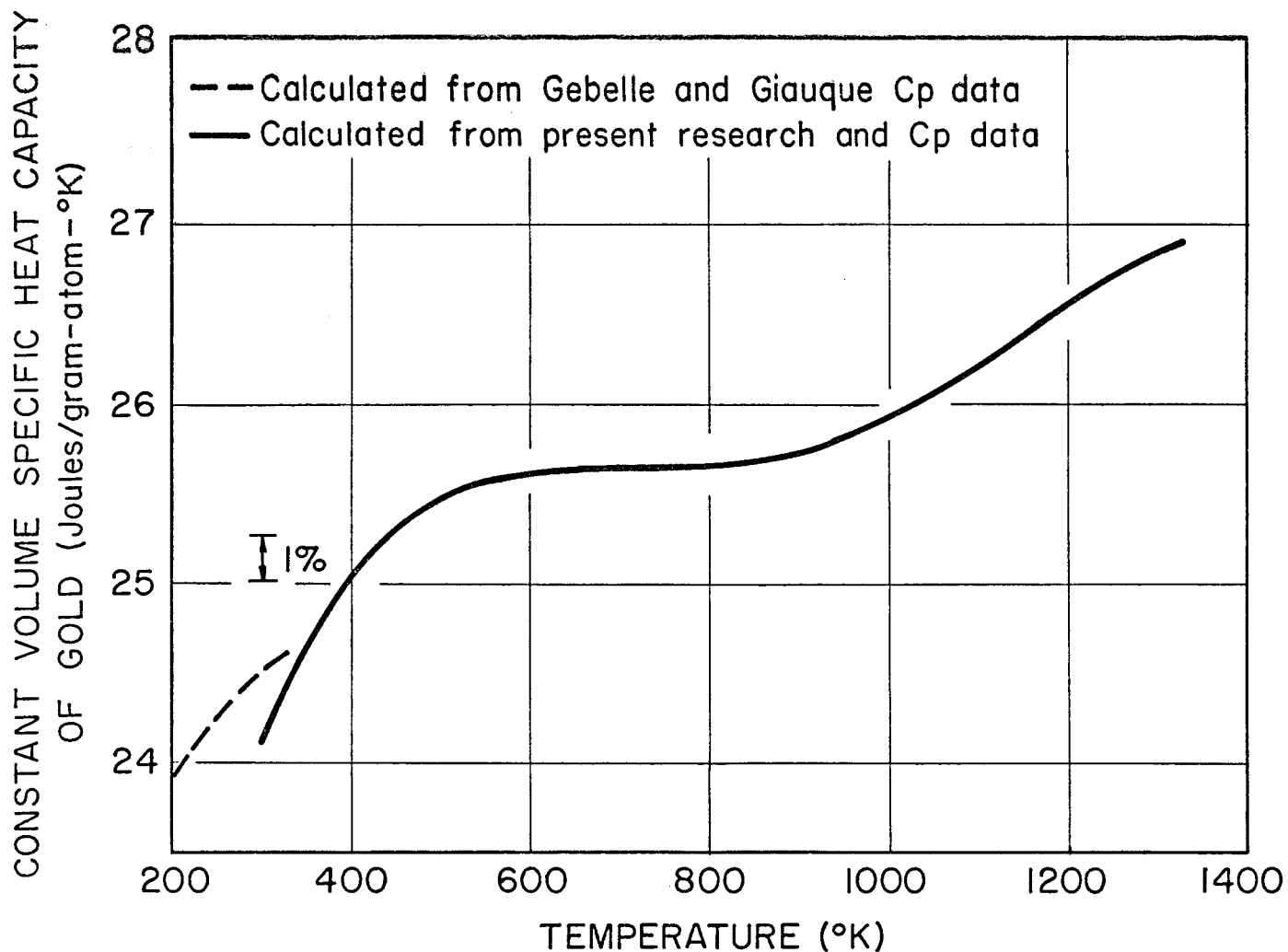


Figure 23. Specific heat capacity at constant volume for gold.

and Balluffi³⁹ and Nix and MacNair³⁷ $\Delta l/l_0$ data differ at high temperature by no more than about one per cent; and

- 3) that the maximum variation in β_v calculated from the uncertainties in K , α_v , C_p and V is two per cent.

The above uncertainties, applied in Equation (9) at 1330°K, indicated that the maximum variation in the dilation term is 0.43 Joules per gram-atom per degree Kelvin (7.0 per cent) which finally would give an error of 1.6 per cent in the calculated specific heat capacity at constant volume.

A ± 1.0 per cent variation in C_p plus the ± 7.0 per cent variation in C^d will cause a maximum variation of ± 2.8 per cent in C_v . The variation of C_p and C^d both with the same positive or negative sign will give a variation of 0.4 per cent in the C_v value.

B. LEAD

a. Coefficient of Volume Thermal Expansion

Measurements on the linear thermal expansion for lead were made in 1941 by Nix and MacNair⁴³ from 85°K to 300°K. The least square curve fitting method was used to determine a polynomial for the $\Delta l/l_0$ data points* given by Nix and MacNair⁴³. The polynomial used is

*The length change was measured with respect to 0°C.

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5 \quad (26)$$

where

$$C_1 = -74.56 \times 10^{-4},$$

$$C_2 = +36.09 \times 10^{-6},$$

$$C_3 = -16.61 \times 10^{-8},$$

$$C_4 = +11.18 \times 10^{-10},$$

$$C_5 = -33.04 \times 10^{-13},$$

$$C_6 = +36.87 \times 10^{-16},$$

and T = temperature in degree Kelvin.

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.13×10^{-4} which represents a 1.6 per cent deviation at 300°K and 0.4 per cent at 400°K .

No further use will be made on the above result since it involves measurements at low temperature; nevertheless, the values determined by Nix and MacNair⁴³ by using the slopes of their $\Delta l/l_0$ versus temperature curves will be used as a mean to check the high temperature α calculations.

$\Delta l/l_0$ measurements were also made by D'Heurle, Feder and Nowick⁴⁴ from 433°K to 600°K . The polynomial obtained by using the least square curve fitting method on their results is

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5 \quad (28)$$

where

$$C_1 = -75.78 \times 10^{-4},$$

$$C_2 = +21.26 \times 10^{-6},$$

$$C_3 = +25.98 \times 10^{-9},$$

$$C_4 = -53.43 \times 10^{-12},$$

$$C_5 = -70.39 \times 10^{-15},$$

$$C_6 = -28.75 \times 10^{-18},$$

and T = temperature in degree Kelvin.

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.2×10^{-5} which represents a 0.2 per cent deviation at 300°K .

Figure 24 shows the low temperature $\Delta l/l_0$ values obtained by Nix and MacNair⁴³ and the polynomial used to fit their data. At around 300°K it is observed that a difference of 6.0×10^{-4} (75 per cent) exists between the data of Nix and MacNair⁴³ and those of Feder and Nowick⁴⁵. It should be emphasized that the per cent difference obtained is high due to very low Δl values at around 300°K , and, as it will be shown later, it produces only a very small difference in the α_v calculations.

Figure 25 shows the high temperature linear thermal expansion $\Delta l/l_0$ where, above 450°K , good agreement is obtained between the results of D'Heurle, Feder and Nowick⁴⁴ and Feder and Nowick⁴⁵ and the polynomials used to fit their data.

Figure 26 shows the results of the linear coefficient of thermal expansion α obtained in different investigations. Nix and MacNair⁴³ measured graphically the α values from their low temperature $\Delta l/l_0$ data. The polynomial calculated to fit their data is given by

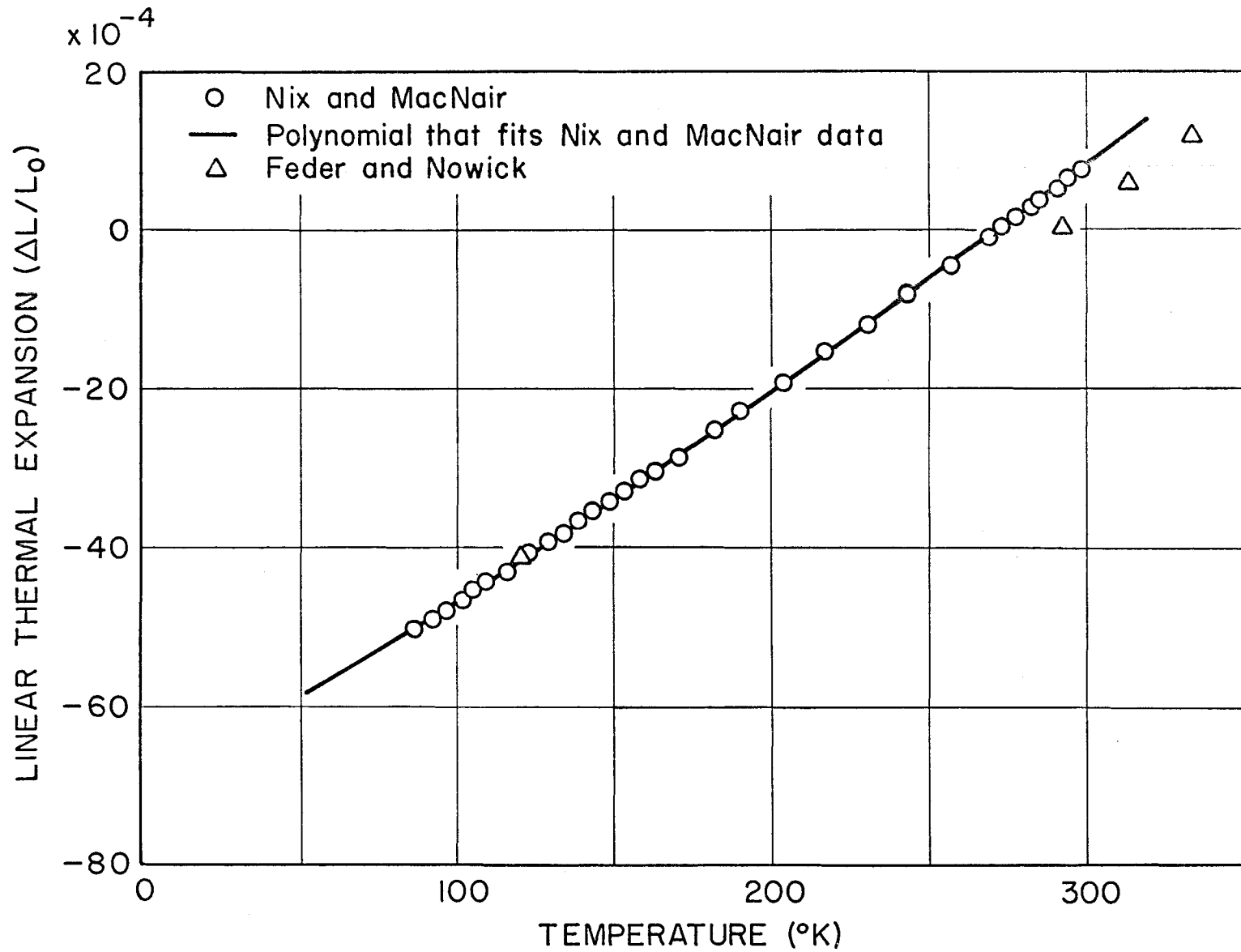


Figure 24. Low temperature linear thermal expansion for lead.

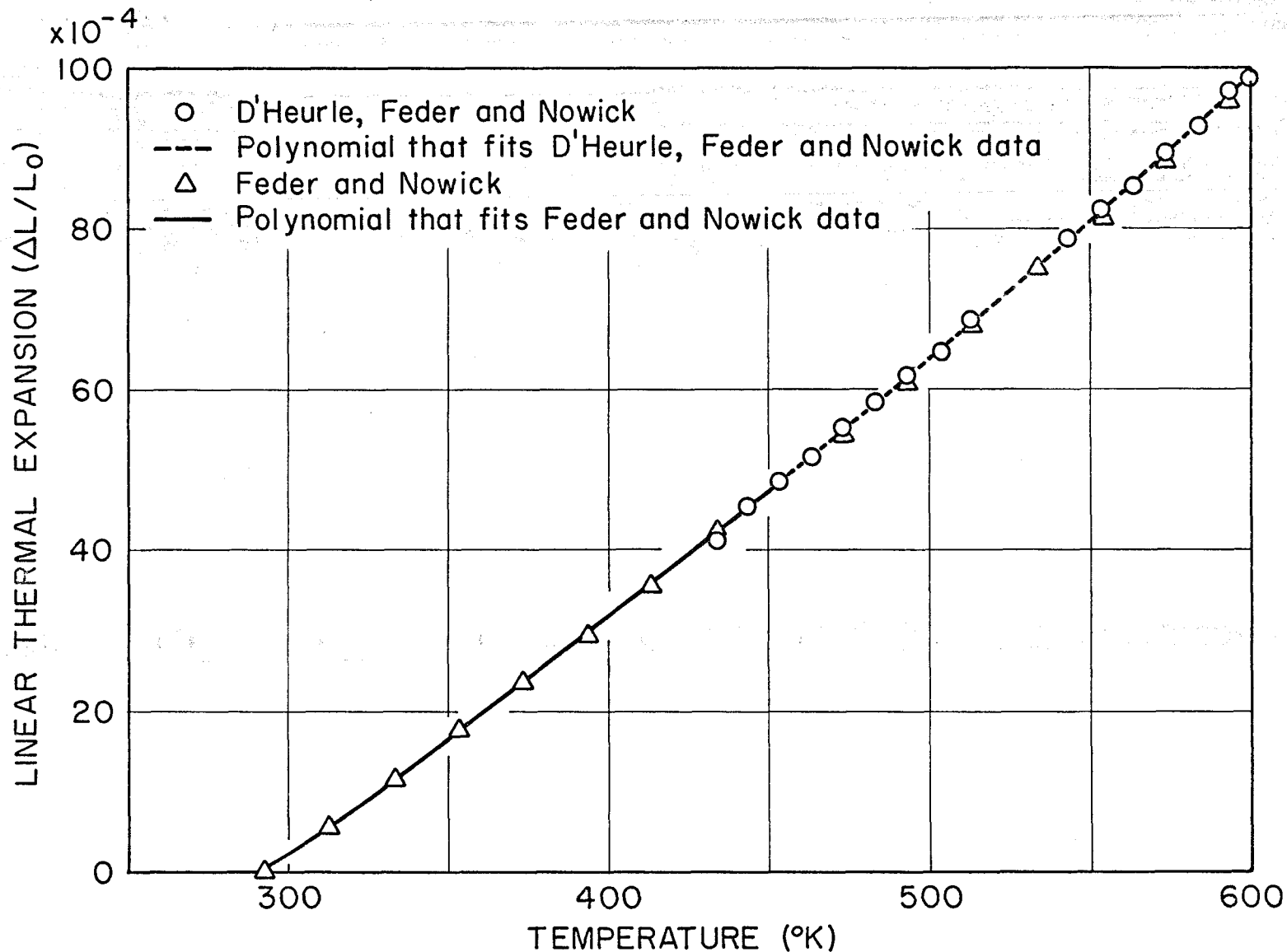


Figure 25. High temperature linear thermal expansion for lead.

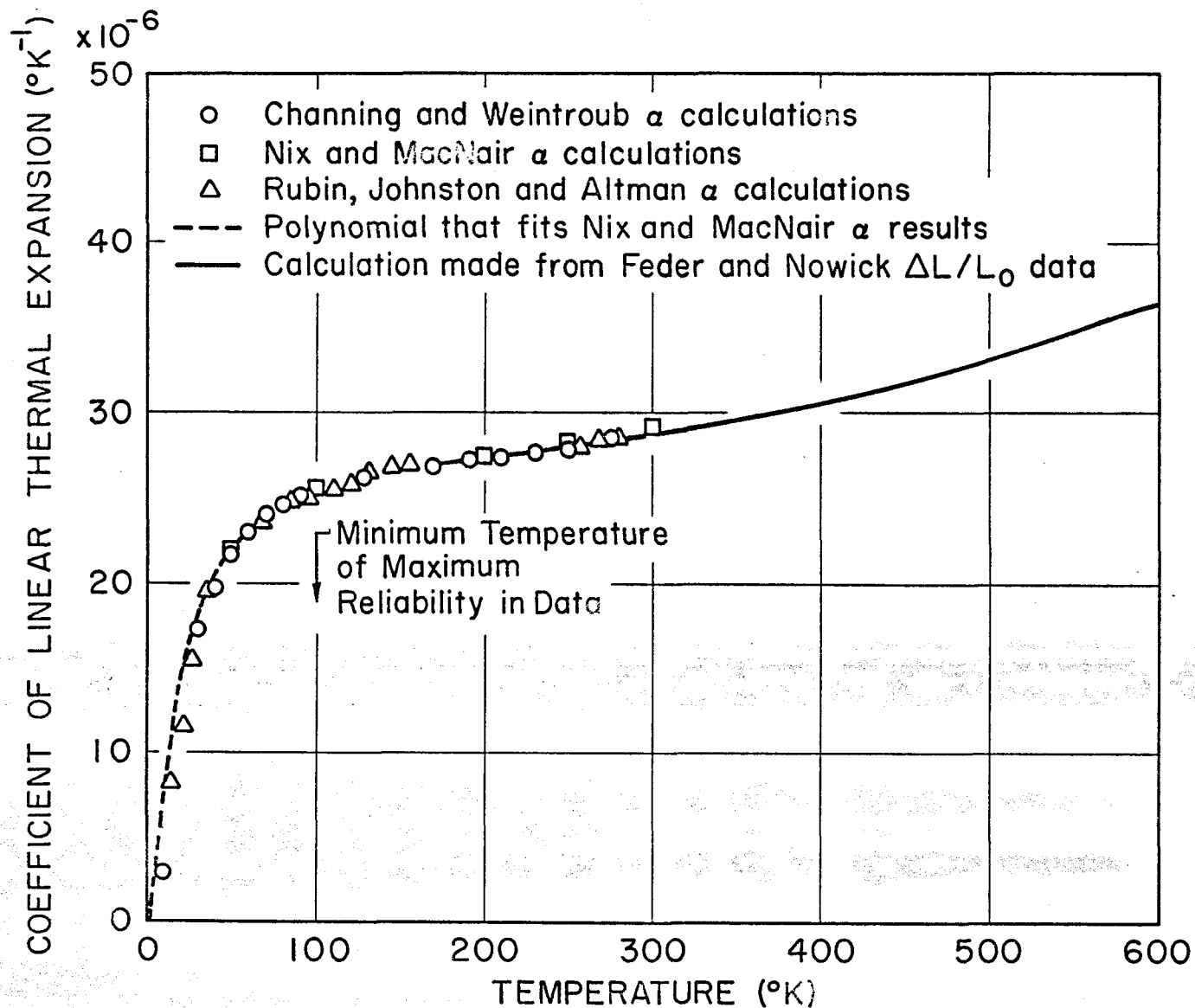


Figure 26. Coefficient of linear thermal expansion for lead.

$$\alpha = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 + c_6 T^5 \quad (29)$$

where, for α in $^{\circ}\text{K}^{-1}$,

$$c_1 = +79.25 \times 10^{-7},$$

$$c_2 = +48.76 \times 10^{-8},$$

$$c_3 = -54.40 \times 10^{-10},$$

$$c_4 = +30.72 \times 10^{-12},$$

$$c_5 = -84.00 \times 10^{-15},$$

$$c_6 = +88.67 \times 10^{-18},$$

and $T = +88.67 \times 10^{-18}$.

The standard deviation of the results of Nix and MacNair⁴³ with respect to the above polynomial is $0.4 \times 10^{-15} \text{ }^{\circ}\text{K}^{-1}$ which represents a deviation of 0.1×10^{-8} per cent at 300°K . Rubin, Johnston and Altman⁴⁶ and Channing and Weintroub⁴⁷ have reported α values at low temperature for lead ($T \leq 300^{\circ}\text{K}$); no length values were reported. Their results are also shown in Figure 26, and are within one per cent of those of Nix and MacNair⁴³. The α curve calculated from the polynomial used to fit the $\Delta l/l_0$ data of Feder and Nowick⁴⁵ (Equation 28), by using Equation (19), is also shown in Figure 26. Since the α curve calculated from Equation (28) by using the procedure summarized in Equation (19), was used for comparison and for future calculations, it was decided to represent the calculated α^* by a simpler polynomial, which is given by

*All calculations involving the use of Equation (19) were made for a temperature interval of ten degrees.

$$\alpha = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 \quad (30)$$

where, for α in $^{\circ}\text{K}^{-1}$,

$$c_1 = +21.50 \times 10^{-6},$$

$$c_2 = +51.08 \times 10^{-9},$$

$$c_3 = -15.98 \times 10^{-11},$$

$$c_4 = +28.08 \times 10^{-14},$$

$$c_5 = -14.46 \times 10^{-17},$$

and T = temperature in degrees Kelvin.

The standard deviation of the calculated α values obtained by using Equation (19) with respect to the above polynomial is $0.1 \times 10^{-10} \text{ }^{\circ}\text{K}^{-1}$ which represents a deviation of 0.3×10^{-4} per cent at 300°K ; this difference shows that the use of the polynomial instead of the calculated α did not produce any appreciable deviation in the α results.

The high temperature α values obtained from Equation (30) were 1.4 per cent below the Nix and MacNair polynomial at 300°K , and this difference decreased to zero at 160°K . The difference at low temperature between the polynomial given by Equation (30) and the α obtained from the work of Rubin, Johnston and Altman⁴⁶ and Channing and Weintroub⁴⁷ is 0.2 per cent.

The coefficient of linear thermal expansion given by Equation (30) and obtained from the polynomial that fits Feder and Nowick⁴⁵ $\Delta l/l_0$ data was used in the determination of the dilation term ($\alpha_v = 3\alpha$). Basically, all the different results were within one per cent for $T \leq 300^{\circ}\text{K}$; for

$T \geq 400^\circ\text{K}$ the α results obtained from the polynomials that fit the $1/l_0$ data of D'Heurle, Feder and Nowick⁴⁴ and Feder and Nowick⁴⁵ agreed within 0.8 per cent. For $300 < T < 400^\circ\text{K}$ no other α but that calculated from the polynomial that fits Feder and Nowick $\Delta 1/l_0$ data was available. It is expected that the maximum variation due to the use of Equation (30) is no greater than one per cent.

b. Molar Volume

As in the case of gold, the molar volume at 25°C was calculated from the lattice parameters given by Pearson⁴⁰ which was used as a reference to calculate the molar volume as a function of temperature by using Equation (21) and the constants C_1, C_2, C_3, C_4, C_5 and C_6 given in Equation (28). The V data points obtained every ten degrees were used to determine a simpler polynomial which was used in the calculation of the dilation term C^d . The polynomial, shown in Figure 27, is

$$V = C_1 + C_2T + C_3T^2 + C_4T^3 \quad (31)$$

where, for V in cubic centimeters per mole, the constants

C_1, C_2, C_3 and C_4 are given by

$$C_1 = +17.81 \times 10^{+0},$$

$$C_2 = +15.74 \times 10^{-4}$$

$$C_3 = -36.33 \times 10^{-6},$$

$$C_4 = +85.51 \times 10^{-9},$$

and T = temperature in degree Kelvin.

The standard deviation of the data points obtained by using

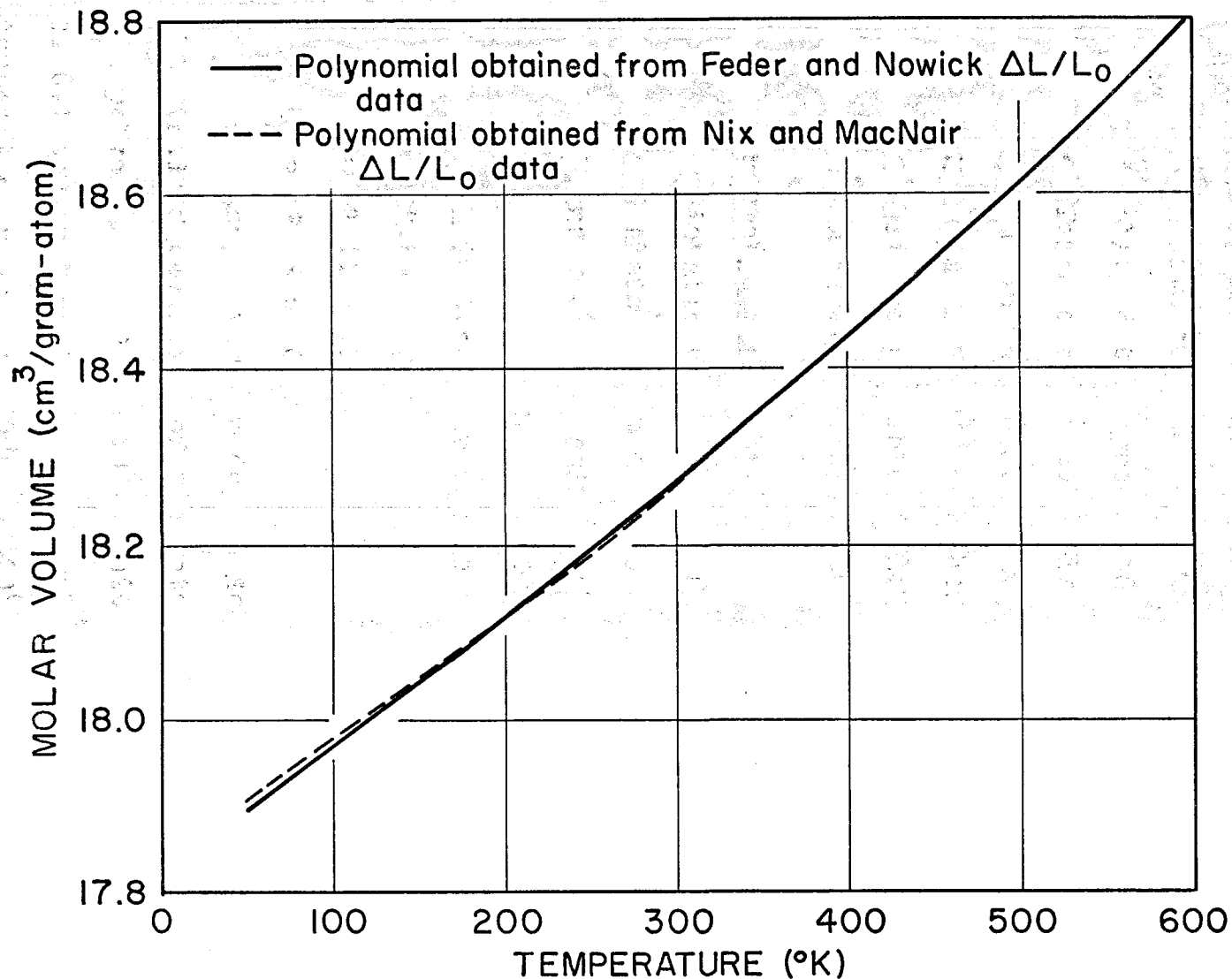


Figure 27. Molar volume for lead as a function of temperature.

Equation (21) with respect to the above polynomial is 0.1×10^{-6} which represents a deviation of 0.6×10^{-5} per cent at 300°K .

Figure 27 also shows the polynomial that was obtained by using the data calculated from Equation (21) and Nix and MacNair⁴³ $\Delta l/l_0$ data represented by Equation (26). The maximum difference above 200°K is 0.04 per cent. The excellent agreement in the molar volume obtained from the $\Delta l/l_0$ data of Nix and MacNair⁴³ and those of Feder and Nowick⁴⁵ indicates that the probable maximum variation in the V results obtained from Equation (31) is no greater than one per cent.

c. Isothermal Compressibility

The adiabatic bulk modulus K for lead was determined by Waldorf and Alers⁴⁸ from elastic constants measurements between 0°K and 300°K . A polynomial that fits their data is

$$K = C_1 + C_2T + C_3T^2 \quad (32)$$

where, for K in dynes per square centimeter,

$$C_1 = +4.89 \times 10^{+12},$$

$$C_2 = -1.21 \times 10^{+9},$$

$$C_3 = -7.55 \times 10^{+5},$$

and T = temperature in degree Kelvin.

The standard deviation of the data points with respect to the polynomial is $0.6 \times 10^{+9}$, which represents a deviation of 0.1 per cent at 300°K . The polynomial was used for a temperature range of 200°K to 600°K , and it is shown in

Figure 28. Since for lead, bulk modulus data exist for temperatures below 300°K , the extrapolation of the polynomial used to represent the data for temperatures above 300°K is not expected to be greater than ± 1.6 per cent. The bulk modulus for lead decreases by around thirteen per cent in the extrapolated region ($300^{\circ} \leq T \leq 600^{\circ}\text{K}$), and an analysis on the decrease of the bulk modulus for zinc, by increasing temperature ($300^{\circ} \leq T \leq 600^{\circ}\text{K}$) shows a decrease of twelve per cent in the bulk modulus. (For zinc the available data was the adiabatic compressibility which is the reciprocal of the bulk modulus. See Section C-c-3). The above comparison give a slight indication that the assumed ± 1.6 per cent variation in the bulk modulus for lead could be a reasonable estimate. The estimated ± 1.6 variation in the bulk modulus was used to determine the effect of this variation in the isothermal compressibility β_v .

The calculation of the high temperature ($T > 300^{\circ}\text{K}$) isothermal compressibility β_v was made by using Equation (7), (30) and (31) in the present chapter, and the polynomial used to represent the present research C_p data of lead (Chapter III). The low temperature ($200^{\circ} \leq T \leq 300^{\circ}\text{K}$) calculation of β_v were made by using Equations (7), (30) and (31) in the present chapter and the low temperature C_p values given by Hultgreen et al.³⁵.

Polynomials were determined for the calculated β_v values for the low and high temperature data. The polynomial

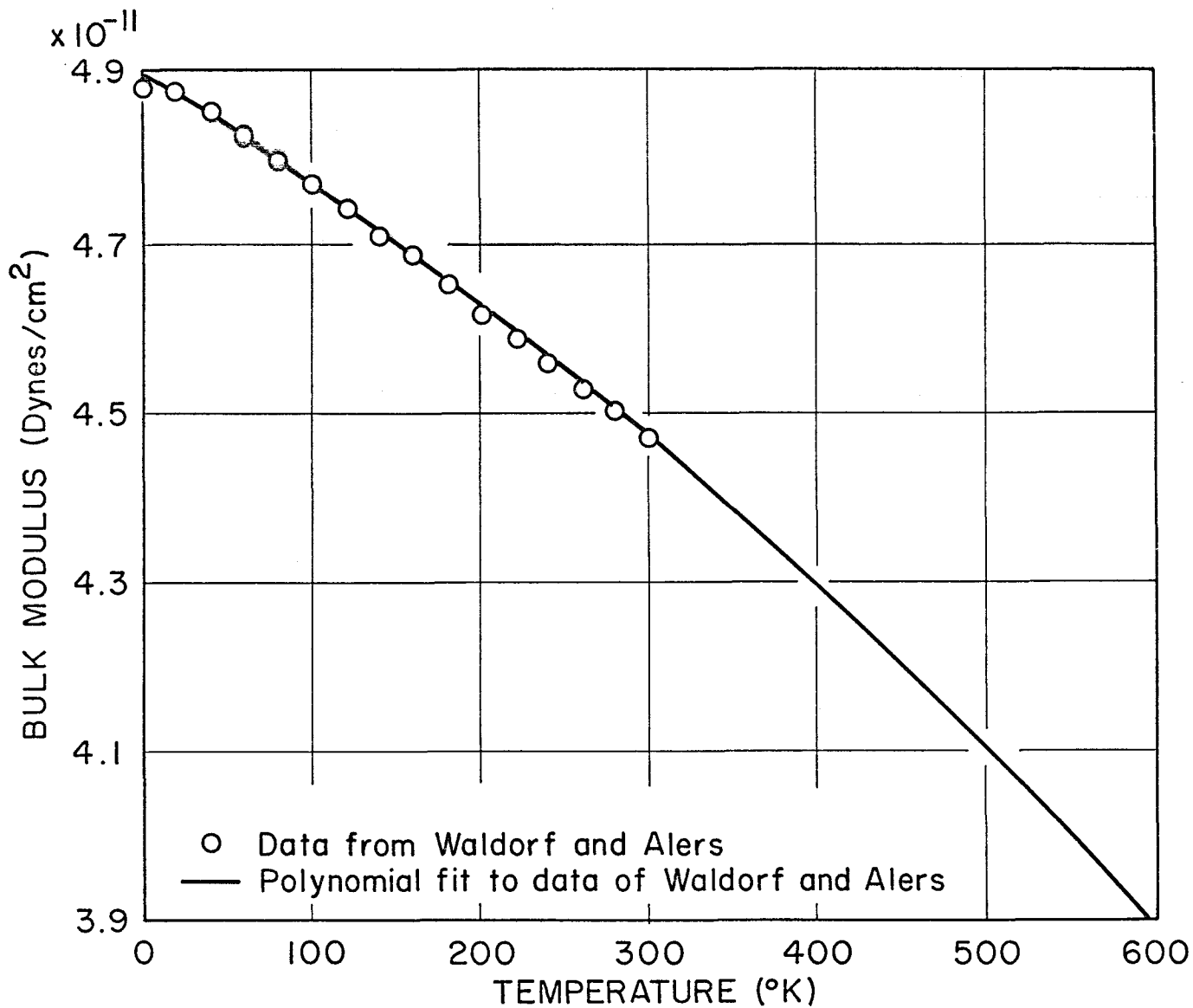


Figure 28. Bulk modulus for lead.

for the low temperature data is

$$\beta_v = c_1 + c_2 T + c_3 T^2 \quad (200 \leq T \leq 300^\circ \text{K}) \quad (33)$$

where, for β_v in square centimeters per degree,

$$c_1 = +20.48 \times 10^{-13},$$

$$c_2 = +83.14 \times 10^{-17},$$

$$c_3 = +10.83 \times 10^{-19},$$

and T = temperature in degree Kelvin.

The standard deviation of the calculated β_v with respect to the above polynomial is 0.1×10^{-24} which represents a deviation of 0.5×10^{-11} at 300°K .

The polynomial for the high temperature data is

$$\beta_v = c_1 + c_2 T + c_3 T^2 + c_4 T^3 \quad (300^\circ \leq T \leq 600^\circ \text{K}) \quad (34)$$

where, for β_v in square centimeters per degree,

$$c_1 = +20.58 \times 10^{-13},$$

$$c_2 = +94.60 \times 10^{-17},$$

$$c_3 = +10.44 \times 10^{-20},$$

$$c_4 = +16.55 \times 10^{-22},$$

and T = temperature in degree Kelvin.

The standard deviation of the calculated β_v with respect to the above polynomial is 0.5×10^{-16} which represents a deviation of 0.2×10^{-2} per cent at 300°K .

Figure 29 shows both the low and the high temperature polynomials used to represent the calculated isothermal compressibilities. Also shown in Figure 29 are the β_v data obtained by a combination of theoretical and experimental

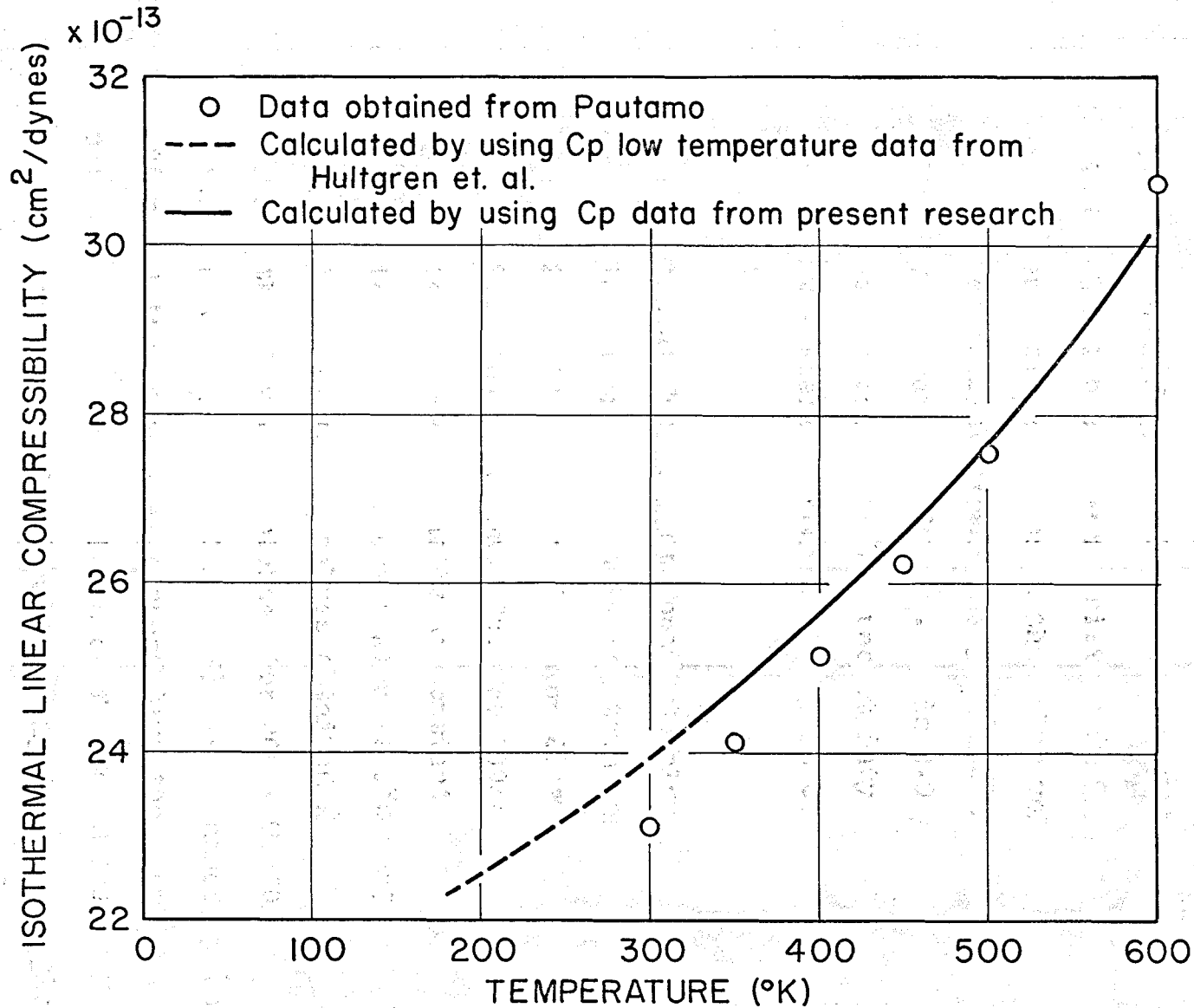


Figure 29. Isothermal compressibility for lead.

calculations made by Pautamo⁴⁹. The difference at low temperature between the polynomial and Pautamo's calculations is 3.3 per cent. The difference decreases at higher temperatures except for the melting point where a three per cent deviation is observed.

At 600°K a 1.6 per cent variation in the bulk modulus, and a one per cent variation in the molar volume, C_p and the coefficient of thermal expansion, produces a maximum uncertainty of two per cent in β_v . This 2.0 per cent variation was used to calculate the uncertainty in the dilation term C^d and the specific heat capacity at constant volume (Section B-e)

d. Specific Heat Capacity at Constant Volume

The calculation of the dilation term was made by using Equations (2), (30), (31) and (33) for $200 \leq T \leq 300^\circ\text{K}$, and Equations (2), (30), (31) and (34) for $300 \leq T \leq 600^\circ\text{K}$.

The specific heat capacity at constant volume was obtained for the low temperature region ($200^\circ \leq T \leq 300^\circ\text{K}$) by using Equation (1), the C_p values obtained from Hultgren et al.³⁵, and the C^d values obtained for $200^\circ \leq T \leq 300^\circ\text{K}$. The high temperature C_v ($300^\circ \leq T \leq 600^\circ\text{K}$) was obtained by using Equation (1) the polynomial representing the present research C_p data and the C^d value calculated for $300^\circ \leq T \leq 600^\circ\text{K}$.

The C_v results at low and high temperature are given in Table V, and are shown in Figure 30. At 300°K the difference between the low and high temperature calculation is 0.2 per cent.

TABLE V

SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME: LEAD

Low Temperature Data		High Temperature Data	
Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)	Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)
200	24.6518	310	24.7100
210	24.6679	320	24.7431
220	24.6824	330	24.7652
230	24.6953	340	24.7838
240	24.7056	350	24.7988
250	24.7162	360	24.8102
260	24.7242	370	24.8184
270	24.7305	380	24.8239
280	24.7353	390	24.8273
290	24.7384	400	24.8295
300	24.7353	410	24.8309
310	24.7397	420	24.8322
		430	24.8341
		440	24.8371
		450	24.8417
		460	24.8483
		470	24.8574
		480	24.8693
		490	24.8842
		500	24.9024
		510	24.9242
		520	24.9497
		530	24.9790
		540	25.0124
		550	25.0498
		560	25.0913
		570	25.1371
		580	25.1872
		590	25.2417
		600	25.3005

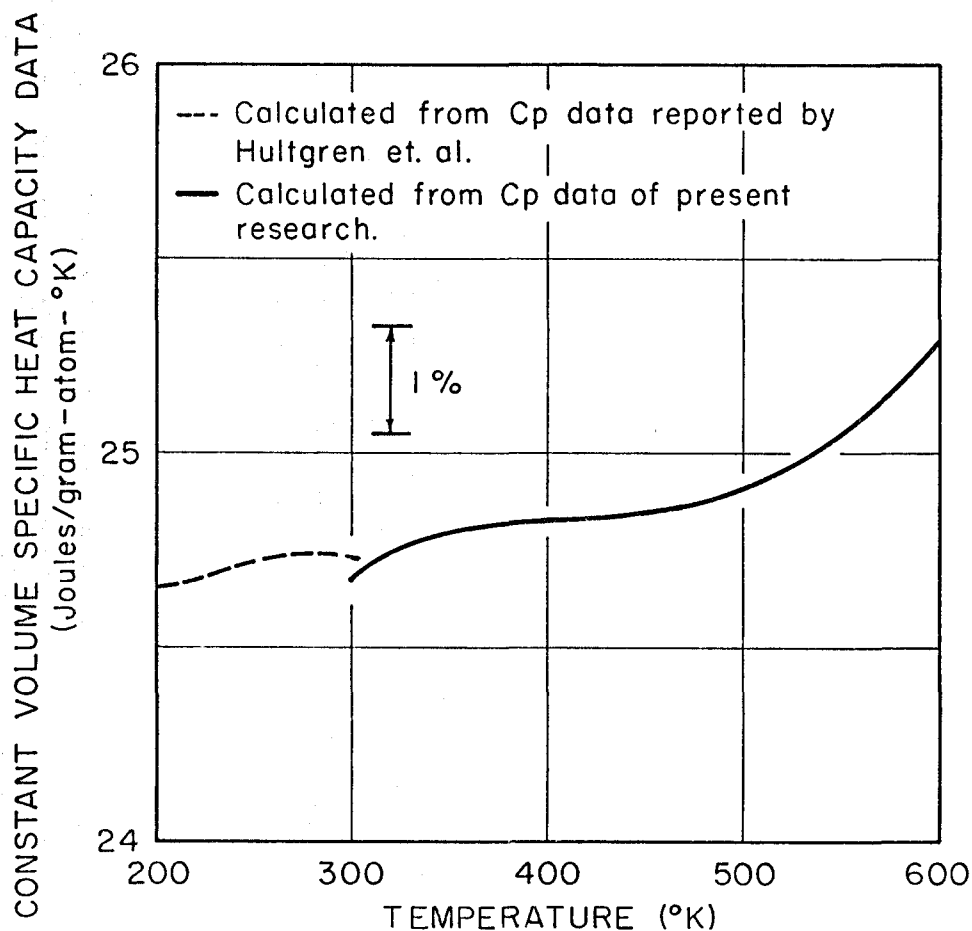


Figure 30. The specific heat capacity at constant volume for lead.

e. Probable Variation in C_V Due to Errors in the Chosen α_V , β_V , V and C_p

Due to the different uncertainties in the different terms involved in the calculation of the dilation term, an analysis was made on the effect of this uncertainties in the calculated C^d and the final C_V .

The analysis made on α_V ($\alpha_V = 3\alpha$), V and β_V (Sections B-a, B-b and B-c) indicated

- 1) that most α values, calculated and obtained from the literature, agreed within one per cent, so the maximum variation of the α_V used in the present research (calculated from the polynomial that fits Feder and Nowick⁴⁵ $\Delta 1/l_0$ data) was not greater than one per cent,
- 2) that a variation no greater than one per cent in the values of the molar volume is expected since the $\Delta 1/l_0$ data of Nix and MacNair⁴³, D'Heurle, Feder and Nowick⁴⁴ and Feder and Nowick⁴⁵ do not differ by more than one per cent, and
- 3) that the maximum variation in β_V calculated from the uncertainties in K , α_V , C_p and V is two per cent.

The above uncertainties, applied to Equation (9) at 600°K, indicated that the maximum variation in the dilation term is ± 0.25 Joules per gram-atom per degree (± 5.6 per cent),

which finally would give an error of one per cent in the calculated specific heat capacity at constant volume. A ± 1.0 per cent variation in C_p plus the ∓ 5.6 per cent variation in C^d will cause a maximum variation of ± 2.2 per cent in C_v . The variation of C_p and C^d , both with the same positive or negative sign will give a variation of ± 0.2 .

C. ZINC

a. Coefficient of Volume Thermal Expansion

The coefficient of volume thermal expansion for zinc was determined from the linear thermal expansion data (along the a and c axis) measured by Gilder and Wallmark⁵⁰ in 1969 from 300°K to 700°K. Since zinc has a hexagonal close-packed structure, the coefficient of volume thermal expansion has to be calculated by

i) determining, separately, the coefficient of linear thermal expansion α_a and α_c from the $\Delta l/l_0$ measurements along the a and c axis, respectively, of single crystals, and

ii) determining the coefficient of volume expansion by using the equation

$$\alpha_v = \frac{1}{V} \frac{dV}{dT} = 2\alpha_a + \alpha_c^* \quad (35)$$

*The derivation of this equation is presented in Appendix F.

1. Coefficient of Linear Thermal Expansion Along the a-axis. The least square curve fitting method was used in the present research to determine the polynomial that fits Gilder and Wallmark⁵⁰ $\Delta l/l_0$ measurements along the a-axis $(\Delta l/l_0)_a$. The polynomial is

$$\left(\frac{\Delta l}{l_0}\right)_a = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 + c_6 T^5 \quad (36)$$

where

$$c_1 = -11.71 \times 10^{-3},$$

$$c_2 = +10.17 \times 10^{-5},$$

$$c_3 = -40.41 \times 10^{-8},$$

$$c_4 = +88.60 \times 10^{-11},$$

$$c_5 = -93.48 \times 10^{-14},$$

$$c_6 = +39.71 \times 10^{-17},$$

and T = temperature in degree Kelvin.

The standard deviation of the $\Delta l/l_0$ data with respect to the above polynomial is 0.6×10^{-5} which represents a 0.5 per cent deviation at 400°K .

Figure 31 shows the linear thermal expansion data for the a-axis $(\Delta l/l_0)_a$ obtained by Gilder and Wallmark⁵⁰, and the polynomial used to represent their data (Equation 36).

The coefficient of linear thermal expansion curve for the a-axis calculated by Gilder and Wallmark⁵⁰ from a graphical differentiation of their $(\Delta l/l_0)_a$ results is shown in Figure 32. They claimed an uncertainty in their

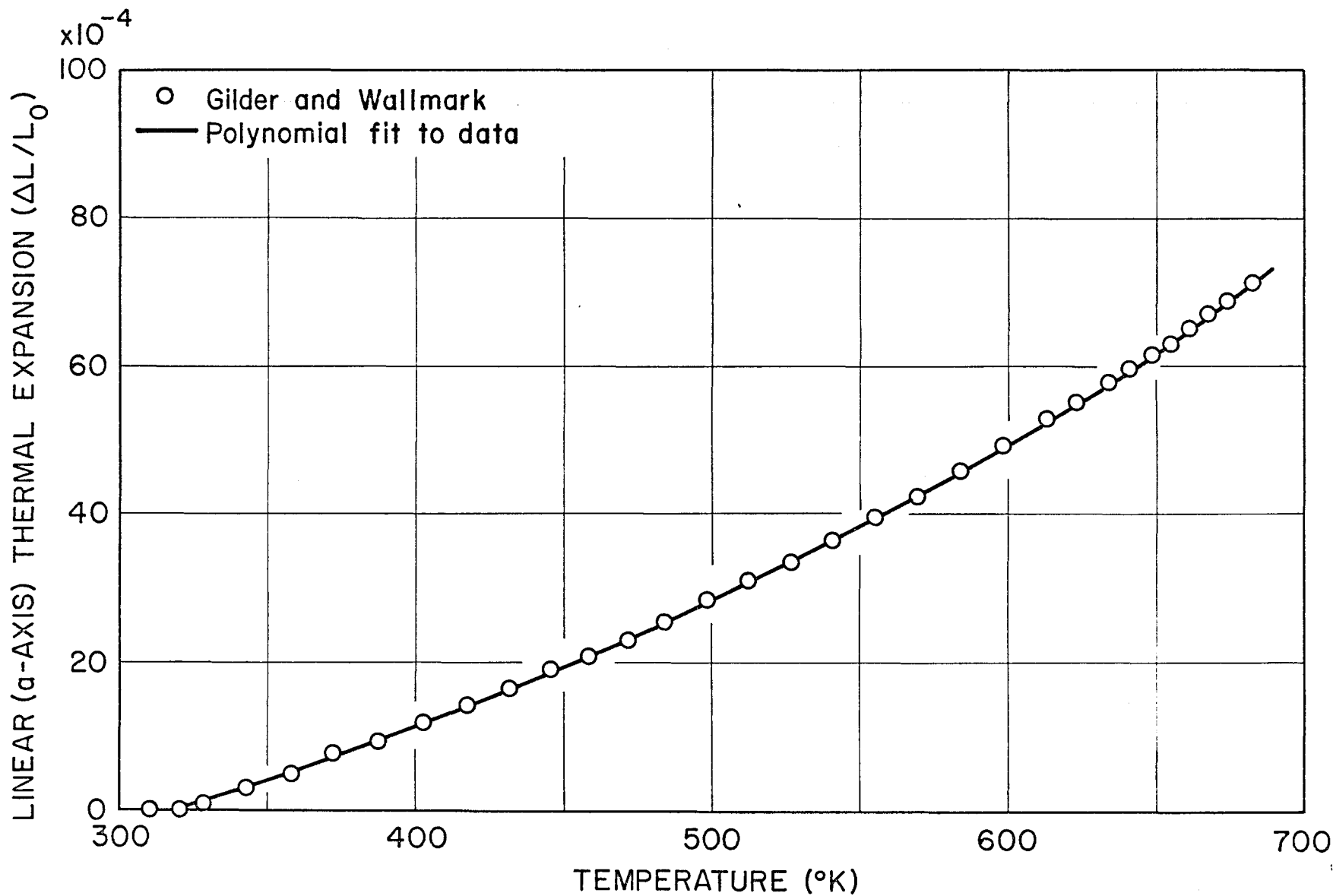


Figure 31. Linear thermal expansion for the a -axis in zinc.

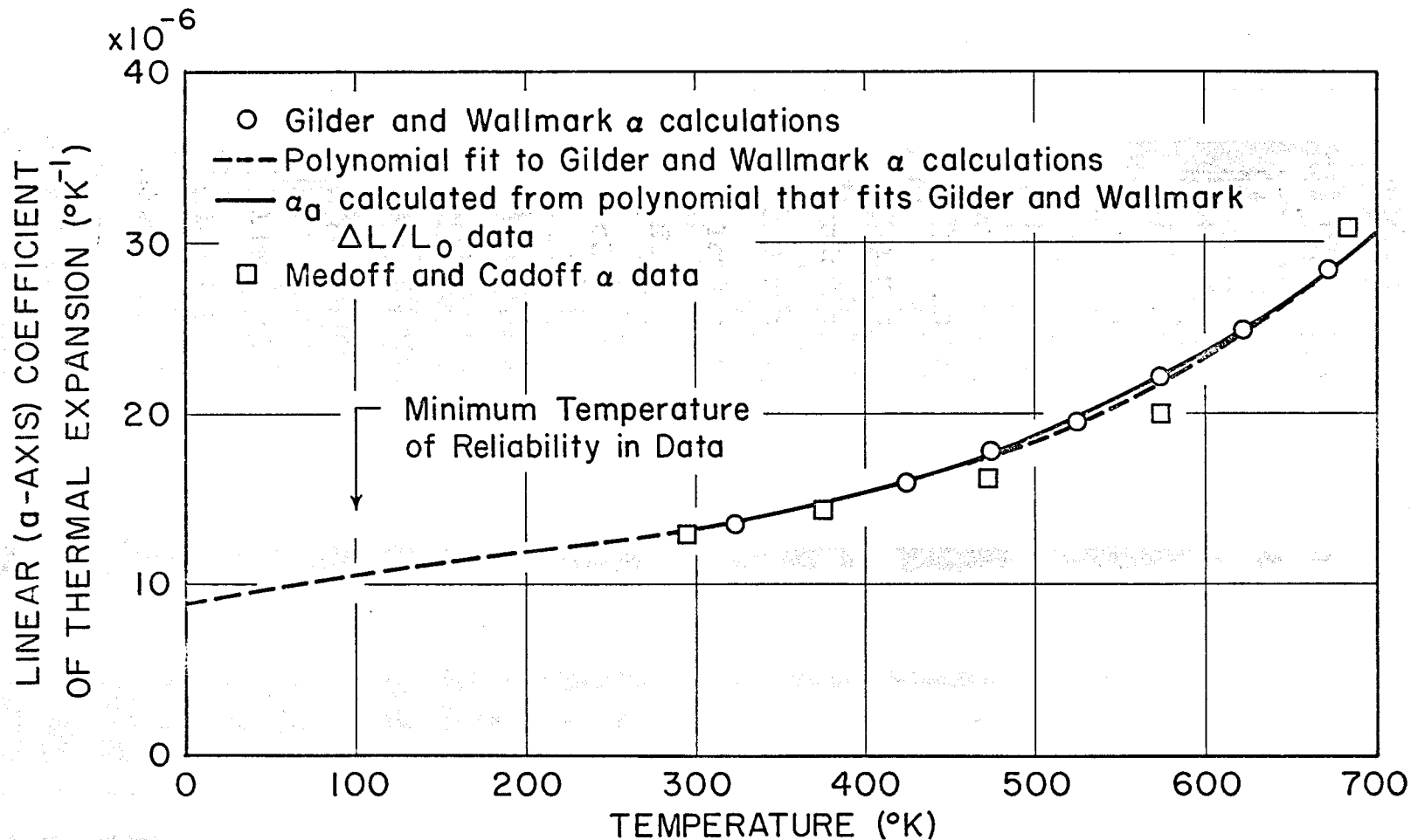


Figure 32. Coefficient of linear thermal expansion for the a-axis, zinc.

α_a results of one per cent. The α_a results obtained by Gilder and Wallmark⁵⁰ were used in the present research to determine a polynomial that could be used to represent their data. The polynomial shown in Figure 32 is given by

$$\alpha_a = C_1 + C_2T + C_3T^2 + C_4T^3$$

where, for α_a in $^{\circ}\text{K}^{-1}$,

$$C_1 = +89.32 \times 10^{-7},$$

$$C_2 = +18.68 \times 10^{-9},$$

$$C_3 = -39.48 \times 10^{-12},$$

$$C_4 = +81.64 \times 10^{-15},$$

and T = temperature in degree Kelvin.

The standard deviation of the α_a results of Gilder and Wallmark⁵⁰ with respect to the above polynomial is 0.2×10^{-6} , which is equivalent to a difference of around 0.2 per cent at 300°K . This difference decreases at higher temperatures.

Figure 32 also shows some α_a values obtained by Medoff and Cadoff⁵¹, who claimed an experimental uncertainty of five per cent in the calculated α_a results. At 573°K their results are ten per cent below those of Gilder and Wallmark⁵⁰, but exhibit closer agreement at other temperatures.

The α_a curve calculated from the polynomial that fits the data of Gilder and Wallmark⁵⁰ $(\alpha_l/l_o)_a$ (Equation (36)) by using Equation (19) is also shown in Figure 32. Since the α_a calculated from Equation (36) by using the procedure summarized in Equation (19) was used for comparison and for future calculations, it was decided to represent the calcu-

lated α_a^* by a simpler polynomial, given by

$$\alpha_a = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4 \quad (38)$$

where, for α_a $^{\circ}\text{K}^{-1}$,

$$C_1 = +10.08 \times 10^{-5},$$

$$C_2 = -80.00 \times 10^{-8},$$

$$C_3 = +26.30 \times 10^{-10},$$

$$C_4 = -36.98 \times 10^{-13},$$

$$C_5 = +19.62 \times 10^{-16},$$

and T = temperature in degree Kelvin.

The standard deviation between the calculated α_a obtained by using Equation (19) and the above polynomial is 0.2×10^{-8} , which produces a variation of 0.01 per cent at 300°K . The variation decreases as the temperature increases. The variations calculated above show that the use of the polynomial instead of the calculated α_a would not produce any appreciable variation in the α_a results. The result obtained by Equation (38) has a maximum variation of 1.4 per cent at 573°K with respect to the α_a calculations made by Gilder and Wallmark⁵⁰. The agreement is excellent at other temperatures. The polynomial given by Equation (38) is, at 573°K , seven per cent above the result obtained by Medoff and Cadoff⁵¹.

The coefficient of linear thermal expansion along the a -axis given by Equation (38) and obtained from the polynomial

*The calculation of the α_a values were made for a temperature interval of ten degrees.

that fits Gilder and Wallmark⁵⁰ ($\Delta l/l_0$) data was used in the determination of the coefficient of volume thermal expansion (Section C-a-3). The α_a results obtained from Equation (38) have a maximum deviation of 1.4 per cent with respect to the graphical determination of α_a made by Gilder and Wallmark⁵⁰. The expected maximum variation in the α_a values obtained from Equation (38) is 1.4 per cent. The per cent difference obtained between the results of Equation (38) and the α_a measured by Medoff and Cadoff⁵¹ was not considered in the chosen estimated error (1.4 per cent) since the latter claimed an uncertainty of five per cent in α_a .

2. Coefficient of Linear Thermal Expansion Along the c-axis. The polynomial determined by the present research to fit Gilder and Wallmark⁵⁰ ($\Delta l/l_0$) measurements along the c-axis ($\Delta l/l_0$)_c is shown in Figure 33 together with Gilder and Wallmark⁵⁰ measurements. The polynomial is given by

$$\left(\frac{\Delta l}{l_0}\right) = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5 \quad (39)$$

where

$$C_1 = -10.33 \times 10^{-3},$$

$$C_2 = -55.68 \times 10^{-6},$$

$$C_3 = + 55.93 \times 10^{-8},$$

$$C_4 = -12.99 \times 10^{-10},$$

$$C_5 = +14.98 \times 10^{-13},$$

$$C_6 = -69.23 \times 10^{-17},$$

and T = temperature in degree Kelvin.

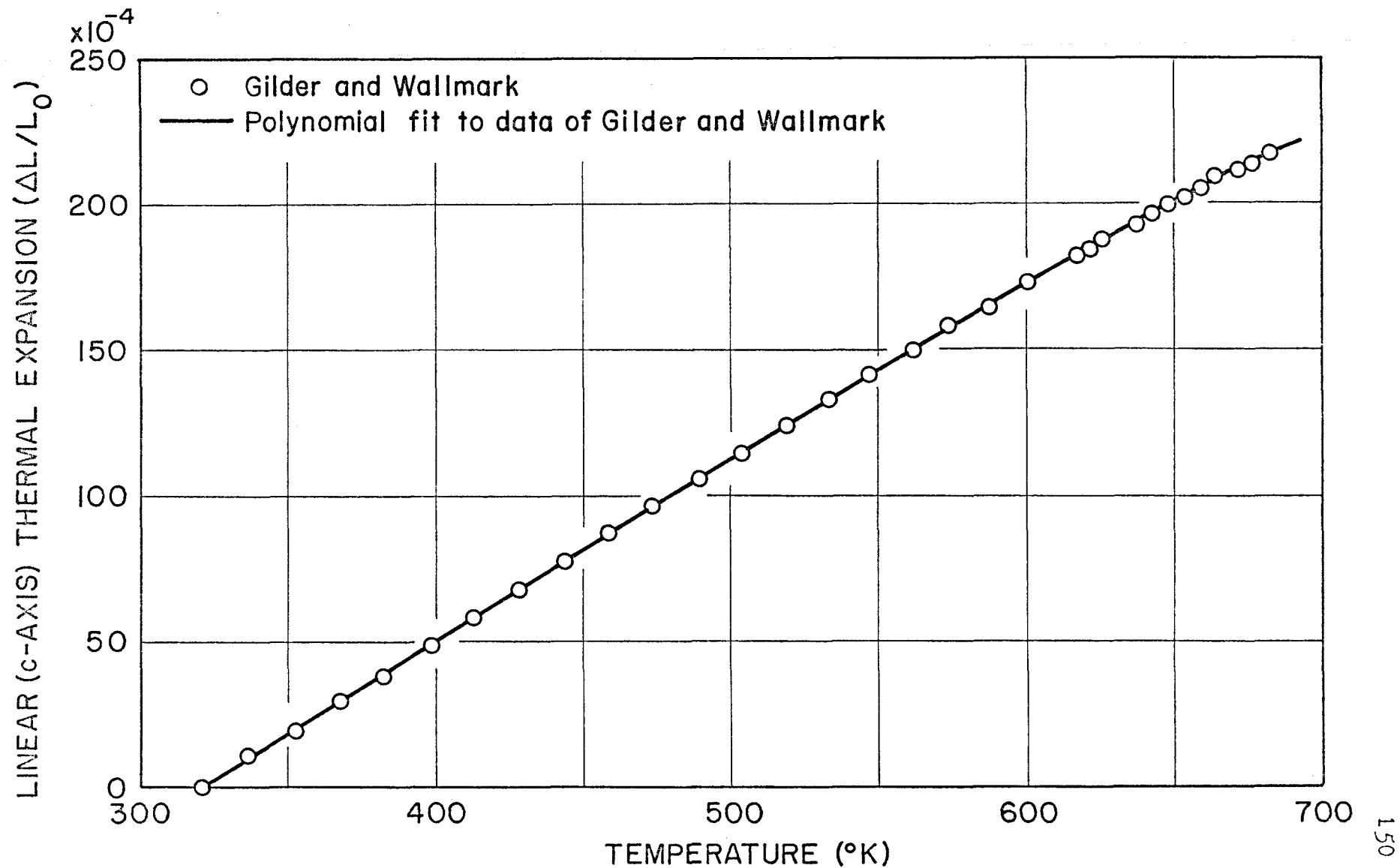


Figure 33. Linear thermal expansion for the c-axis in zinc.

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.4×10^{-8} which represent a deviation of 0.8×10^{-4} per cent at 400°K .

The coefficient of linear thermal expansion for the c -axis calculated by Gilder and Wallmark⁵⁰ from a graphical differentiation of their $(\Delta l/l_0)_c$ results is shown in Figure 34. The uncertainty claimed by Gilder and Wallmark⁵⁰ on the α_c results is one per cent.

Also shown in Figure 34 is the polynomial determined in this research to represent Gilder and Wallmark α_c results. The polynomial is given by

$$\alpha_c = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 + c_6 T^5 \quad (40)$$

where for, α_c in $^\circ\text{K}^{-1}$,

$$c_1 = +21.00 \times 10^{-3},$$

$$c_2 = -17.66 \times 10^{-5},$$

$$c_3 = +83.54 \times 10^{-8},$$

$$c_4 = -19.52 \times 10^{-10},$$

$$c_5 = +22.60 \times 10^{-13},$$

$$c_6 = -10.47 \times 10^{-15},$$

and T = temperature in degree Kelvin.

The standard deviation of the α_c data with respect to the above polynomial was 0.6×10^{-8} which produces a variation of 0.05 per cent at 300°K .

The α_c values calculated by Medoff and Cadoff⁵¹, who claimed an uncertainty of five per cent, are also shown in Figure 34. Most of their α_c results, for temperatures below

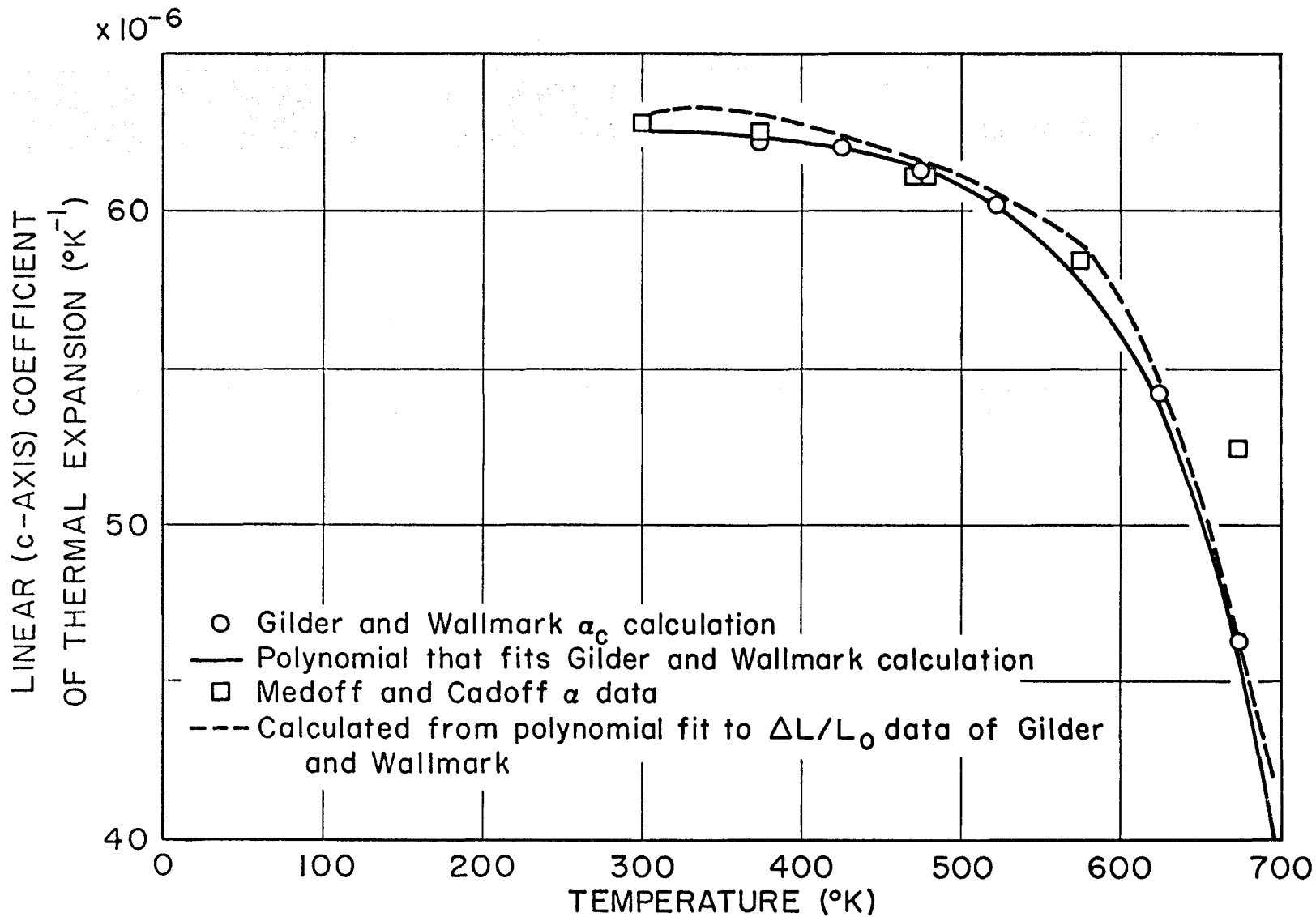


Figure 34. Coefficient of linear thermal expansion for the c-axis, zinc

600°K, are 1.4 per cent above the α_c determined by Gilder and Wallmark⁵⁰. Above 600°K the difference between both α_c results increases to around ten per cent.

The α_c calculated from the polynomial used to fit the data of Gilder and Wallmark⁵⁰ $(\Delta l/l_0)_c$ (Equation (39)), by using Equation (19), is also shown in Figure 34, where it is observed that a difference of 1.4 per cent exists with respect to the α_c graphical measurements made by Gilder and Wallmark⁵⁰, for temperatures below 680°K, and a difference of 3.4 per cent at 693°K.

Since the α_c calculated from Equation (39) by using the procedure summarized in Equation (19) was used for comparison and for future calculations, it was decided to represent the calculated α_c^* by a simpler polynomial which is given by

$$\alpha_c = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 \quad (41)$$

where for, α_c in °K⁻¹,

$$C_1 = -50.71 \times 10^{-6},$$

$$C_2 = +10.80 \times 10^{-7},$$

$$C_3 = -37.74 \times 10^{-10},$$

$$C_4 = +58.07 \times 10^{-13},$$

$$C_5 = -33.52 \times 10^{-16},$$

and T = absolute temperature in degree Kelvin.

The standard deviation of the calculated α_c by using Equa-

*The α_c calculations were made for a ten degrees temperature interval.

tion (19) and the above polynomial is 0.4×10^{-10} which at 690°K produces a variation equal to zero within three decimal places. This indicates that the use of the polynomial given by Equation (41) instead of the calculated α_c does not produce any appreciable deviation in the α_c results. The maximum deviation expected by using Equation (41) in the calculation of the coefficient of thermal expansion (Section C-a-3) is 3.4 per cent, which represent the maximum deviation of Equation (38) with respect to the graphical measurements of α_c made by Gilder and Wallmark⁵⁰. The deviation between Equation (38) and α_c results of Medoff and Cadoff was not considered in the chosen estimated error (3.4 per cent), since the latter claimed an uncertainty of five per cent in α_c .

3. Coefficient of Volume Thermal Expansion. The coefficient of volume thermal expansion was determined by substituting Equations (38) and (41) in Equation (35); the average coefficient of thermal expansion, shown in Figure 35, is equal to one third of the α_v calculated by using Equation (35).

Also shown in Figure 35 are the $\alpha_v/3$ results obtained from the α_a and α_c calculations of Gilder and Wallmark⁵⁰ and those of Medoff and Cadoff⁵¹. The difference between Gilder and Wallmark⁵⁰ α_a and α_c results (obtained by graphical differentiation) and the present research calculations (made by using the polynomial that fits Gilder and

$\times 10^{-6}$

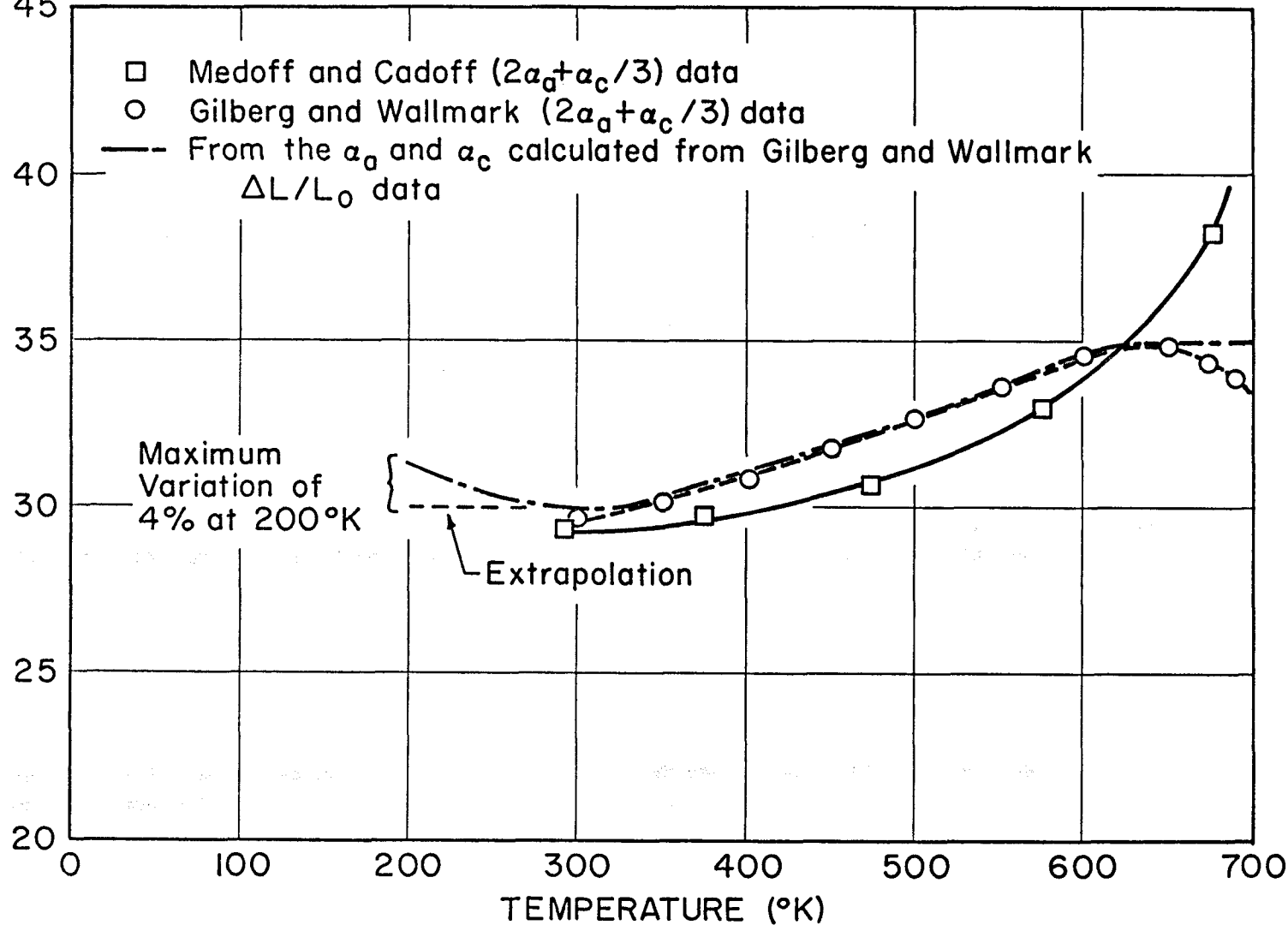


Figure 35. Average coefficient of linear thermal expansion for zinc.

Wallmark $(\Delta l/l_0)_a$ and $(\Delta l/l_0)_c$ measurements) is around one per cent for temperatures below 660°K; at the melting point the difference is around three per cent.

The results obtained from the α_a and α_c results of Medoff and Cadoff⁵¹ are five per cent below the present research calculations for temperatures below 600°K, and at the melting point, their data are around ten per cent above this research calculations.

The 1.4 and 3.4 per cent variation estimated for α_a and α_c will produce a maximum variation of two per cent in the coefficient of volume thermal expansion.

b. Molar Volume

The molar volume at 25°C was calculated from the lattice parameter data given by Pearson⁴⁰ at 25°C, and was used as a reference to calculate the molar volume as a function of temperature. The calculation was made by using the polynomials that fit Gilder and Wallmark⁵⁰ $(\Delta l/l_0)_a$ and $(\Delta l/l_0)_c$ measurements and the following equation

$$V = V_{298} \frac{(l_a)^2 l_c}{(l_a)_R^2 (l_c)_R} \quad (42)$$

where l_a and l_c are obtained by substituting the constants of Equation (36) and (39), respectively, into Equation (17); $(l_a)_R$ and $(l_c)_R$ are obtained by substituting the constants of Equations (36) and (39), respectively in Equation (17) for T equal to 298°K (25°C). The data points obtained by using

Equation (42) were represented in a simpler polynomial (shown in Figure 36) given by

$$V = C_1 + C_2T + C_3T^2 + C_4T^3 \quad (43)$$

where, for V in cubic centimeters per mole,

$$C_1 = +89.77 \times 10^{-1},$$

$$C_2 = +55.31 \times 10^{-5},$$

$$C_3 = +47.98 \times 10^{-8},$$

$$C_4 = -14.59 \times 10^{-11},$$

and T = temperature in degree Kelvin.

The standard deviation of the V calculated by using Equation (42) with respect to the above polynomial is 0.2×10^{-3} which represents a variation of 0.002 per cent at 300°K .

Figure 36 also shows a polynomial representing Owen and Yates⁵² V calculations; the maximum difference is 0.5 per cent at 500°K . The agreement between Owen and Yates⁵² results and those obtained in the present research indicates that the deviation obtained by using Equation (43) to calculate C^d should not be greater than one per cent.

c. Isothermal Compressibility

The adiabatic linear compressibility had been calculated by Alers and Neighbours⁵³ from measurements of elastic constants for temperatures between 4.2°K and 670°K . Polynomials were calculated in order to represent the results of Alers and Neighbours⁵³ along the a and c axis.

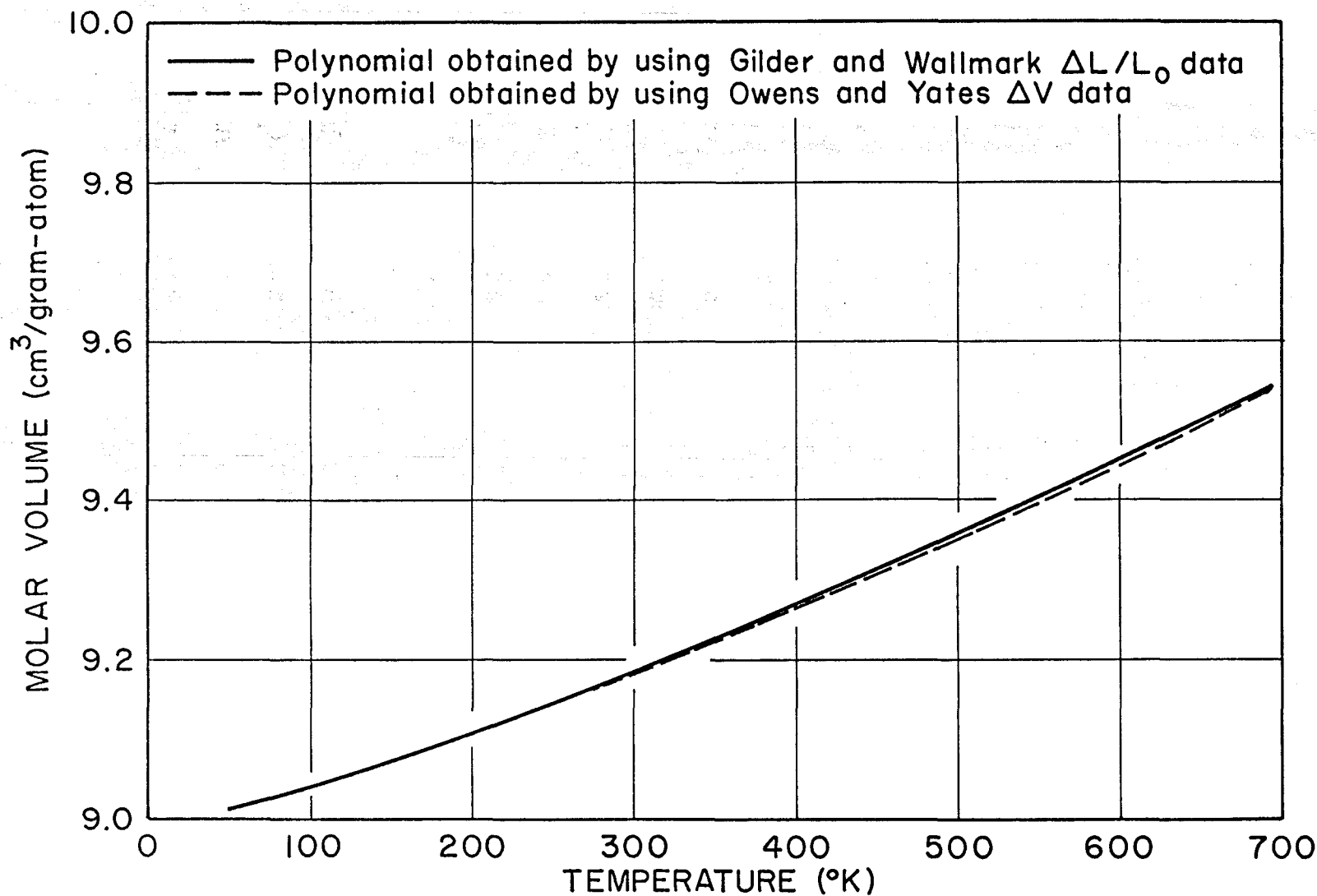


Figure 36. Molar volume for zinc.

1. Adiabatic Linear Compressibility Along the a-axis

$(\beta_A)_a$. The polynomial calculated to represent Alers and Neighbours⁵³ $(\beta_A)_a$ data is

$$(\beta_A)_a = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4 + C_6T^5 \quad (44)$$

where, for $(\beta_A)_a$ in square centimeters per degree Kelvin,

$$C_1 = +15.33 \times 10^{-14},$$

$$C_2 = -27.30 \times 10^{-18},$$

$$C_3 = -81.68 \times 10^{-20},$$

$$C_4 = +50.95 \times 10^{-22},$$

$$C_5 = -90.35 \times 10^{-25},$$

$$C_6 = +48.31 \times 10^{-28},$$

and T = temperature in degree Kelvin.

Figure 37 shows Alers and Neighbours⁵³ data and the above polynomial used to represent their data. The standard deviation of the data obtained by Alers and Neighbours⁵³ with respect to the polynomial given by Equation (44) is 0.6×10^{-15} which, at 300°K , gives a variation of 0.4 per cent.

It is expected that the use of Equation (44) to give the $(\beta_A)_a$, results in a maximum variation of one per cent. This value is used in a subsequent calculation of the uncertainty in the adiabatic volume compressibility.

2. Adiabatic Linear Compressibility Along the c-axis

$(\beta_A)_c$. The polynomial calculated to represent Alers and Neighbours⁵³ $(\beta_A)_a$ data is shown in Figure 38 together with

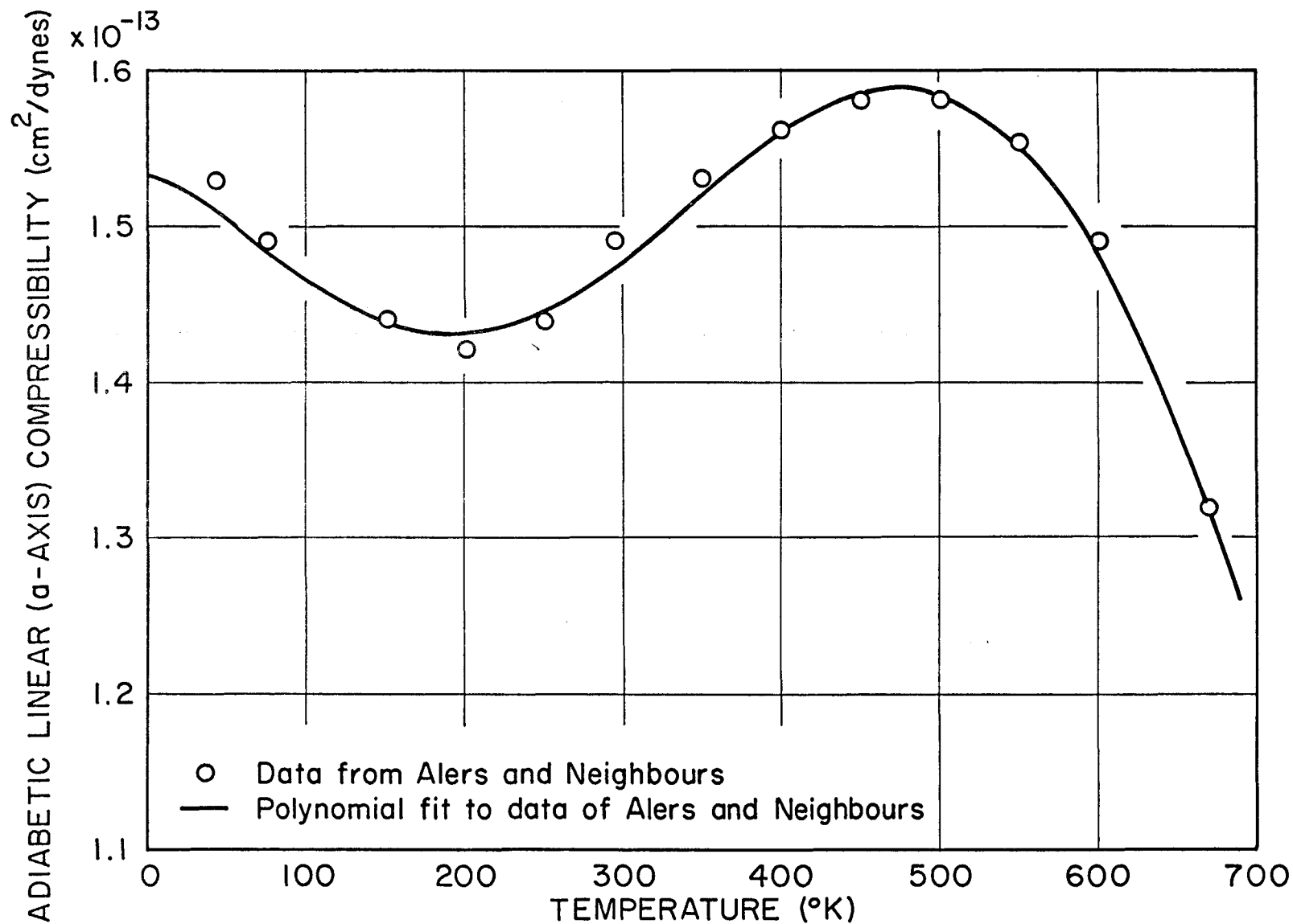


Figure 37. Adiabatic linear compressibility along the a -axis for zinc.

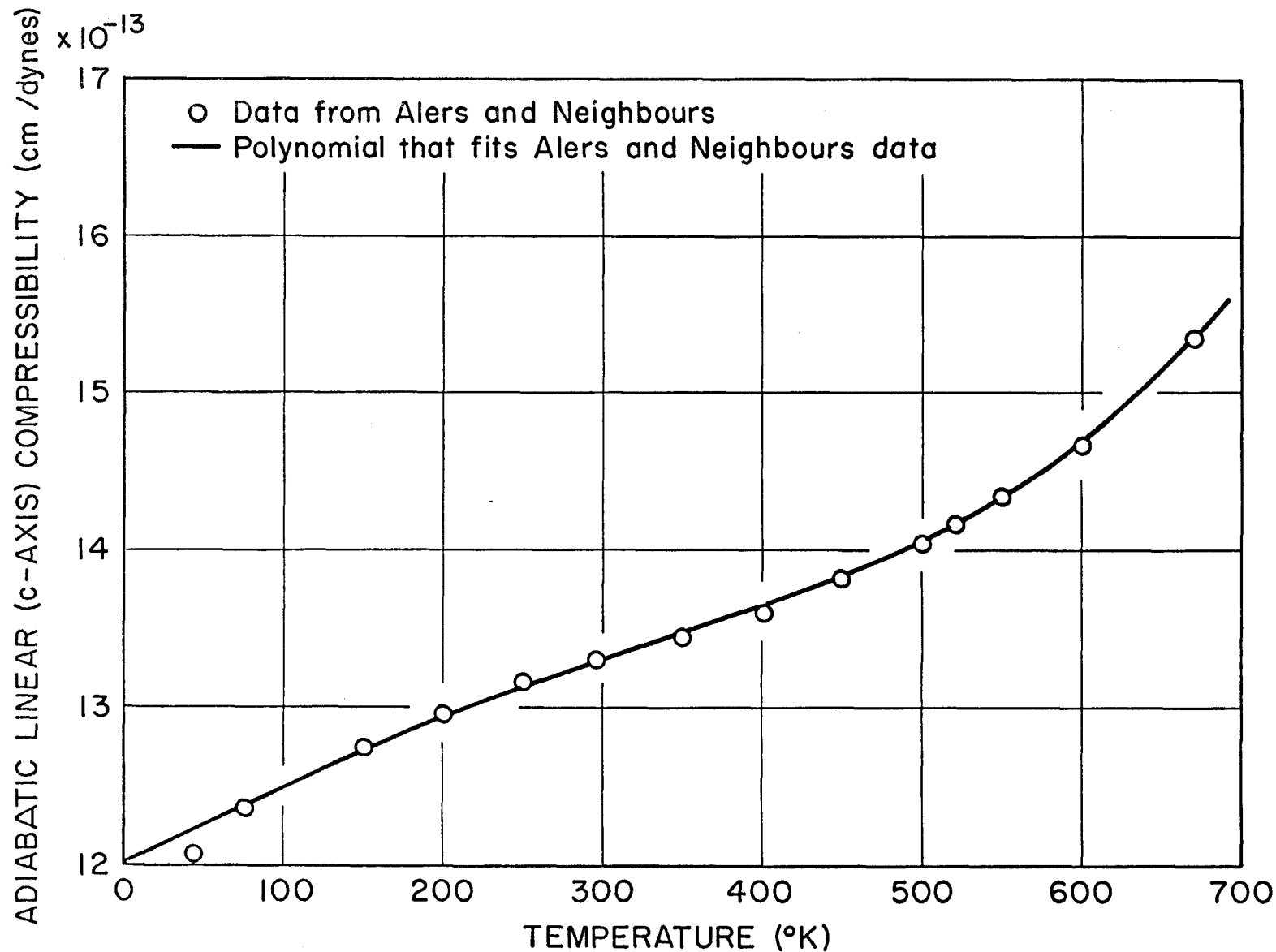


Figure 38. Adiabatic linear compressibility along the c-axis for zinc.

their data. The polynomial is

$$(\beta_A)_c = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4 \quad (45)$$

where, for $(\beta_A)_c$ in square centimeters for dyne,

$$C_1 = +12.03 \times 10^{-13},$$

$$C_2 = +45.03 \times 10^{-17},$$

$$C_3 = +25.73 \times 10^{-20},$$

$$C_4 = -19.94 \times 10^{-22},$$

$$C_5 = +25.33 \times 10^{-25},$$

and T = temperature in degree Kelvin.

The standard deviation of the data obtained by Alers and Neighbours⁵³ $(\beta_A)_c$ with respect to the above polynomial is 0.2×10^{-14} which, at 300°K , would produce a variation of 0.1 per cent.

It is expected that the use of Equation (45) to give the $(\beta_A)_c$, results in a maximum variation of one per cent. This calculation is used in a subsequent calculation of the uncertainty in the adiabatic compressibility.

3. Adiabatic Volume Compressibility. β_A . The adiabatic compressibility is given by

$$\beta_A = 2(\beta_A)_a + (\beta_A)_c^* \quad (46)$$

where $(\beta_A)_a$ and $(\beta_A)_c$ are the results obtained by using Equations (44) and (45), respectively. Figure 39 shows the β_A results.

*The derivation of this equation is similar to that of Equation (35).

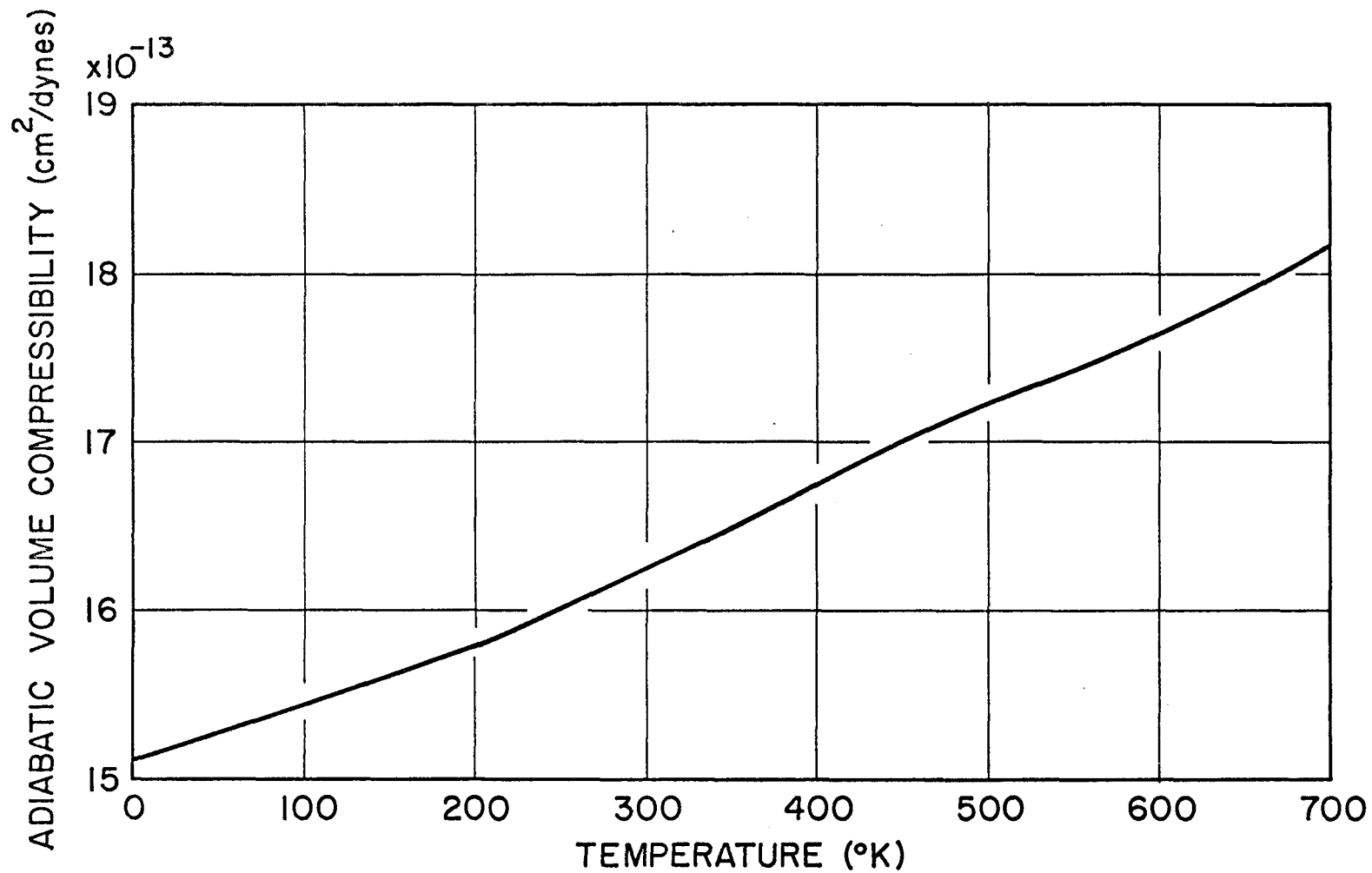


Figure 39. Adiabatic volume compressibility for zinc.

The estimated one per cent variation in $(\beta_A)_a$ and $(\beta_A)_c$ will produce a variation of one per cent in the β_A results.

4. Isothermal Volume Compressibility. The isothermal volume compressibility β_V for zinc was calculated at low temperature ($200^\circ \leq T \leq 300^\circ \text{K}$) by using Equation (7) and the low temperature C_p data of Schimpft⁵⁴. A polynomial was calculated to represent these β_V data and it is

$$\beta_V = C_1 + C_2T + C_3T^2, \quad 200^\circ \leq T \leq 300^\circ \text{K} \quad (47)$$

where, for β_V in square centimeters per degree,

$$C_1 = +15.90 \times 10^{-13},$$

$$C_2 = +54.84 \times 10^{-18},$$

$$C_3 = +11.79 \times 10^{-19},$$

and T = temperature in degree Kelvin.

The standard deviation of the data calculated by using Equation (47) with respect to the above polynomial is 0.8×10^{-18} which produces a variation of 0.5×10^{-4} per cent at 300°K .

The high temperature ($300^\circ \leq T \leq 693^\circ \text{K}$) isothermal volume compressibility β_V was calculated by using Equation (7) in the present chapter and the polynomial used to represent the C_p data of the present research (Chapter III). The result was then used to obtain a polynomial to represent the high temperature β_V as a function of temperature. This polynomial is given by

$$\beta_V = C_1 + C_2T + C_3T^2 + C_4T^3, \quad 300^\circ \leq T \leq 693^\circ \text{K} \quad (48)$$

where, for β_v in cubic centimeters per degree,

$$C_1 = +15.41 \times 10^{-13},$$

$$C_2 = +24.64 \times 10^{-17},$$

$$C_3 = +13.67 \times 10^{-19},$$

$$C_4 = -96.47 \times 10^{-23},$$

and T = temperature in degree Kelvin.

The standard deviation of the β_v data obtained from Equation (47) with respect to the above polynomial is 0.9×10^{-15} , which at 300°K would give a variation of 0.05 per cent. This variation decreases with increasing temperature. The low and high temperature β_v results are shown in Figure 40. At 320°K a difference of 0.2 per cent exists between the β_v calculated from the low temperature polynomial and the β_v calculated from the high temperature polynomial.

The estimated one per cent variation in β_A , v , a_v and C_p will produce a maximum uncertainty of two per cent in β_v at 690°K .

d. The Specific Heat Capacity at Constant Volume

The calculation of the dilation term C^d at low temperature ($200^\circ \leq T \leq 300^\circ\text{K}$) was made by using Equations (2), (35)*, (43) and (47); the C^d at high temperature ($300^\circ \leq T \leq 693^\circ\text{K}$) was obtained by using Equation (2), (35)*, (43) and (48).

The specific heat capacity at constant volume was ob-

* a_a and a_c in Equation (35) are substituted by Equation (38) and (41), respectively.

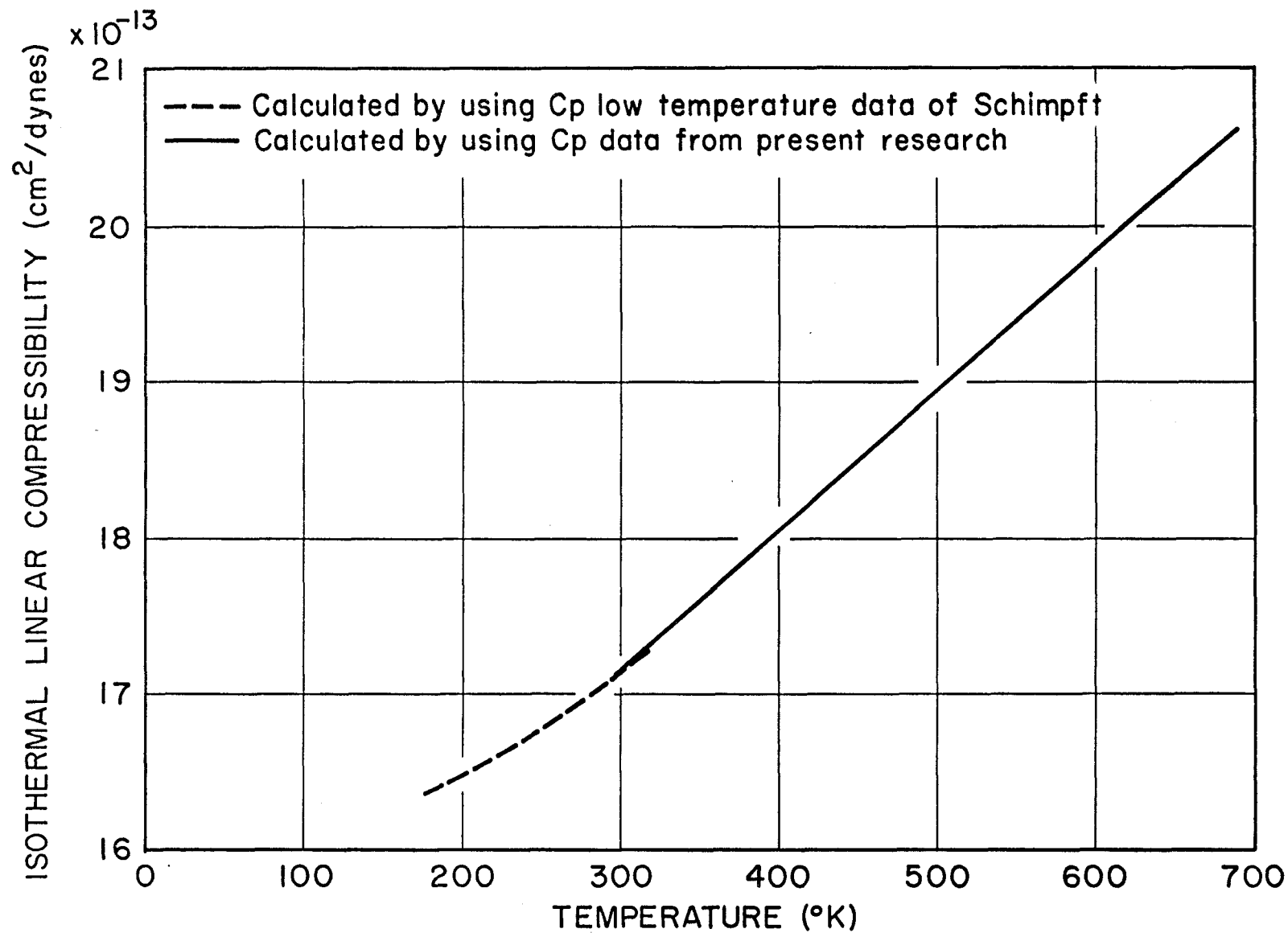


Figure 40. Isothermal volume compressibility for zinc.

tained for the low temperature region ($200^{\circ} \leq T \leq 300^{\circ} \text{K}$) by using Equation (1) in the present chapter, the C_p values obtained by Schimpft⁵⁴ and the C^d values obtained for $200 \leq T \leq 300^{\circ} \text{K}$. The high temperature C_v ($300^{\circ} \text{K} \leq T \leq 693^{\circ} \text{K}$) was obtained by using Equation (1), the polynomial representing the C_p data obtained in the present research and the C^d values obtained for $300^{\circ} \leq T \leq 693^{\circ} \text{K}$.

The results in the low and high temperature ranges are given in Table VI, and are shown in Figure 41. At 320°K the low temperature C_v results obtained from the Schimpft⁵⁴ C_p data are one per cent higher than the value calculated from the C_p determined in the present research.

e. Probable Variations in C_v Due to Errors in the Chosen α_v , β_v , V and C_p

Due to the different uncertainties in the different terms involved in the calculation of the dilation term, an analysis was made on the effect of this uncertainties in the calculated C^d and the final C_v .

The analysis made on α_v , V and β_v (Section C-a, C-b and C-c) indicated

- 1) that the variation in α_v due to a variation of 1.4 and 3.4 per cent in α_a and α_c was two per cent,
- 2) that a variation no greater than one per cent is expected in the molar volume, and
- 3) that the maximum variation in β_v due to a one per cent variation in C_p , V and β_A and a two per cent

TABLE VI

SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME: ZINC

Low Temperature Data		High Temperature Data	
Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)	Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)
200	22.1980	320	23.8248
210	22.4747	330	23.9350
220	22.7301	340	24.0614
230	22.9645	350	24.1911
240	23.1779	360	24.3157
250	23.3705	370	24.4299
260	23.5425	380	24.5310
270	23.6939	390	24.6178
280	23.8250	400	24.6902
290	23.9357	410	24.7491
300	24.0264	420	24.7957
310	24.0971	430	24.8317
		440	24.8591
		450	24.8798
		460	24.8958
		470	24.9091
		480	24.9217
		490	24.9354
		500	24.9520
		510	24.9730
		520	25.0001
		530	25.0346
		540	25.0778
		550	25.1309
		560	25.1950
		570	25.2710
		580	25.3600
		590	25.4626
		600	25.5796
		610	25.7116
		620	25.8593
		630	26.0230
		640	26.2032
		650	26.4004
		660	26.6148
		670	26.8466
		680	27.0962
		690	27.3637

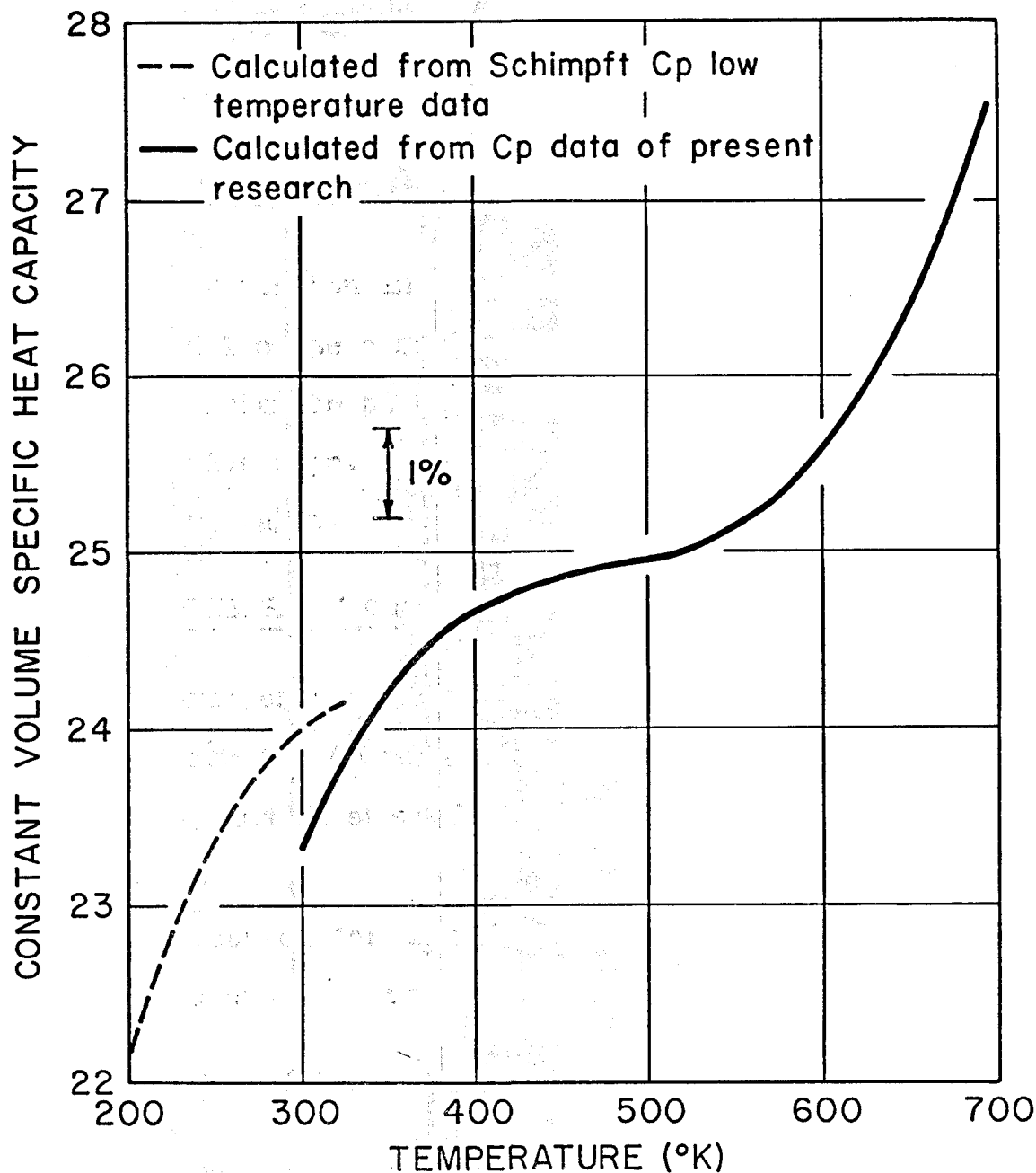


Figure 41. The specific heat capacity at constant volume for zinc.

variation in α_v was two per cent.

The above uncertainties, applied in Equation (9) at 690°K , indicated that the maximum variation in the dilation term is 0.25 Joules per gram-atom per degree Kelvin (7.3 per cent) which finally would give an error of 0.9 per cent in the calculated C_v .

A ± 1.0 variation in C_p plus the ± 7.3 per cent variation in C^d will cause a maximum variation of ± 2.0 per cent in C_v . The variation of C_p and C^d , both with the same positive or negative sign, will give a variation of ± 0.9 per cent in the C_v value.

D. GRUNEISEN'S CONSTANT Γ : EFFECT ON C_v

The Gruneisen's constant for gold, lead and zinc was calculated from the C_v results obtained in parts A, B, and C respectively, and is shown in Figure 42 as a function of temperature.

The expression for C_v using Gruneisen's constant, from Equations (1) and (3), is

$$C_v = \frac{C_p}{1 + \frac{C_p}{\Gamma \alpha_v T}} \quad (49)$$

The terms used to calculate Γ are all available at 300°K , so by assuming Γ to be constant, the C_v as a function of temperature can be calculated. As is observed in Figure 42, Γ changes considerably with temperature, so by assuming it to be constant, an error is made in the approximation.

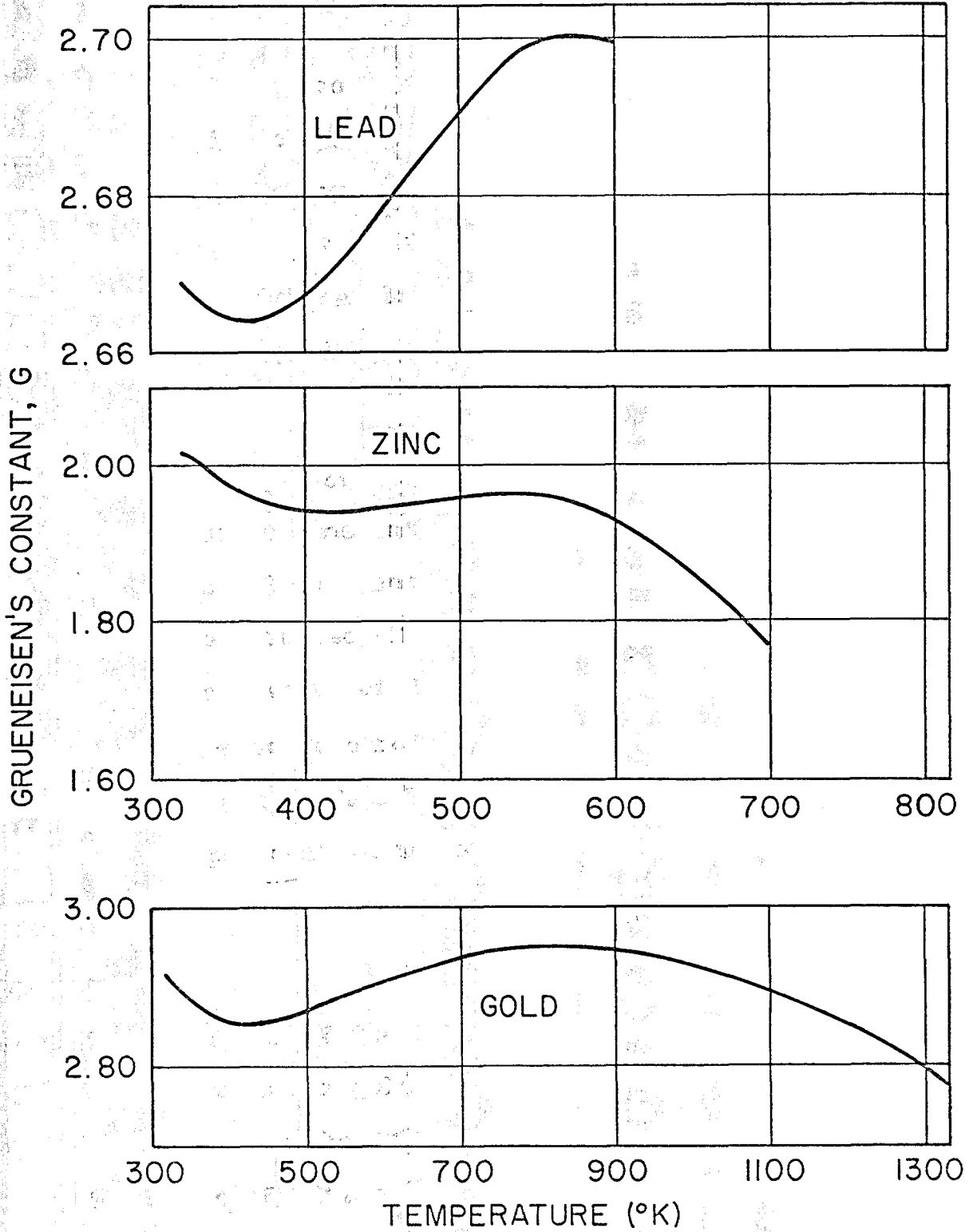


Figure 42. The Gruneisen's constant as a function of Temperature for gold, lead and zinc.

a. Gold

The use of the Gruneisen's constant at 300°K to calculate C_v at 1330°K gives a value of 26.60 Joules per gram-atom per degree, which compared to the value 26.96 Joules per gram-atom per degree in Table IV (Page 121) gives an error of around 1.3 per cent in the specific heat capacity at constant volume. Note that between 320°K and 1330°K , Gruneisen's constant, varies by five per cent.

b. Lead

For lead, it is observed that a smaller variation exists in the Gruneisen's constant with temperature than for gold. At 600°K Γ is 1.1 per cent lower than the value of 300°K . The use of the Gruneisen's constant at 300°K to calculate C_v at 600°K gives a value of 25.43^* Joules per gram-atom per degree, which when compared to the value 25.30 Joules per gram-atom per degree from Table V (Page 140), gives an error of 0.5 per cent in the specific heat capacity at constant volume.

c. Zinc

The variation of the Gruneisen's constant for zinc is even greater than for gold or lead. At 693°K Γ is 12.0 per cent less than the value at 320°K .

The use of Equation (49) to determine the specific heat

*The calculation was made by using Equation (49).

capacity at constant volume at 690°K by using the Γ value at 320°K gives a result of 27.35 Joules per gram-atom per degree, which when compared to the value 27.36 Joules per gram-atom per degree from Table VI (Page 168), gives an error of 1.1 per cent in the specific heat Capacity C_v .

E. THE EFFECT OF THE USE OF THE NERNST-LINDEMANN

APPROXIMATION ON C_v

Another approximation which could have been used to calculate C_v is the Nernst-Lindemann approximation given by Equation (6). The use of this constant A would have been possible since data of α_v , $V C_p$ and β_v exist around 300°K to allow its calculation.

Figure 43 shows the variation of the constant A as a function of temperature, as calculated from the C_v obtained in part A, B and C for gold, lead and zinc, respectively.

a. Gold

For gold the use of the Nernst-Lindemann approximation to calculate C_v at high temperature would have caused a high value of C_v due to the sharp increase in A around 320°K. A maximum variation of 17 per cent exists in the A value given by Equation (6) (Figure 43).

If the A value at 320°K were used to calculate C_v at 1330°K, the error in C_v would be around two per cent. This approximation is obviously better for gold than the use of the Gruneisen's constant.

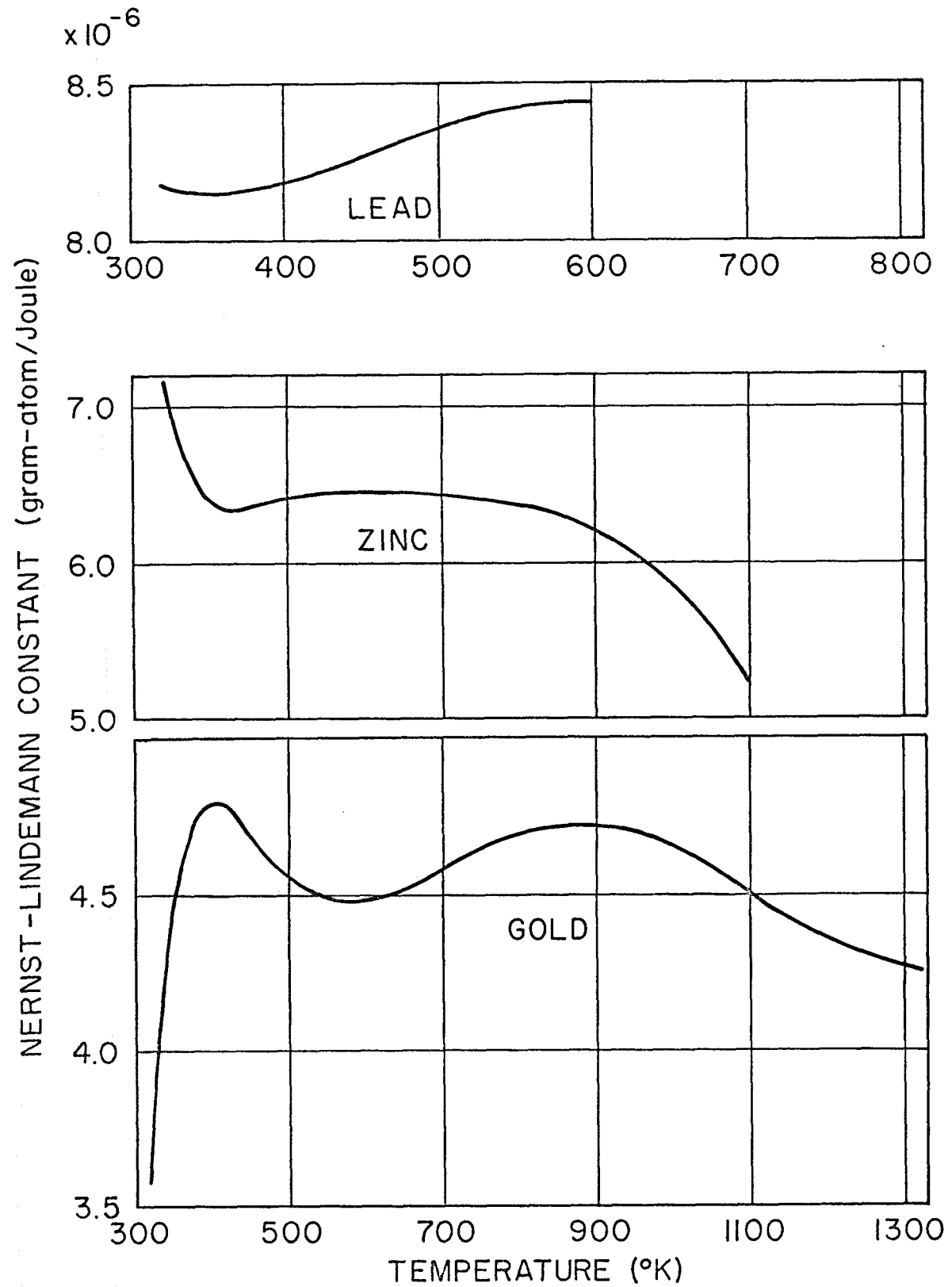


Figure 43. The Nernst-Lindemann constant as a function of temperature, for gold, lead and zinc.

b. Lead

For lead, the maximum variation of the A value given by Equation (6) is four per cent (Figure 43). The use of A at 320°K to calculate C_v at 600°K produces an error of around one per cent in the specific heat capacity at constant volume. This approximation works reasonably well for lead, as it did for gold.

c. Zinc

A variation of 28.0 per cent exists in A for zinc (Figure 43). The calculation of the specific heat capacity at constant volume by using the A value at 320°K produces an error of four per cent in C_v at 690°K .

THEORETICAL CONTRIBUTIONS TO THE SPECIFIC HEAT CAPACITY
AT CONSTANT VOLUME: RESULTS AND CONCLUSIONS

For gold, lead and zinc the different theoretical contributions to the specific heat capacity (discussed in detail in Chapter I) were determined after the necessary parameters (Debye temperature Θ_D , electronic heat capacity constant γ , formation energies of monovacancies and divacancies, Δh_{1v} and Δh_{2v} respectively, and the entropy change due to the formation of monovacancies and divacancies, ΔS_{1v} and ΔS_{2v} , respectively) were obtained from the literature. The analysis was made assuming all contributions to C_v lattice, electronic, formation of imperfections (monovacancies and divacancies) to be independent from each other. Then the anharmonic contribution was obtained by subtracting the theoretical contributions from the experimental C_v , which was calculated from the experimental C_p .

The formula that relates $(C_v)_{\text{experimental}}$ to all the different contributions is

$$(C_v)_{\text{experimental}} = (C_L)_v + (C_E)_v + (C_{1v})_v + (C_{2v})_v + (C_{\text{anharmonic}})_v \quad (1)$$

or

$$(C_{\text{anharmonic}})_v = (C_v)_{\text{experimental}} - (C_L)_v - (C_E)_v - (C_{1v})_v - (C_{2v})_v \quad (2)$$

The lattice contribution is

$$(C_L)_v = 3Nk \left[3 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{e^x x^4 dx}{(e^x - 1)^2} \right]^* \quad (3)$$

where N = Avogadro's number,

k = Boltzman's constant,

and T = temperature in degree Kelvin

The electronic contribution is

$$(C_E)_v = \gamma T \left[1 - \frac{3\pi^2}{10} \left(\frac{kT}{\zeta_0} \right)^2 \right] \quad (4)$$

where

$$\gamma = \frac{1}{2} \pi^2 R^k \frac{\zeta_0}{\zeta_0} Z,$$

ζ_0 = Fermi Energy,

and Z = number of free electrons per atom.

The contribution due to the formation of monovacancies is

$$(C_{1v})_v = (N e^{\Delta S_{1v}/k}) \left(\frac{\Delta h_{1v}^2}{kT^2} \right) e^{-\Delta h_{1v}/kT} \quad (5)$$

and the contribution due to the formation of divacancies is

$$(C_{2v})_v = (N \frac{Z}{2} e^{\Delta S_{ev}/k}) \left(\frac{\Delta h_{2v}^2}{kT^2} \right) e^{-\Delta h_{2v}/kT}, \quad (6)$$

*The computer program that was used⁷³ to calculate the integral is able to perform numerical integration of any analytic function by sixteen point Gaussian quadrature. The integrals are broken into two regions and the limits of integration for a desired integral are given as two arguments of a subroutine call statement.

where

$$\Delta h_{2v} = 2\Delta h_{1v} - B,$$

B = binding energy for two vacancies,

z = coordination number

and T = temperature in degree Kelvin.

At relatively low temperature ($T < 400^\circ\text{K}$) $(C_{1v})_v$ and $(C_{2v})_v$ are negligible. Further, in the present treatment $(C_{\text{anharmonic}})_v$ is assumed to be very small at low temperature. Then, for these temperatures, Equation (2) becomes

$$C_v)_{\text{experimental}} = (C_L)_v + (C_E)_v \quad (7)$$

Due to the wide range of values given in the literature for θ_D and γ^* , these parameters were chosen to give values for $[(C_L)_v + (C_E)_v]$ that were the closest to the experimental C_v obtained in this research, for temperatures close to 300°K . For all three metals studied during this investigation, around 300°K the sum of the lattice and electronic contributions to the specific heat capacity was closest to the experimental C_v when the θ_D value used was the highest and the γ value used was the lowest. An examination was then made of the effect of the variation of θ_D and γ on the total theoretical lattice and electronic contributions to C_v , and on the difference ΔC_v obtained between the theoretical specific heat capacity at constant volume and the $(C_v)_{\text{experimental}}$. The effect of the variation in θ_D and

* The γ is determined experimentally at low temperatures and the present treatment assumes that no appreciable varia-

on γC_v was examined at two or three different temperatures.

It is emphasized that the variation of θ_D is due to the different temperatures at which its determination has been made (its variation being especially large for temperatures around 0°K), and to the method employed for its determination. It will be shown, for gold, lead and zinc, that above 300°K the variation in θ_D and γ does not affect appreciably the lattice plus electronic contributions to C_v . Analyses of the variation of θ_D with temperature and method employed for its determination have been made by Gschneidner⁵⁶, Herbstein⁵⁷ and Kelly and MacDonald⁵⁸.

In the present treatment the θ_D and γ values were obtained from a compilation of data and analysis made by Gschneidner⁵⁶.

The contribution to C_v due to the formation of monovacancies was determined by using one of the Δh_{1v} and ΔS_{1v} values given in the literature for a given metal; the effect on C_v due to a variation in these Δh_{1v} and ΔS_{1v} values was then analyzed. The contribution to C_v due to the formation of divacancies was obtained by assuming the binding energy B for two vacancies to be within the limit $\Delta h_{1v}/6$ and $E_c/6^*$, as explained by Bartlett and Dienes⁵⁵. The rea-

tion exists when this experimental γ result is assumed to be constant, independent of volume changes produced by increasing temperature.

* E_c is the lattice cohesive energy.

son for this choice of B will be explained during the analysis of the $(C_{2v})_v$ contribution for gold.

A. RESULTS

a. Gold

1. Lattice and Electronic Contributions to C_v . θ_D
 values for gold have been obtained by specific heat capacity, elastic constants, electrical resistivity and thermal expansion measurements⁵⁶; the values range from 156°K (calculated from elastic constants measurements at 298°K) to 203°K (calculated from electrical resistivity measurements at 100°K). The relatively closest $(C_L)_v$ value to the experimental C_v results were obtained with a θ_D equal to 203°K; the theoretical $(C_L)_v$ result being at 320°K 0.3 Joules per gram-atom per degree Kelvin above the present research $(C_v)_{\text{experimental}}$. Any other θ_D smaller than 203°K will increase that difference. The use of a θ_D value equal to 156°K produces a $(C_L)_v$ result that, when compared to those obtained with θ_D equal to 203°K, is higher by 0.23 Joules per gram-atom per degree Kelvin at 300°K (0.94 per cent), 0.13 at 400°K (0.53 per cent), 0.08 at 500°K (0.32 per cent), and 0.01 at 1330°K (0.04 per cent). The $(C_L)_v$ results with θ_D equal to 203°K are listed in Table VII. The difference between $(C_v)_{\text{experimental}}$ and $(C_L)_v$ is increased when the electronic contributions $(C_E)_v$ is added to

TABLE VII

LATTICE AND ELECTRONIC CONTRIBUTIONS TO THE SPECIFIC HEAT
CAPACITY AT CONSTANT VOLUME: GOLD

Temperature (Degree Kelvin)	$(C_L)_v$ *	$(C_E)_v$ **	$(C_L)_v + (C_E)_v$
200	23.7014	0.1470	23.8484
220	23.9100	0.1617	24.0717
240	24.0704	0.1764	24.2468
260	24.1963	0.1911	24.3874
280	24.2969	0.2058	24.5027
300	24.3785	0.2205	24.5990
320	24.4455	0.2352	24.6807
340	24.5013	0.2499	24.7512
360	24.5482	0.2646	24.8128
380	24.5880	0.2793	24.8673
400	24.6220	0.2940	24.9160
420	24.6514	0.3087	24.9601
440	24.6768	0.3234	25.0002
460	24.6991	0.3381	25.0372
480	24.7186	0.3528	25.0714
500	24.7359	0.3675	25.1034
520	24.7512	0.3822	25.1334
540	24.7649	0.3969	25.1618
560	24.7772	0.4116	25.1888
580	24.7882	0.4263	25.2145
600	24.7981	0.4410	25.2391
620	24.8071	0.4557	25.2628
640	24.8153	0.4704	25.2857
660	24.8227	0.4801	25.3078
680	24.8295	0.4998	25.3293
700	24.8357	0.5145	25.3502
720	24.8414	0.5292	25.3706
740	24.8467	0.5439	25.3906
760	24.8515	0.5586	25.4101
780	24.8560	0.5733	25.4293
800	24.8602	0.5880	25.4482
820	24.8640	0.6027	25.4667
840	24.8676	0.6174	25.4850
860	24.8709	0.6323	25.5030
880	24.8740	0.6468	25.5208
900	24.8769	0.6615	25.5384
920	24.8797	0.6762	25.5559
940	24.8822	0.6909	25.5731

TABLE VII (continued)

Temperature (Degree Kelvin)	$(C_L)_v^*$	$(C_E)_v^{**}$	$(C_L)_v + (C_E)_v$
960	24.8846	0.7056	25.5902
980	24.8868	0.7203	25.6071
1000	24.8890	0.7350	25.6240
1020	24.8910	0.7497	25.6406
1040	24.8928	0.7644	25.6572
1060	24.8946	0.7791	25.6737
1080	24.8963	0.7938	25.6901
1100	24.8978	0.8085	25.7063
1120	24.8993	0.8232	25.7225
1140	24.9008	0.8379	25.7387
1160	24.9021	0.8526	25.7547
1180	24.9034	0.8673	25.7707
1200	24.9046	0.8820	25.7866
1220	24.9058	0.8967	25.8025
1240	24.9069	0.9114	25.8183
1260	24.9079	0.9261	25.8340
1280	24.9089	0.9408	25.8497
1300	24.9099	0.9555	25.8654
1320	24.9108	0.9702	25.8810
1330	24.9113	0.9776	25.8888

*The calculation of $(C_L)_v$ was made with Θ_D equal to 203°K. $(C_L)_v$ is given in Joules per gram-atom per degree Kelvin.

**The calculation of $(C_E)_v$ was made with γ equal to 0.735×10^{-3} Joules per gram atom per degree Kelvin squared. $(C_E)_v$ is given in Joules per gram-atom per degree Kelvin.

$(C_L)_v$ in order to obtain the total theoretical specific heat capacity at constant volume (see next paragraph).

The γ values obtained from Gschneidner⁵⁶ range from 0.735×10^{-3} to 0.761×10^{-3} Joules per gram-atom per degree Kelvin squared. The lowest value, 0.735×10^{-3} , was chosen in this research since, as observed above, the electronic contribution will increase the difference between the theoretical and experimental C_v in the temperature range (temperature close to 300°K) where the theoretical and experimental values should be very close to each other. The $(C_E)_v$ results obtained with γ equal to 0.735×10^{-3} Joules per gram-atom per degree Kelvin squared are shown in Table VII together with the $(C_L)_v$ and $[(C_L)_v + (C_E)_v]$ results.

The difference between the $[(C_L)_v + (C_E)_v]$ results obtained when the γ value is changed from 0.735×10^{-3} (Table VII) to 0.761×10^{-3} Joules per gram-atom per degree Kelvin squared (θ_D remaining equal to 203°K) is 0.03 Joules per gram atom per degree Kelvin (0.11 per cent) at 1330°K . The difference in the $[(C_L)_v + (C_E)_v]$ results obtained with the two different γ values decreases with decrease in temperature.

The calculation of $(C_E)_v$ was made by neglecting the least term in Equation (4)* since, by assuming the effective valence to be one, this last term becomes, at 1330°K , 0.13

$$\frac{*3\pi^2}{10} \quad \frac{kT^2}{\zeta_0}$$

per cent of the $(C_E)_V$ term $\left(0.005 \text{ per cent of } [(C_E)_V + (C_L)_V]\right)$.

Figure 44 shows the comparison of the $(C_V)_{\text{experimental}}$ with the $[(C_E)_V + (C_L)_V]$ obtained with γ and θ_D equal to 0.735×10^{-3} Joules per gram-atom per degree Kelvin squared and 203°K , respectively.

2. Excess Specific Heat Capacity at Constant Volume.

The difference (ΔC_V) between $(C_V)_{\text{experimental}}$ and the theoretical $[(C_L)_V + (C_E)_V]$ contributions to C_V is shown in Table VIII and Figure 45. This excess specific heat capacity ΔC_V can be associated with the formation of lattice defects (monovacancies and divacancies) and/or anharmonic lattice vibrations.

i) Contributions due to the formation of equilibrium lattice defects.

The excess energy is very dependent on the type of model used to calculate the theoretical contributions to the specific heat capacity at constant volume, and any variation in the C_V results obtained by using different models, has a tremendously great influence on the type of mechanisms to which the excess ΔC_V could be attributed. It was shown in Chapter IV that an uncertainty of 2.8 per cent exists for $(C_V)_{\text{experimental}}$. It was also emphasized in the analysis of the theoretical contribution that a variation of 0.32 per cent could exist at 500°K due to the use of a θ_D different by 23 per cent from the one used to calculate the $(C_L)_V$ contribution (Page 181) and that this variation

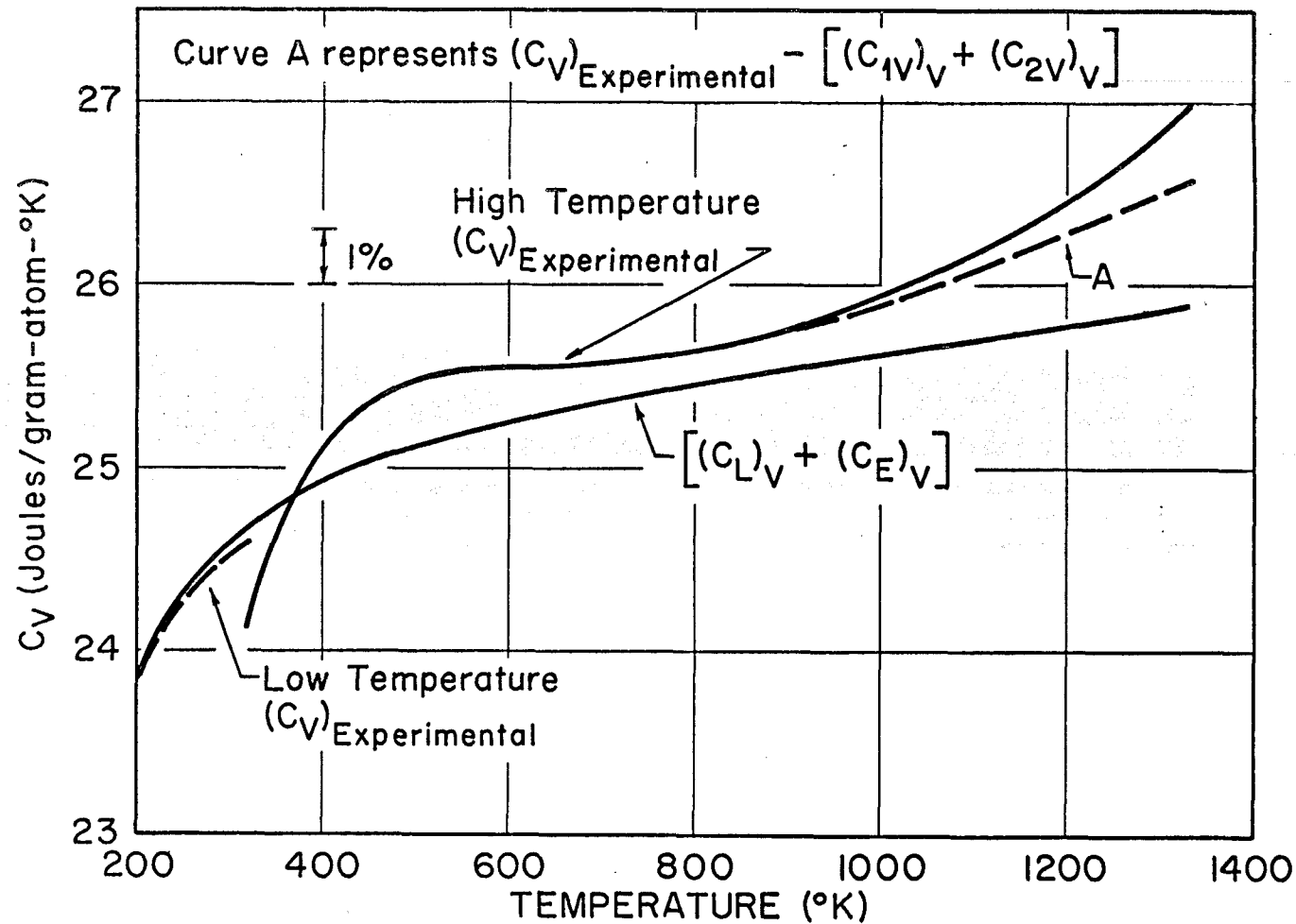


Figure 44. Specific heat capacity at constant volume for gold : theoretical and experimental.

TABLE VIII
EXCESS SPECIFIC HEAT CAPACITY AT
CONSTANT VOLUME: GOLD

Temperature (Degree Kelvin)	Excess C_v^*	
	ΔC_v	$(\Delta C_v)_A^{**}$
380	0.096	0.096
400	0.208	0.208
420	0.285	0.285
440	0.335	0.335
460	0.365	0.365
480	0.379	0.379
500	0.381	0.381
520	0.374	0.374
540	0.362	0.362
560	0.344	0.344
580	0.325	0.325
600	0.304	0.304
620	0.284	0.284
640	0.263	0.263
660	0.244	0.244
680	0.227	0.227
700	0.212	0.211
720	0.199	0.198
740	0.188	0.186
760	0.181	0.179
780	0.177	0.174
800	0.175	0.171
820	0.175	0.169
840	0.180	0.172
860	0.187	0.177
880	0.196	0.183
900	0.210	0.195
920	0.225	0.205
940	0.243	0.218
960	0.264	0.233
980	0.288	0.251
1000	0.314	0.269
1020	0.343	0.289
1040	0.375	0.311
1060	0.408	0.332
1080	0.445	0.356
1100	0.484	0.380

TABLE VIII (continued)

Temperature (Degree Kelvin)	Excess C_v^*	
	ΔC_v	$(\Delta C_v)_A^{**}$
1120	0.524	0.404
1140	0.567	0.429
1160	0.612	0.454
1180	0.659	0.477
1200	0.708	0.502
1220	0.760	0.528
1240	0.813	0.553
1260	0.867	0.566
1280	0.923	0.598
1300	0.983	0.622
1320	1.042	0.640
1330	1.073	0.653

*The units are Joules per gram-atom per degree Kelvin.

** $(\Delta C_v)_A = \Delta C_v - (C_{1v})_v - (C_{2v})_v$. $(C_{1v})_v$ was calculated by using Δh_{1v} equal to 0.97 e.v. and ΔS_{1v} equal to 1.2k; $(C_{2v})_v$ was calculated by using Δh_{1v} equal to 1.84 e.v. and ΔS_{2v} equal to 1.5k.

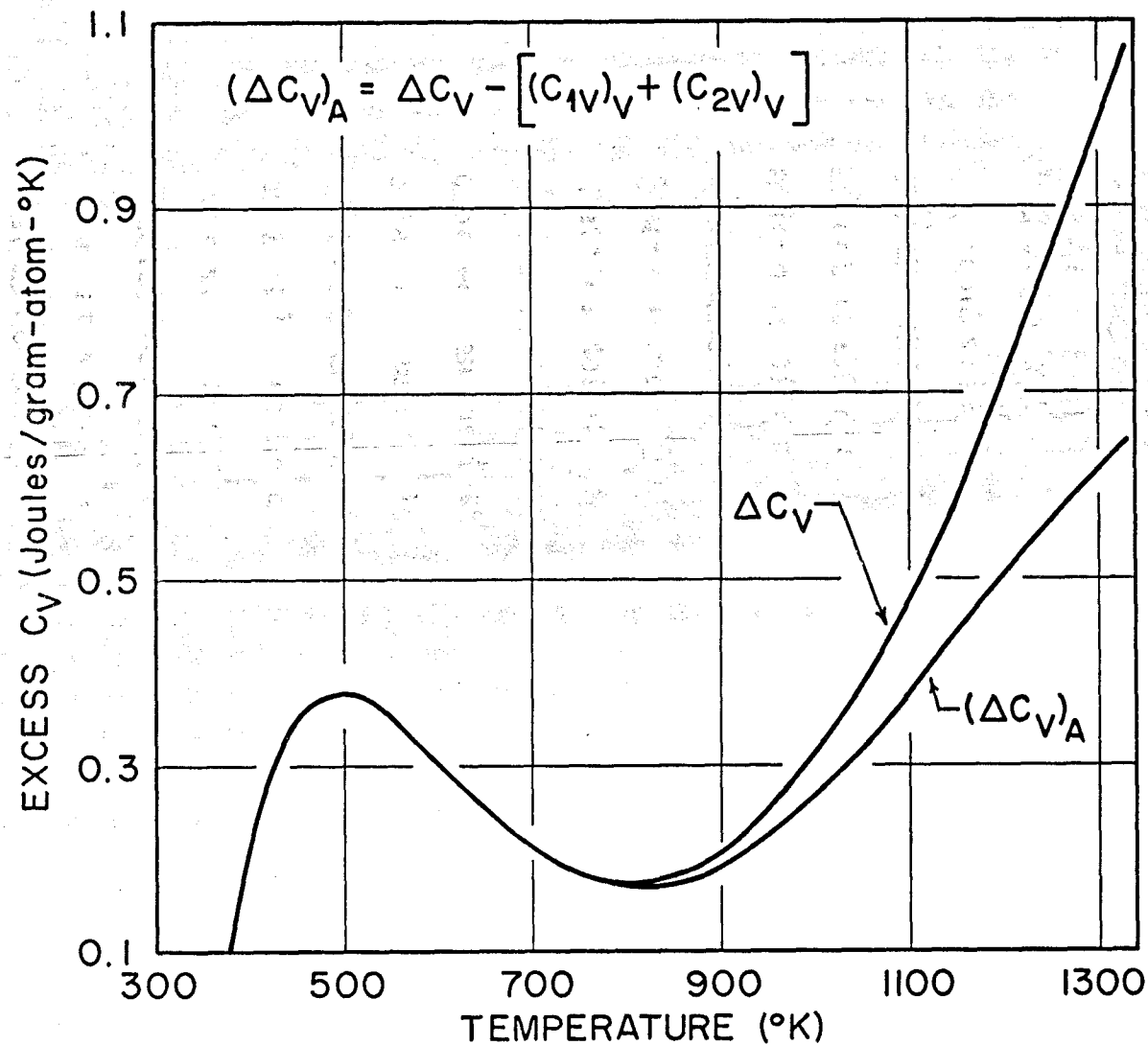


Figure 45. Excess specific heat capacity C_V : gold.

in $(C_L)_V$ increased for lower temperatures. Due to the above considerations, and because of the small ΔC_V values obtained for temperatures below 800°K , no attempt was made to try to justify the low temperature results of a plot of $\log_e (\Delta C_V)T^2$ versus $1/T^*$ (discussed below). It is emphasized that the following analysis made on the high temperature ΔC_V results is also affected considerably by the variations of the different terms in the theoretical model used for the calculation of the excess C_V . The effect of these variations is discussed in detail later.

If it is assumed that the excess specific heat capacity at constant volume ΔC_V is due only to one type of equilibrium lattice defect (i.e. monovacancies), a plot of $\log_e (\Delta C_V)T^2$ versus $1/T$ will be linear. The energy Δh_{1V} for monovacancies can be determined from the slope of the plot in the temperature region where only the one defect contribution is significant. Figure 46 shows this plot and above around 1040°K the formation of one defect is characterized by the more or less straight line which identifies the monovacancies in gold; the slope of the line gives 67,500 Joules per gram-atom (0.7 e.v.), and the variation involved in the graphical measurement of this slope is ± 14.0 per cent. No other type of defect at high temperature is observed from the plot of $\log_e (\Delta C_V)T^2$ versus $1/T$. It is

*A detailed analysis of the uncertainties in ΔC_V is made later in this section and the section dealing with the anharmonic contributions to C_V .

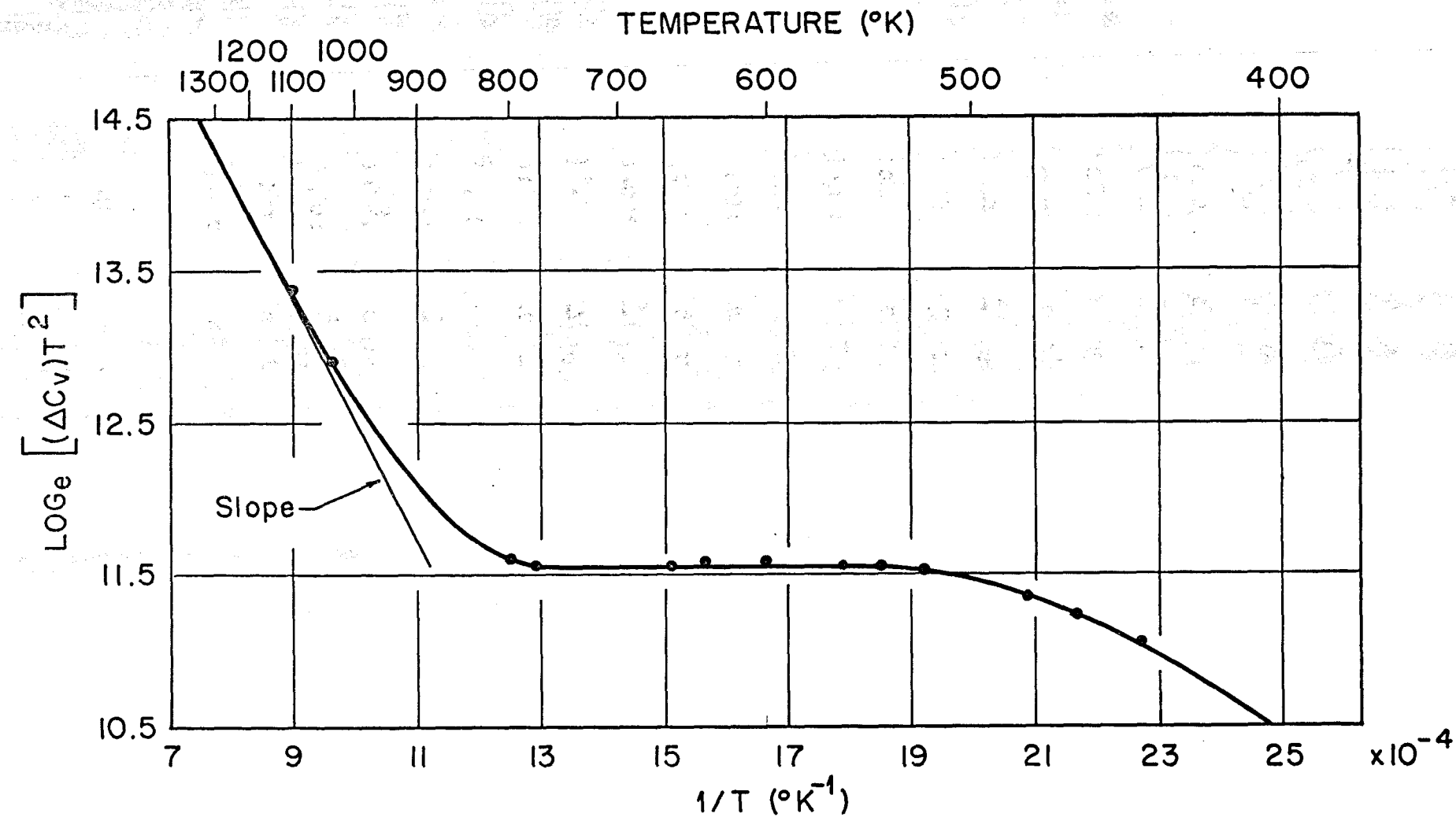


Figure 46. Logarithm of $(\Delta C_v)T^2$ versus $1/T$ for gold.

emphasized that this Δh_{1v} value calculated from the slope of the plot of the $\log_e(\Delta C_v)T^2$ versus $1/T$ is not recommended since considerable error is involved every time a set of data is transformed into logarithmic values, which have a tendency to give straight lines for any given set of data that do not differ appreciably in magnitude; further, as was stated at the beginning of this section, the variations in the calculated ΔC_v increases considerably the uncertainties in the Δh_{1v} calculated above. The measured 0.7 e.v. is 14.0 to 33.0 per cent below the Δh_{1v} values obtained from different more reliable techniques used to determine the energy of formation of point defects.

Since other experimental techniques give much more precise Δh_{1v} values, the analysis of the contributions of monovacancies was made using the Δh_{1v} and ΔS_{1v} values measured by Simmons⁵⁹ ($\Delta h_{1v} = 0.97 \pm 0.04$ e.v., $\Delta S_{1v} = 1.2 \pm 0.2k$)*. The Δh_{1v} values of other investigations are: 0.95 e.v. by Bradshaw and Pearson⁶⁰, 0.96 e.v. by Baverle and Koeler⁶¹, 0.97 ± 0.1 e.v. by De Sorbo⁶², 0.94 e.v. by Simmons and Balluffi³⁹, 0.95 to 1.03 e.v. by Mori, Meshii and Kauffman⁶³, 0.8 e.v. by Misek and Polak⁶⁴, 0.96 e.v. by De Jong and Koehler⁶⁵, and 0.85 to 0.88 e.v. by Seeger and Mehrer⁶⁶. Simmons and Balluffi³⁹ suggested from their results a ΔS_{1v} value of 1.0k, and Seeger and Mehrer⁶⁶ a value

* k is the Boltzmann constant.

of 1.0k, and Seeger and Mehrer⁶⁶ a value of 0.5 k.

The selection of Δh_{2v} was more difficult since the binding energy B^* for two vacancies as determined in different investigations gives values for B that range from 0.1 to 0.4 e.v. The determination of B in the different investigations was based on:

i-i) an analysis on the conservation of the total amount of vacancies made on quenched samples (Koehler, Seitz and Bauerle⁶⁷, where B is between 0.1 and 0.2 e.v.);

i-ii) an analysis of the clustering vacancies made on the recovery of the electrical resistivity of quenched samples after annealing (Mori, Meshii and Kauffman^{68, 69}, where B is greater than 0.3 e.v.);

i-iii) an analysis of the decrease in quenched-in resistivity observed during the transient process in which single vacancies and divacancies come into equilibrium with one another (De Jong and Koehler⁶⁵, where $B = 0.1 \pm 0.03$ e.v.); and

i-iv) an analysis of self diffusion and quenching studies in gold (Stoebe and Dawson⁷⁰, where $B = 0.3$ e.v., Seeger and Mehrer⁶⁶, where $B = 0.16$ e.v., and Wang, Seidman and Balluffi⁷¹, where $B = 0.4$ e.v.).

An analysis of the limit values for B, similar to that made for copper by Bartlett and Dienes⁵⁵ where

$$^* \Delta h_{2v} = 2 \Delta h_{1v} - B$$

$\Delta h_{1v}/6 \leq B \leq E_c/6^*$, gives for gold the limit values 0.16 and 0.56 e.v. Since the experimental results concerning divacancies can not yet give an specific value for B which could be compared with theoretical calculations, it was not necessary to go into very complicated calculations in order to determine the binding energy of the vacancies to form divacancies. For the divacancy contribution the value of 0.1 e.v. was chosen and an analysis was made concerning the effect of a variation of B on $(C_{2v})_v$ and ΔC_v .

The value 1.5k for ΔS_{2v} was chosen from the work of Seeger and Mehrer⁶⁶ since it was the value used during the determination of their B value ($B \leq 0.16$ e.v.). Table VIII (Page 186) and Figure 46 (Page 190) show the $(\Delta C_v)_A$ remaining after the contributions due to monovacancies and divacancies were subtracted from ΔC_v . Figure 44 (Page 185) shows the effect of monovacancies and divacancies on the $(C_v)_{\text{experimental}}$. The calculations for the contributions due to the monovacancies and divacancies were then made by using

$$\Delta h_{1v} = 0.97 \text{ e.v.}, \quad \Delta S_{1v} = 1.2k \quad (8a)$$

$$\Delta h_{2v} = 2(0.97) - 0.1 = 1.84, \quad \Delta S_{2v} = 1.5k \quad (8b)$$

The contributions due to the formation of monovacancies started being noticeable (within three decimal places) at 700°K and the contributions due to the formation of divacancies at 1180°K.

* E_c is the cohesive energy (sublimation energy).

In order to observe the effect of a different Δh_{1v} value on the $(C_{1v})_v$ contribution to the specific heat capacity, a Δh_{1v} value of 0.85 e.v. (determined by Seeger and Mehrer⁶⁶) was used to calculate at 1330°K the $(C_{1v})_v$ contribution. The ΔS_{1v} value was not change for this new calculation ($\Delta S_{1v} = 1.2k$). The use of Δh_{1v} equal to 0.85 e.v. will increase, at 1330°K, the contribution due to monovacancies by 0.495 Joules per gram-atom per degree Kelvin, above the value calculated when using the Δh_{1v} value given in Equation (8a). The above increase is 118.0 per cent of the total value of the contributions due to monovacancies and divacancies as calculated by using Δh_{1v} equal to 0.97 e.v., and it decreases the calculated $(\Delta C_v)_A$ value at 1330°K by 76.0 per cent, to a new value of 0.158 Joules per gram-atom per degree Kelvin. Furthermore, an increase of the ΔS_{1v} by 0.2k together with the use of Δh_{1v} equal to 0.85 e.v. will increase the contributions due to monovacancies by 0.645 Joules per gram-atom per degree Kelvin (155.0 per cent); this increase in $(C_{1v})_v$ produces a decrease in $(\Delta C_v)_A$ to 0.011 Joules per gram-atom per degree Kelvin (99.0 per cent).

At 1330°K the contribution of divacancies, by using the values in Equation (8b), is 0.003 Joules per gram-atom per degree Kelvin which represents 0.7 per cent of the total contributions due to both monovacancies and divacancies (0.420 Joules per gram-atom per degree Kelvin). The use of a binding energy B equal to 0.4 e.v. increases the contribu-

tions due to divacancies by 0.024 Joules per gram-atom per degree Kelvin. This increment in $(C_{2v})_v$ together with the use of Δh_{1v} equal to 0.85 e.v. and ΔS_{1v} equal to 1.4 will decrease $(\Delta C_v)_A$ to zero which means that within the uncertainty of the Δh_{1v} , ΔS_{1v} , B and ΔS_{2v} , the excess ΔC_v can be attributed to the formation of lattice defects. It is emphasized that an increase in Δh_{1v} and a decrease in B, ΔS_{1v} and ΔS_{2v} with respect to the values used (Equations (8a) and (8b)) will increase the $(\Delta C_v)_A$.

ii) Anharmonic contributions.

In Chapter IV it was stated that a variation of ± 2.8 per cent in the calculated $(C_v)_{\text{experimental}}$ could be expected due to the ± 1.0 per cent absolute error of C_p and to variations in the different terms used in the dilation term. This 2.8 per cent variation in C_v , if negative, reduces ΔC_v from 1.073 to 0.319 Joules per gram-atom per degree Kelvin at 1330°K. This new value is easily surpassed by the contributions due to imperfections in the lattice, which means that, within these uncertainties, $(\Delta C_v)_A$ could be negative.

The variations in the $(C_v)_{\text{experimental}}$ and $[(C_{1v})_v + (C_{2v})_v]$ gives a range in the calculated $(\Delta C_v)_A$ of ± 1.4 Joules per gram-atom per degree at 1330°K. The variation decreases with decreasing temperature and at 700°K the variation in $(\Delta C_v)_A$ is ± 0.8 Joules per gram-atom per degree Kelvin.

For temperatures around 700°K a decrease of 1.5 per

cent in the $(C_v)_{\text{experimental}}$ or an increment by the same percentage in $(C_L)_v + (C_E)_v$ will decrease to zero the ΔC_v and $(\Delta C_v)_A$ values at this temperature. The variation in $(C_v)_{\text{experimental}}$ and/or $[(C_L)_v + (C_E)_v]$ needed to decrease to zero the $(\Delta C_v)_A$ value, is less than 1.5 per cent for temperatures below 700°K .

For gold, the $(\Delta C_v)_A$ results obtained in this research (Table VIII in Page 186) could be attributed to anharmonic contributions, but due to the high uncertainties involved in the $(\Delta C_v)_A$ calculations it is difficult to predict with assurance the veracity of such a statement.

b. Lead

1. Lattice and Electronic Contributions to C_v . The characteristic Debye temperature for lead had been calculated from specific heat capacity, elastic constants, electrical resistivity, thermal expansion and X-ray intensity measurements⁵⁶, at temperatures ranging from 0° to 298°K . The θ_D values range from 670°K (calculated from X-ray intensity data at 298°K) to 107°K (calculated from specific heat measurements at 0°K). The relatively closest $(C_L)_v$ values to the experimental results were obtained with a θ_D equal to 107°K , the theoretical $(C_L)_v$ result being at 300°K 0.1 Joules per gram-atom per degree Kelvin above the present research $(C_v)_{\text{experimental}}$. Any θ_D smaller than 107°K will increase the above difference. The use of θ_D value equal to

67°K produces a $(C_L)_V$ result which, when compared to that obtained with Θ_D equal to 107°K, is higher by 0.1 Joules per gram-atom per degree Kelvin at 300°K (0.39 per cent), 0.05 at 400°K (0.22 per cent), 0.04 at 500°K (0.14 per cent) and 0.02 at 600°K (0.1 per cent). The $(C_L)_V$ results with Θ_D equal to 108°K are shown in Table IX. The 0.1 Joules per gram-atom per degree Kelvin difference between $(C_V)_{\text{experimental}}$ and $(C_L)_V$ was increased when the electronic contribution $(C_E)_V$ was added to $(C_L)_V$ in order to obtain the total theoretical specific heat capacity at constant volume.

The γ values given by Gschneidner⁵⁶ range from 2.99×10^{-3} to 3.29×10^{-3} Joules per gram-atom per degree Kelvin squared. The value chosen in this research was 2.99×10^{-3} Joules per gram-atom per square degree Kelvin, since as observed above, the electronic contributions will increase the difference between the theoretical and experimental C_V in the temperature range (temperatures close to 300°K) where the theoretical and experimental values should be very close to each other. The $(C_E)_V$ results obtained with γ equal to 2.99×10^{-3} Joules per gram-atom per degree Kelvin squared are shown in Table IX together with the $(C_L)_V$ and $[(C_L)_V + (C_E)_V]$ results.

The difference between the $(C_L)_V + (C_E)_V$ results obtained when the γ value is changed from 2.99×10^{-3} (Table IX) 3.29×10^{-3} Joules per gram atom per degree Kelvin squared (Θ_D remaining equal to 107°K) is 0.18 Joules per gram-atom

TABLE IX

LATTICE AND ELECTRONIC CONTRIBUTIONS TO THE SPECIFIC
HEAT CAPACITY AT CONSTANT VOLUME: LEAD

Temperature Degree Kelvin	$(C_L)_v^*$	$(C_E)_v^{**}$	$(C_L)_v + (C_E)_v$
200	24.5870	0.5980	25.1850
220	24.6478	0.6578	25.3056
240	24.6941	0.7176	25.4117
260	24.7303	0.7774	25.5077
280	24.7591	0.8372	25.5963
300	24.7823	0.8970	25.6793
320	24.8014	0.9568	25.7582
340	24.8172	1.0166	25.8338
360	24.8304	1.0764	25.9068
380	24.8417	1.1362	25.9779
400	24.8513	1.1960	26.0473
420	24.8595	1.2558	26.1153
440	24.8667	1.3156	26.1823
460	24.8729	1.3754	26.2483
480	24.8784	1.4352	26.3136
500	24.8832	1.4950	26.3783
520	24.8875	1.5548	26.4423
540	24.8914	1.6146	26.5060
560	24.8948	1.6744	26.5692
580	24.8979	1.7342	26.6321
600	24.9007	1.7940	26.6947

*The calculation of $(C_L)_v$ was made with Θ_D equal to 107°K. $(C_L)_v$ is given in Joules per gram atom per degree Kelvin.

**The calculation of $(C_E)_v$ was made with γ equal to 2.99×10^{-3} Joules per gram-atom per degree Kelvin squared. $(C_E)_v$ is given in Joules per gram-atom per degree Kelvin.

per degree Kelvin (0.67 per cent) at 600°K . The difference in the $[(C_L)_v + (C_E)_v]$ results obtained with the two different γ values decreases with a decrease in temperature.

The calculation of $(C_E)_v$ was made by neglecting the last term in Equation (3)* since, by assuming the effective valence for lead to be two, this last term becomes at 600°K , 0.02 per cent of the $(C_E)_v$ term $[0.8 \times 10^{-5}$ per cent of $(C_E)_v + (C_L)_v]$.

Figure 47 shows the comparison of the $(C_v)_{\text{experimental}}$ with the $(C_E)_v + (C_L)_v$ obtained with γ and θ_D equal to 2.99×10^{-3} Joules per gram-atom per degree Kelvin squared. and 107°K respectively.

2. Excess Specific Heat Capacity at Constant Volume.

The difference (ΔC_v) between $(C_v)_{\text{experimental}}$ and the theoretical $(C_L)_v + (C_E)_v$ contributions to C_v is shown in Table X and Figure 48. This excess specific heat capacity ΔC_v is negative for lead and the contributions due to the formation of monovacancies and divacancies increase this difference for temperatures above 360°K , indicating a probable negative anharmonic contribution.

i) Contributions due to the formation of equilibrium lattice defects.

As it was stated in the analysis made of the contribu-

* $\frac{3\pi^2}{10} \frac{KT^2}{\zeta_0}$

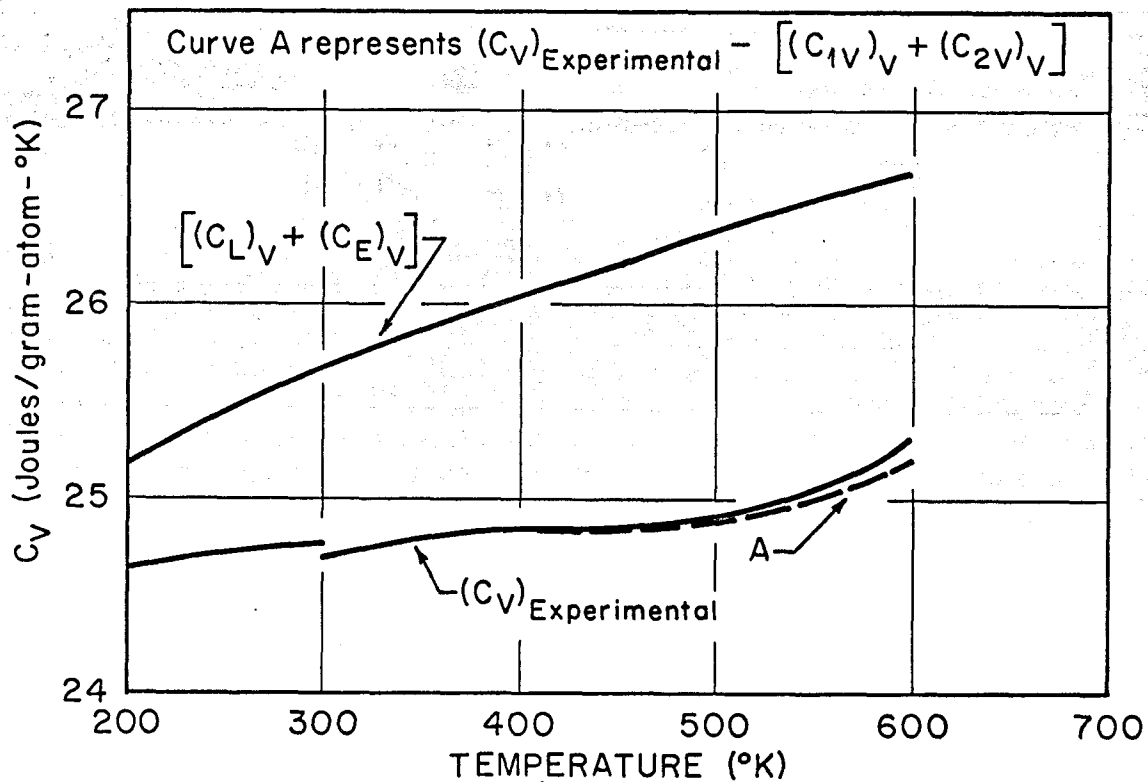


Figure 47. Specific heat capacity at constant volume for lead: theoretical and experimental.

The uncertainty in the dilation term due to any possible error in α_v , β_v and V can be determined by assuming that each of them is independent from the others. Differentiating Equation (2) and assuming small errors in α_v , β_v and V , the error in C^d at a given temperature will be given by

$$\Delta C^d = \frac{2\alpha_v}{\beta_v} T V (\Delta \alpha_v) + \frac{\alpha_v^2}{\beta_v} T (\Delta V) - \frac{\alpha_v^2}{\beta_v^2} T V (\Delta \beta_v) \quad (8)$$

Equation (8) will give the maximum variation in C^d by using the maximum positive values of α_v and V , and the maximum negative value of β_v . That is, Equation (8) can then be written as

$$\Delta C^d = \frac{2\alpha_v}{\beta_v} T V \cdot |\Delta \alpha_v| + \frac{\alpha_v^2}{\beta_v} T \cdot |\Delta V| + \frac{\alpha_v^2}{\beta_v^2} T V |\Delta \beta_v| \quad (9)$$

A. GOLD

a. Coefficient of Volume Thermal Expansion

The least square curve fitting method was used to fit a polynomial to the $\Delta l/l_0^*$ data points given by Nix and MacNair³⁷ from 86 to 1003°K. The polynomial used is

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 \quad (10)$$

where

*The length change $\Delta l = l - l_0$ at any temperature T was measured with respect to the length of the bar l_0 measured at 0°C.

$$C_1 = -34.75 \times 10^{-4},$$

$$C_2 = +11.70 \times 10^{-6},$$

$$C_3 = +34.40 \times 10^{-10},$$

and T = temperature in degree Kelvin.

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.20×10^{-4} which represents a three per cent deviation at 300°K and 0.7 per cent at 700°K .

$\Delta l/l_0$ measurements were also made in 1941 by Esser and Eusterbrock³⁸ from 323°K to 1223°K . Their data were fitted to the least square curve fitting method to obtain the polynomial

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5 \quad (11)$$

where

$$C_1 = -93.33 \times 10^{-5},$$

$$C_2 = +61.54 \times 10^{-7},$$

$$C_3 = -15.03 \times 10^{-9},$$

$$C_4 = +21.68 \times 10^{-12},$$

$$C_5 = -14.49 \times 10^{-15},$$

$$C_6 = +37.08 \times 10^{-19},$$

and T = temperature in degrees Kelvin

The standard deviation of the $\Delta l/l_0$ data point with respect to the above polynomial is 0.21×10^{-4} which represent a four per cent deviation at 300°K and 0.4 per cent at 723°K .

In a more recent investigation made in 1961 by Simmons and Balluffi³⁹, measurements of $\Delta l/l_0$ were made from 323°K

to 1333°K. The polynomial obtained by using their data is

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 \quad (12)$$

where

$$C_1 = -31.91 \times 10^{-4},$$

$$C_2 = +10.35 \times 10^{-6},$$

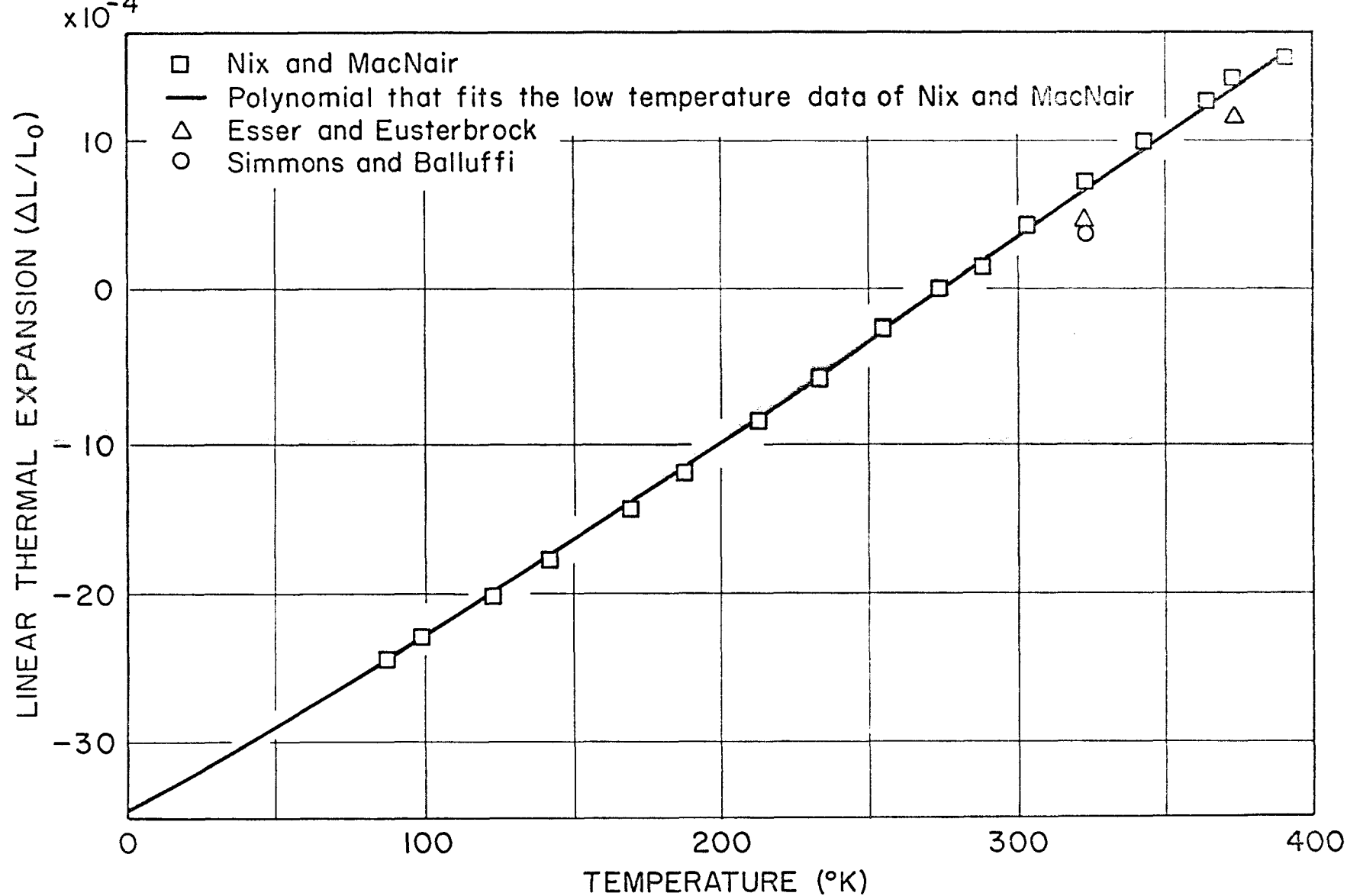
$$C_3 = +43.25 \times 10^{-10},$$

and T = temperature in degrees Kelvin

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.50×10^{-4} which represents an eleven per cent deviation at 300°K and 0.7 per cent at 723°K.

Figure 17 shows the low temperature $\Delta l/l_0$ values obtained by Nix and MacNair³⁷ and the polynomial determined from their data. At 323°K a difference of 2.3×10^{-4} (30 per cent) exists between the values of Esser and Eusterbrock³⁸ and Simmons and Balluffi³⁹. It is emphasized that the difference is high due to the very low values of Δl near 300°K, and it will be seen later that this difference produces only a very small error in the α_v calculation.

Figure 18 shows the high temperature linear thermal expansion $\Delta l/l_0$ where it is observed that a reasonable agreement exists between the data of Nix and MacNair³⁷ and those of Simmons and Balluffi³⁹ for temperatures above 400°K. The difference between the polynomial that fits the data of Nix and MacNair³⁷ and the polynomial that fits those of Simmons and Balluffi³⁹ remains constant at four per cent for temperatures above 500°K.



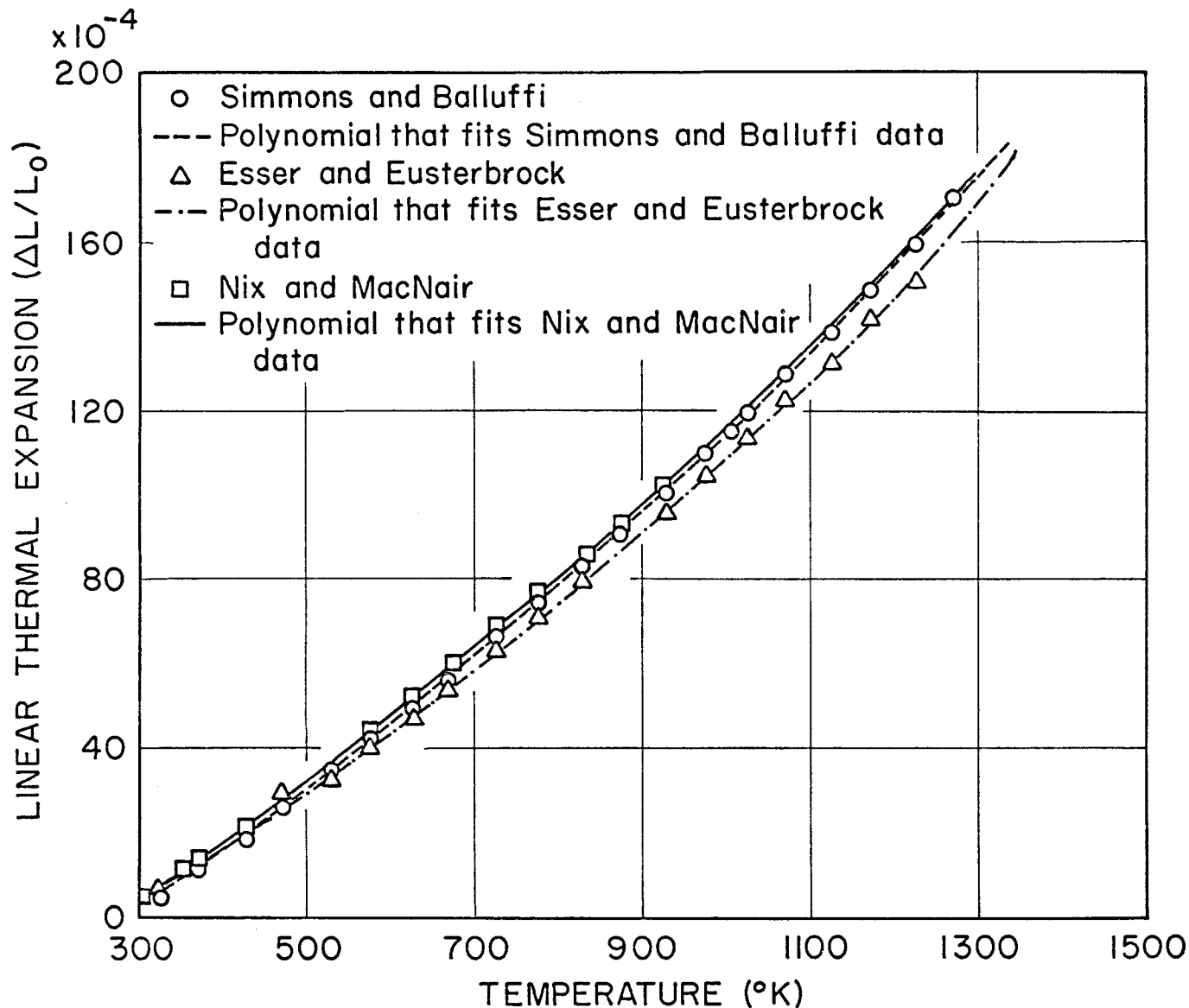


Figure 18. High temperature linear thermal expansion for gold.

The polynomial that fits the data of Esser and Eusterbrock³⁸ deviates farther from those data points of Nix and MacNair with increasing temperature. The polynomial calculated in this research to represent Esser and Eusterbrock³⁸ data gives results that are 0.1×10^{-6} per cent away from the polynomial calculated by them, which they used to calculate the linear coefficient thermal expansion α , so, no further use of Equation (11) will be made in the calculation of α and α_v ($\alpha_v = 3\alpha$).

The coefficient of linear thermal expansion α as a function of temperature is shown in Figure 19, where the results of Nix and MacNair³⁹ and Esser and Eusterbrock³⁸ are shown. Nix and MacNair determined the coefficients of linear thermal expansion at a given temperature by graphically measuring the slopes of the curve given by $\Delta l/l_0$ versus temperature. The α values given by Esser and Eusterbrock³⁸ were determined from a polynomial they fitted to their $\Delta l/l_0$ data. The results of Nix and MacNair³⁷ and those of Esser and Eusterbrock³⁸ differ by around one per cent from 300°K to around 900°K. Above 900°K, the difference increases to be four per cent at 1100°K. The polynomials that fit both Nix and MacNair³⁷ and Esser and Eusterbrock α data are shown in Figure 19. The polynomial that fits the α data of Nix and MacNair is given by

$$\alpha = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 + c_6 T^5 \quad (13)$$

where for, α in $^{\circ}\text{K}^{-1}$,

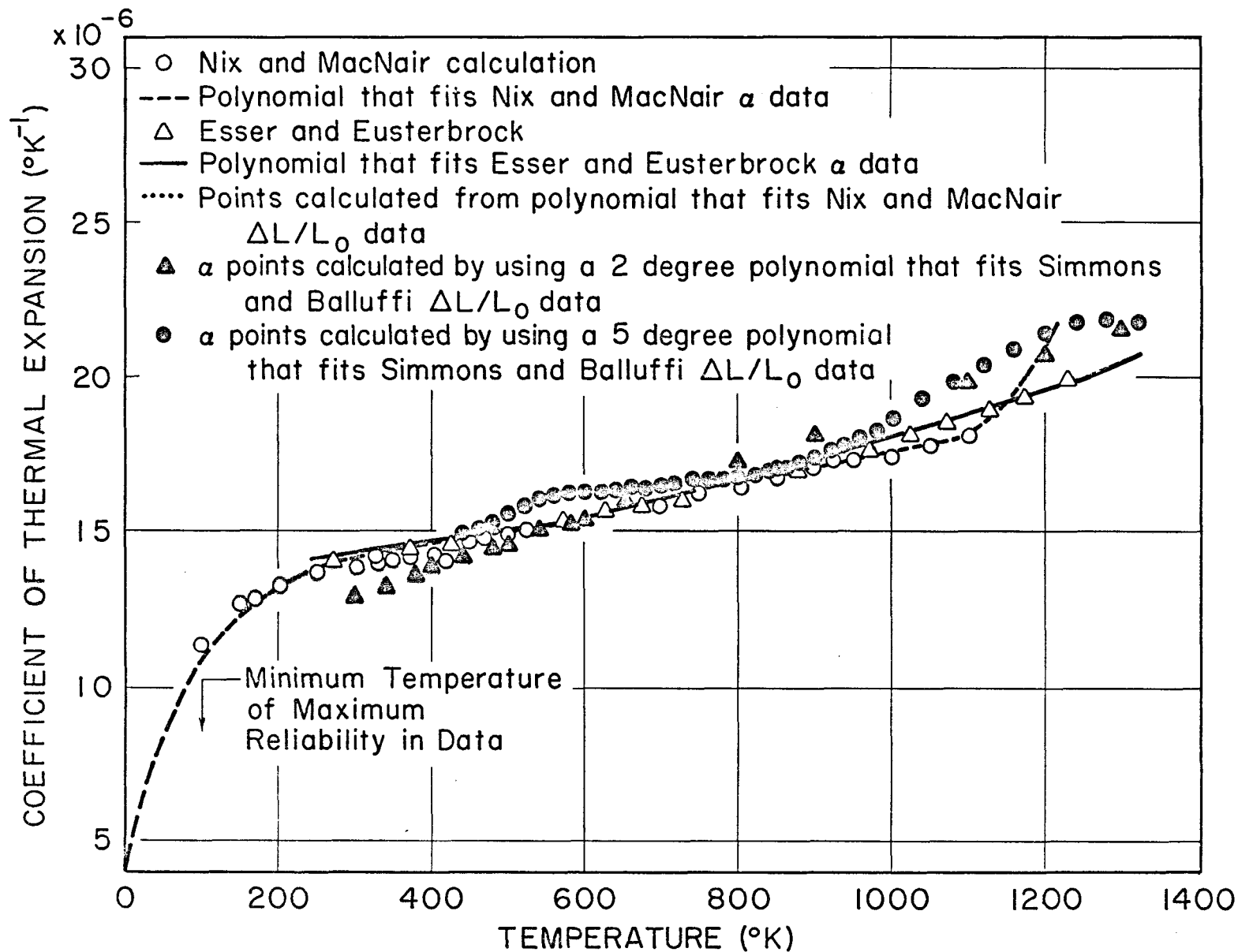


Figure 19. Coefficient of linear thermal expansion for gold.

$$C_1 = +43.97 \times 10^{-7},$$

$$C_2 = +94.20 \times 10^{-9},$$

$$C_3 = -35.33 \times 10^{-11},$$

$$C_4 = +63.31 \times 10^{-14},$$

$$C_5 = -52.25 \times 10^{-17},$$

$$C_6 = +16.14 \times 10^{-20},$$

and T = temperature in degrees Kelvin.

The polynomial that fits the α data obtained by Esser and Eusterbrock is given by

$$\alpha = C_1 + C_2 T + C_3 T^2 \quad (14)$$

where for, α in $^{\circ}\text{K}^{-1}$,

$$C_1 = +13.54 \times 10^{-6},$$

$$C_2 = +13.25 \times 10^{-10},$$

$$C_3 = +31.00 \times 10^{-13},$$

and T = temperature in degrees Kelvin.

The standard deviation of the polynomial used to fit the α data of Nix and MacNair³⁷ was 0.23, which would give a variation of around two per cent at 300 $^{\circ}\text{K}$. It was impossible to obtain a better fit to the α data of Nix and MacNair due to the irregularity of the α values which they determined by using a graphical method. The standard deviation of the polynomial used to fit the data of Esser and Eusterbrock³⁸ was 0.004 which gives a variation of 0.06 per cent at 300 $^{\circ}\text{K}$. It is clear that the method used by Esser and Eusterbrock³⁸ is more precise since a more exact slope is determined from the polynomial used to fit the greater amount of $\Delta l/l_0$ data points obtained experimentally, than by reading approximately

the values of the tangents at a given temperature from a curve drawn through a lesser number of data point.

The polynomials used in the present research to fit the $\Delta l/l_0$ data of Nix and MacNair³⁷ and Simmons and Balluffi (Equations (10) and (12)) were used to determine α as follows.

In general, let $\Delta l/l_0$ be given by

$$\frac{\Delta l}{l_0} = c_1 + c_2 T + c_3 T^2 + \dots c_n T^{n-1} \quad (15)$$

then

$$\Delta l = l_0 (c_1 + c_2 T + c_3 T^2 + \dots c_n T^{n-1}) \quad (16)$$

From Equation (16), the length l at a temperature T is given by

$$l = l_0 (1 + c_1 + c_2 T + c_3 T^2 + \dots c_n T^{n-1}) \quad (17)$$

Differentiating Equation (17) with respect to T

$$\frac{dl}{dT} = l_0 (c_2 + 2c_3 T + \dots (n-1) c_n T^{n-2}) \quad (18)$$

The linear coefficient of thermal expansion α is given by

$$\alpha = \frac{1}{l} \frac{dl}{dT} + (c_2 + 2c_3 T + \dots (n-1) c_n T^{n-2}) / (1 + c_1 + c_2 T + c_3 T^2 + \dots c_n T^{n-1}) \quad (19)$$

The α calculated from the polynomial used to fit the $\Delta l/l_0$ data of Nix and MacNair³⁷ (Equation (10)), by using Equation (19), is also shown in Figure 19, where it is observed that a difference of six per cent was obtained with respect to the graphical measurements of α made by Nix and MacNair³⁷ at 300°K. This difference decreases to zero per

cent at around 500°K and increases again to four per cent at 1100°K . The α calculated from the polynomial (Equation 10) maintains a difference of one per cent with respect to the values calculated by Esser and Eusterbrock³⁸ over the entire temperature range (300°K to 1330°K).

Since the α calculated from Equation (10) by using the procedure summarized in Equation (19) was used for comparison and for future calculations, it was decided to represent the calculated α^* by a simpler polynomial, given by

$$\alpha = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 \quad (20)$$

where, for α in $^{\circ}\text{K}^{-1}$,

$$c_1 = +11.74 \times 10^{-6},$$

$$c_2 = +67.67 \times 10^{-10},$$

$$c_3 = -11.99 \times 10^{-14},$$

$$c_4 = -21.97 \times 10^{-18},$$

$$c_5 = +72.21 \times 10^{-23},$$

and T = temperature in degrees Kelvin.

The standard deviation of the α values calculated from the polynomial used to represent the $\Delta l/l_0$ data of Nix and MacNair, by using Equation (19), with respect to those obtained by using the above polynomial (Equation (20)), is $0.2 \times 10^{-19} ^{\circ}\text{K}^{-1}$ which represents a variation of 0.1×10^{-12} per cent at 300°K ; this difference shows that the use of the polynomial instead of the calculated α did not produce any appreciable

*All calculations involving the use of Equation (19) were made for a temperature interval of ten degrees.

deviation in the α results.

The α calculated from the polynomial that fits Simmons and Balluffi³⁹ $\Delta l/l_0$ data (Equation (12)) by using Equation (19) is also shown in Figure 19 (Page 107).

A deviation of six per cent exists at 300°K between the values defined by Equation (20) and those calculated from the $\Delta l/l_0$ data of Simmons and Balluffi³⁹. The difference decreases to zero at around 750°K and increases again to four per cent at 1200°K. It is observed that except for the ends of the temperature range used in the present research (300°K to 1330°K) the agreement is reasonably good and the difference is mainly due to:

- 1) Errors near 300°K in the shape of the polynomial curve fitted to Simmons and Balluffi³⁹ $\Delta l/l_0$ data points. The fact that the $\Delta l/l_0$ data by Nix and MacNair³⁷ are given for temperatures as low as 80°K gives a much more reasonable polynomial fit for their data for temperatures around 300°K. Simmons and Balluffi³⁹ data start at 323°K so a great amount of different curves with different slopes can fit this first set of data points.
- 2) Error in the polynomial used to fit the highly separated Simmons and Balluffi³⁷ $\Delta l/l_0$ data points. The more separated the data points, usually the higher the standard deviation of the polynomial of a given order used to represent the data. A polynomial of very high order used to lower the standard deviation

tion of the very separated set of data points results in a wavy curve that give erroneous slopes. To observe this effect, a five degree polynomial was used to fit the $\Delta l/l_0$ data of Simmons and Balluffi; α was then calculated, and the result (Figure 19) showed that, even with a lower standard deviation, the irregularity in the α with respect to temperature, and the difference in these values with respect to the other calculations, increased considerably. At 1200°K, the difference in the α obtained from the second and fifth degree polynomial fit to Simmons and Balluffi³⁷ $\Delta l/l_0$ data is four per cent ($0.8 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$). The same analysis made on Nix and MacNair $\Delta l/l_0$ data give a difference of 0.4 per cent ($0.09 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$).

The above analysis indicates that the larger the number of data points, and the smaller the ΔT intervals, the higher the probability of finding the right α values.

The coefficient of linear expansion given by Equation (20) and obtained from the polynomial that fits Nix and MacNair $\Delta l/l_0$ data was used in the determination of the dilation term ($\alpha_v = 3\alpha$). Since basically most α results given in Figure 19 (Page 107) agree within one per cent, except for the end points (300°K and 1300°K) calculated from Simmons and Balluffi³⁸ $\Delta l/l_0$ data, an estimated maximum variation ± 2.0 per cent was given to the values obtained by Equation (20) in order to see the effect that this variation has on the

specific heat capacity at constant volume (Section A-e).

b. Molar Volume

The molar volume at 25°C was calculated from the lattice parameters data given by Pearson⁴⁰, and was used as a reference to calculate the molar volume as a function of temperature. For gold, the calculation was based on the use of Equation (17) as follows:

$$C = V_{298} \frac{1 + C_1 + \dots + C_n T^{n-1}}{1 + C_1 + \dots + C_n T_R^{n-1}} \quad (21)$$

where

V = molar volume at a temperature T ,

V_{298} = reference molar volume at 298°K (25°C),

T_R = reference temperature (298°K)

Using Equation (21) values of molar volume were calculated at ten degrees intervals, and the values were fitted to a polynomial curve. The resulting polynomial, shown in Figure 20, is given by

$$V = C_1 + C_2 T + C_3 T^2 + C_4 T^3 \quad (22)$$

where, for V in cubic centimeters per gram atom,

$$C_1 = +10.101 \times 10^{+0},$$

$$C_2 = +35.567 \times 10^{-5},$$

$$C_3 = +10.874 \times 10^{-8},$$

$$C_4 = +26.961 \times 10^{-13},$$

and T = temperature in degree Kelvin.

The standard deviation of the data points obtained by using Equation (21) with respect to the above polynomial is

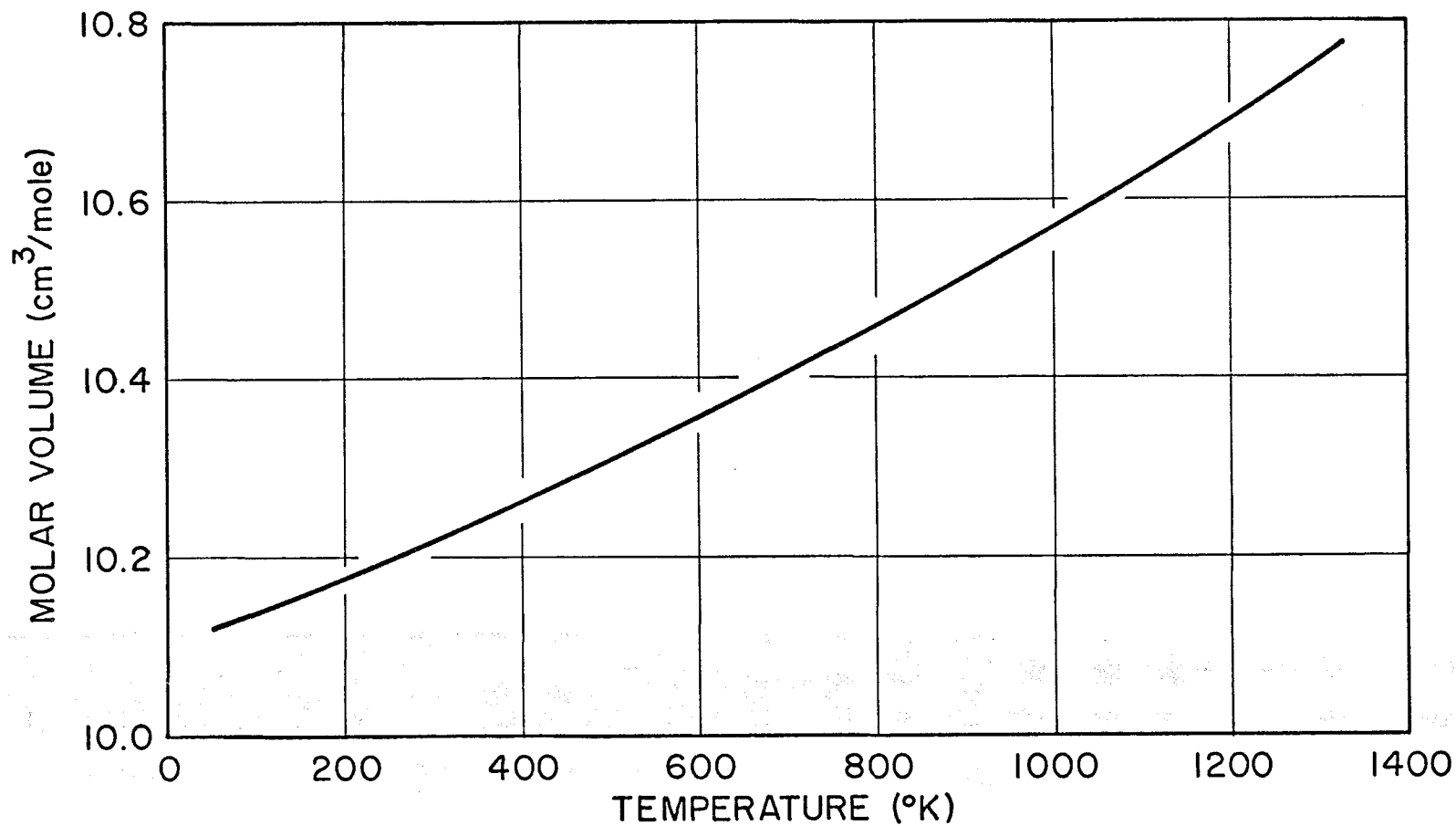


Figure 20. Molar volume for gold.

0.2×10^{-7} which represents a variation of 0.2×10^{-6} per cent at 300°K .

The good agreement between the $\Delta l/l_0$ data of Nix and MacNair³⁷ and those of Esser and Eusterbrock³⁸, where for high temperatures the maximum variation is of one per cent, indicates that the maximum uncertainty in the molar volume is no greater than one per cent. This uncertainty was used to calculate the variation of the calculated C_v (Section A-e).

c. Isothermal Compressibility

The adiabatic bulk modulus K for gold was determined by Chang and Himmel⁴¹ from the elastic constant measurements for temperatures between 300°K and 800°K . Their data were fitted by the polynomial.

$$K = C_1 + C_2T + C_3T^2 \quad (23)$$

where, for K in dynes per square centimeters,

$$C_1 = +17.83 \times 10^{+11},$$

$$C_2 = -17.89 \times 10^{+7},$$

$$C_3 = -88.58 \times 10^{+3},$$

and T = temperature in degree Kelvin.

The standard deviation of the data points with respect to the polynomial is 0.003×10^{-12} dynes per square centimeters (around 0.2 per cent). The polynomial was used for a temperature range of 200°K to 1330°K and is shown in Figure 21.

The maximum deviation of the extrapolated bulk modulus is assumed not to be greater than one per cent at 1330°K . The adiabatic compressibility β_A is the reciprocal of K .

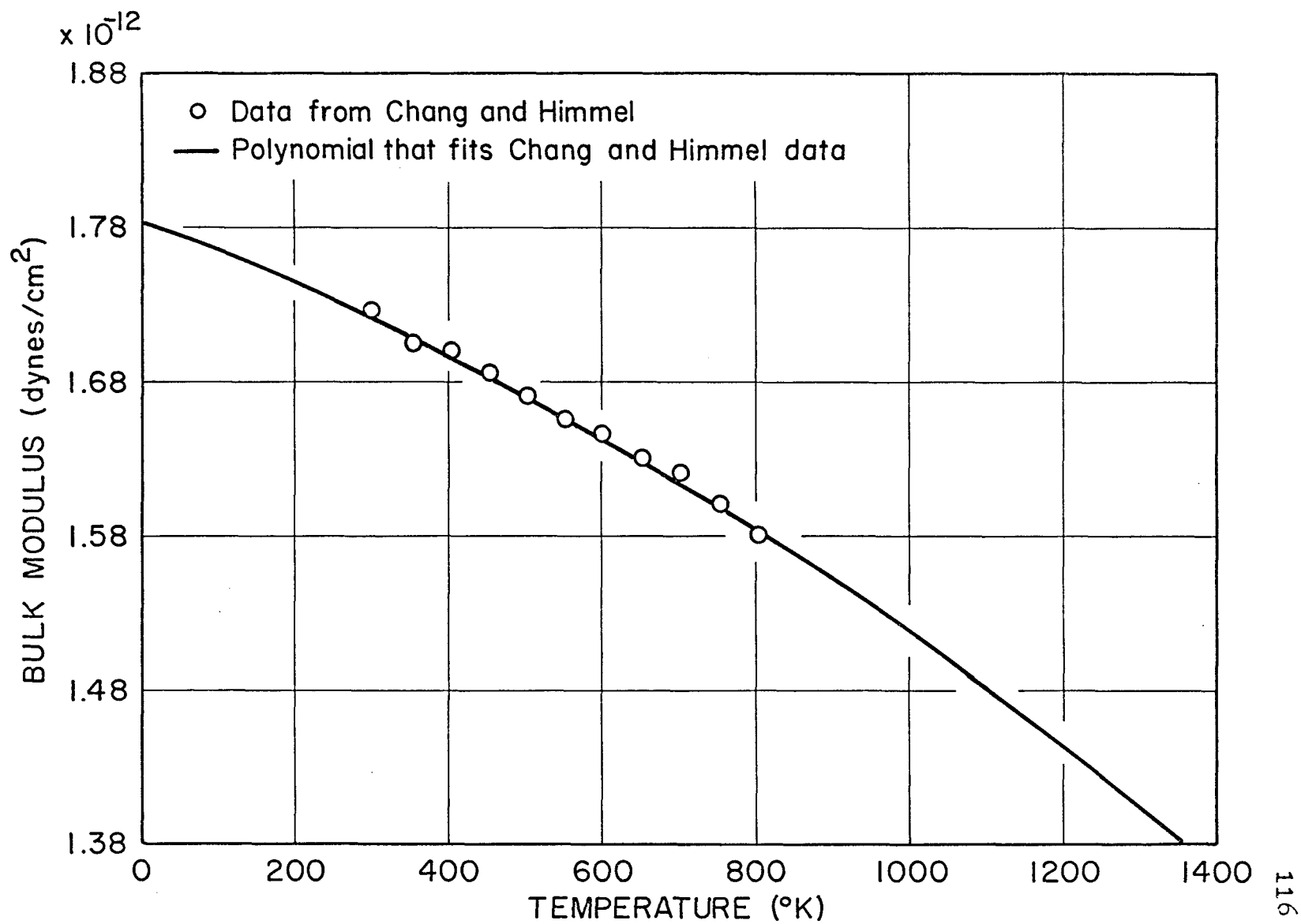


Figure 21. Bulk modulus for gold.

The high temperature ($T > 300^\circ\text{K}$) calculation of the isothermal compressibility β_v was made by using Equation (7), (20) and (22) and the C_p data given by Equation (1) in Chapter III. The low temperature range (200°K to 300°K) β_v was obtained by using Equations (7), (19), and (22) and the low temperature C_p data by Geballe and Giauque⁴².

Polynomials were determined for the calculated β_v values for the low and high temperature data. The polynomial for the low temperature data is given by

$$\beta_v = C_1 + C_2T + C_3T^2 \quad (200 \leq T \leq 300^\circ\text{K}) \quad (24)$$

where, for β_v in square centimeters per degree, the constants are

$$C_1 = +5.610 \times 10^{-13},$$

$$C_2 = +1.092 \times 10^{-16},$$

$$C_3 = +8.443 \times 10^{-20},$$

and T = absolute temperature in degree Kelvin.

The standard deviation of the calculated β_v points with respect to the above polynomial is 0.2×10^{-18} square centimeters per dyne which represents a variation of 0.3×10^{-4} per cent.

The polynomial for the high temperature data is given by

$$\beta_v = C_1 + C_2T + CT^2 \quad (300^\circ \leq T \leq 1333^\circ\text{K}) \quad (25)$$

where, for β_v in square centimeters per dyne, the constants are given by

$$C_1 = 5.660 \times 10^{-13},$$

$$C_2 = 8.463 \times 10^{-16},$$

$$C_3 = 11.567 \times 10^{-20},$$

and T = absolute temperature in degree Kelvin.

The standard deviation of the calculated data points at high temperature with respect to the polynomial representing the data points is 0.1×10^{-15} square centimeters per dyne which represents a variation of 0.1 per cent at 300°K .

Figure 22 shows the polynomial for the low and high temperature β_v data.

The difference in the isothermal compressibility at 300°K calculated by using the low and high temperature polynomials representing the β_v value is 0.2 per cent.

At 1330°K , a one per cent variation in the bulk modulus, molar volume and C_p , and a two per cent variation in α_v , produces a maximum uncertainty of two per cent in β_v . This two per cent variation in β_v was used to calculate the uncertainty in the dilation term C^d and the specific heat capacity at constant volume (Section A-e).

d. Specific Heat Capacity at Constant Volume

The calculation of the dilation term was made by using Equations (2), (20), (22) and (24) for $200^\circ \leq T \leq 300^\circ\text{K}$ and Equations (2), (20), (22) and (25) for $300^\circ \leq T \leq 1333^\circ\text{K}$. The specific heat at constant volume was obtained for the low temperature region ($200^\circ \leq T \leq 300^\circ\text{K}$) by using Equation (1), the C_p values obtained by Geballe and Giauque⁴² and the C^d

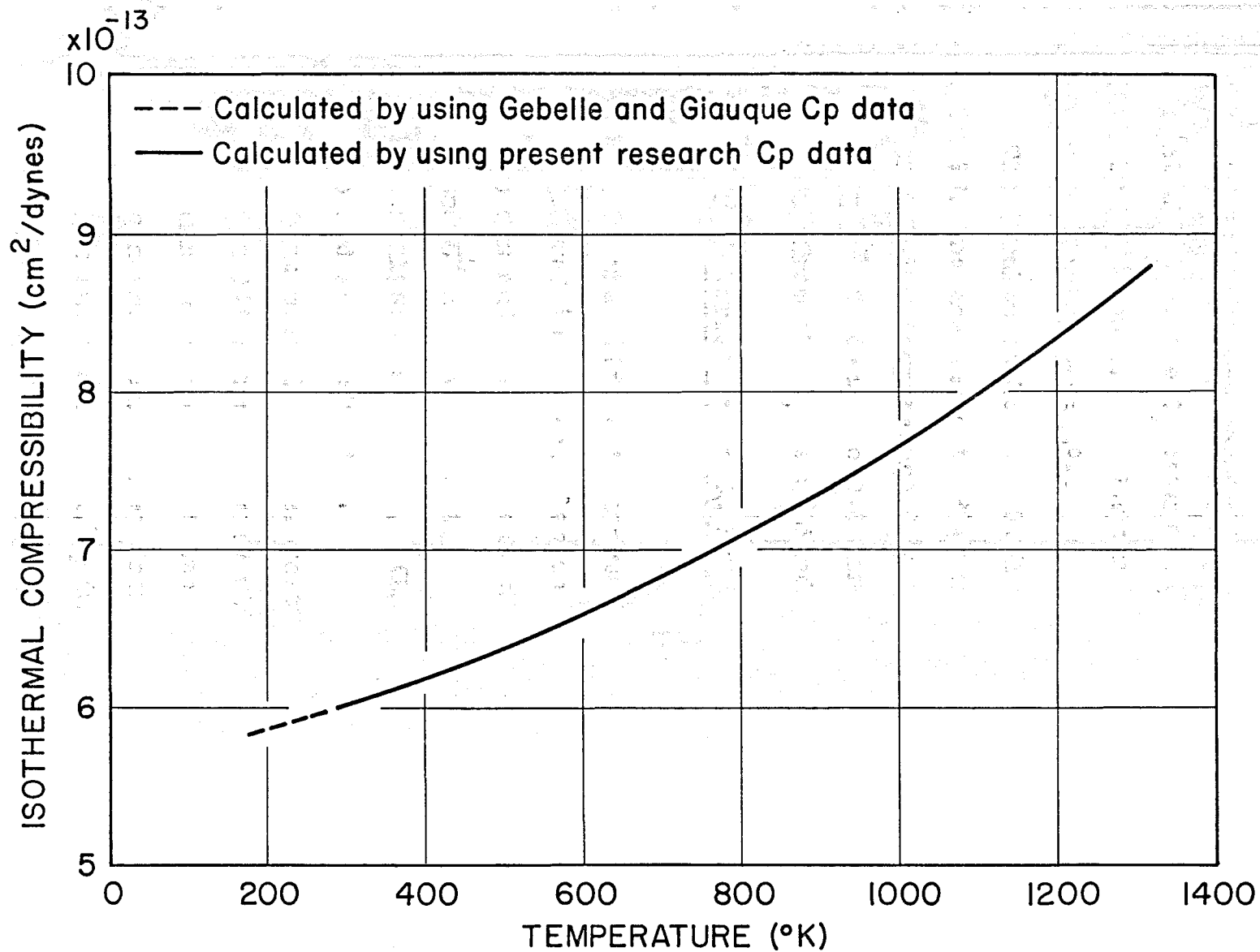


Figure 22. Isothermal compressibility for gold.

value obtained for $200^{\circ} \leq T \leq 300^{\circ}\text{K}$. The high temperature C_v ($300^{\circ} \leq T \leq 1333^{\circ}\text{K}$) was obtained by using Equation (1) in the present chapter, the C_p obtained in the present research and given by Equation (1) in Chapter III and the C^d values obtained for $300^{\circ} \leq T \leq 1333^{\circ}\text{K}$.

The results at low and high temperature are given in Table IV, and are shown in Figure 23. At 320°K the difference between the low temperature C_v results obtained from Geballe and Giauque⁴² C_p data are 2.0 per cent higher than the value calculated from the C_p determined in the present research.

e. Probable Variation in C_v Due to Error in the α_v , β_v and v

Due to the different uncertainties in the different terms involved in the calculation of the dilation term, an analysis was made on the effect of this uncertainties in the calculated C^d and the final C_v .

The analysis made on α_v ($\alpha_v = 3\alpha$), v and β_v (Section A-a, A-b and A-c) indicated:

- 1) that most α values, calculated and obtained from the literature, agreed within one per cent so the maximum variation of the α_v used in the present research (calculated from the polynomial that fits Nix and MacNair $\Delta l/l_0$ data) was no greater than two per cent;
- 2) that a variation no greater than one per cent in the values of the molar volume is expected since Simmons

TABLE IV

SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME: GOLD

Low Temperature Data		High Temperature Data			
Temperature	C_v	Temperature	C_v	Temperature	C_v
(degree Kelvin)	(Joules/gram-atom/degree Kelvin)	(degree Kelvin)	(Joules/gram-atom/degree Kelvin)	(degree Kelvin)	(Joules/gram-atom/degree Kelvin)
200	23.8995	320	24.1253	570	25.5363
210	23.9811	330	24.3132	580	25.5391
220	24.0330	340	24.4789	590	25.5414
230	24.0887	350	24.6247	600	25.5432
240	24.1606	360	24.7528	610	25.5448
250	24.2279	370	24.8651	620	25.5462
260	24.2948	380	24.9633	630	25.5475
270	24.3612	390	25.0491	640	25.5489
280	24.4232	400	25.1238	650	25.5504
290	24.4762	410	25.1887	660	25.5521
300	24.5288	420	25.2449	670	25.5540
310	24.5771	430	25.2935	680	25.5563
320	24.6175	440	25.3353	690	25.5590
		450	25.3711	700	25.5620
		460	25.4417	710	25.5656
		470	25.4277	720	25.5696
		480	25.4497	730	25.5742
		490	25.4682	740	25.5793
		500	25.4836	750	25.5850
		510	25.4965	760	25.5912
		520	25.5070	770	25.5982
		530	25.5157	780	25.6057
		540	25.5226	790	25.6139
		550	25.5283	800	25.6227
		560	25.5328	810	25.6322

TABLE IV (continued)

Low Temperature Data		High Temperature Data			
Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)	Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)	Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)
		820	25.6423	1090	26.1620
		830	25.6531	1100	26.1897
		840	25.6646	1110	26.2179
		850	25.6767	1120	26.2466
		860	25.6896	1130	26.2759
		870	25.7031	1140	26.3057
		880	25.7172	1150	26.3360
		890	25.7321	1160	26.3668
		900	25.7476	1170	26.3981
		910	25.7637	1180	26.4299
		920	25.7806	1190	26.4622
		930	25.7980	1200	26.4949
		940	25.8162	1210	26.5281
		950	25.8350	1220	26.5618
		960	25.8544	1230	26.5960
		970	25.8744	1240	26.6306
		980	25.8951	1250	26.6657
		990	25.9164	1260	26.7012
		1000	25.9383	1270	26.7371
		1010	25.9608	1280	26.7735
		1020	25.9839	1290	26.8103
		1030	26.0076	1300	26.8475
		1040	26.0319	1310	26.8851
		1050	26.0568	1320	26.9232
		1060	26.0823	1330	26.9616
		1070	26.1083		
		1080	26.1349		

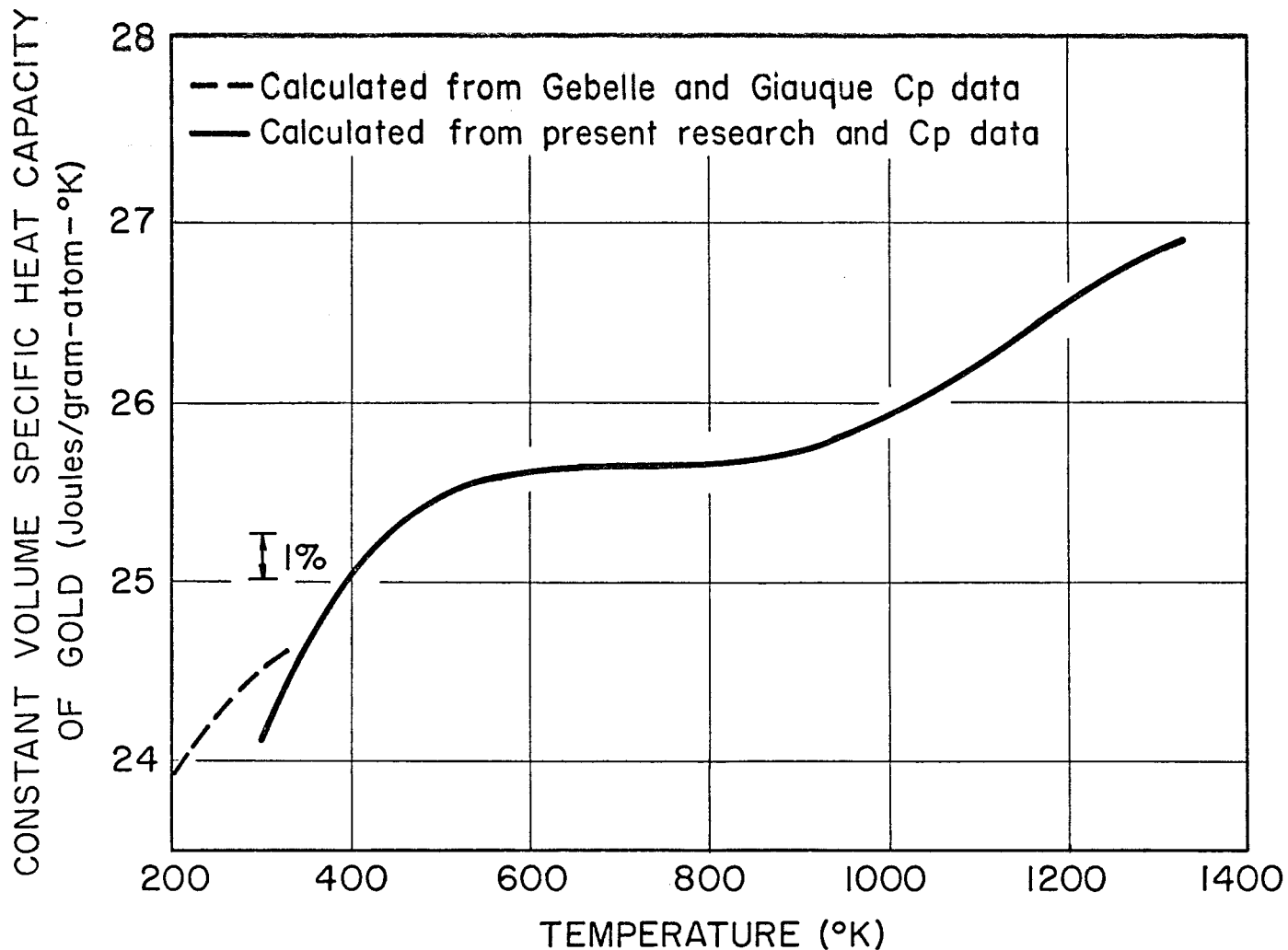


Figure 23. Specific heat capacity at constant volume for gold.

and Balluffi³⁹ and Nix and MacNair³⁷ $\Delta l/l_0$ data differ at high temperature by no more than about one per cent; and

- 3) that the maximum variation in β_v calculated from the uncertainties in K , α_v , C_p and V is two per cent.

The above uncertainties, applied in Equation (9) at 1330°K, indicated that the maximum variation in the dilation term is 0.43 Joules per gram-atom per degree Kelvin (7.0 per cent) which finally would give an error of 1.6 per cent in the calculated specific heat capacity at constant volume.

A ± 1.0 per cent variation in C_p plus the ± 7.0 per cent variation in C^d will cause a maximum variation of ± 2.8 per cent in C_v . The variation of C_p and C^d both with the same positive or negative sign will give a variation of 0.4 per cent in the C_v value.

B. LEAD

a. Coefficient of Volume Thermal Expansion

Measurements on the linear thermal expansion for lead were made in 1941 by Nix and MacNair⁴³ from 85°K to 300°K. The least square curve fitting method was used to determine a polynomial for the $\Delta l/l_0$ data points* given by Nix and MacNair⁴³. The polynomial used is

*The length change was measured with respect to 0°C.

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5 \quad (26)$$

where

$$C_1 = -74.56 \times 10^{-4},$$

$$C_2 = +36.09 \times 10^{-6},$$

$$C_3 = -16.61 \times 10^{-8},$$

$$C_4 = +11.18 \times 10^{-10},$$

$$C_5 = -33.04 \times 10^{-13},$$

$$C_6 = +36.87 \times 10^{-16},$$

and T = temperature in degree Kelvin.

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.13×10^{-4} which represents a 1.6 per cent deviation at 300°K and 0.4 per cent at 400°K .

No further use will be made on the above result since it involves measurements at low temperature; nevertheless, the values determined by Nix and MacNair⁴³ by using the slopes of their $\Delta l/l_0$ versus temperature curves will be used as a mean to check the high temperature α calculations.

$\Delta l/l_0$ measurements were also made by D'Heurle, Feder and Nowick⁴⁴ from 433°K to 600°K . The polynomial obtained by using the least square curve fitting method on their results is

$$\frac{\Delta l}{l_0} = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5 \quad (28)$$

where

$$C_1 = -75.78 \times 10^{-4},$$

$$C_2 = +21.26 \times 10^{-6},$$

$$C_3 = +25.98 \times 10^{-9},$$

$$C_4 = -53.43 \times 10^{-12},$$

$$C_5 = -70.39 \times 10^{-15},$$

$$C_6 = -28.75 \times 10^{-18},$$

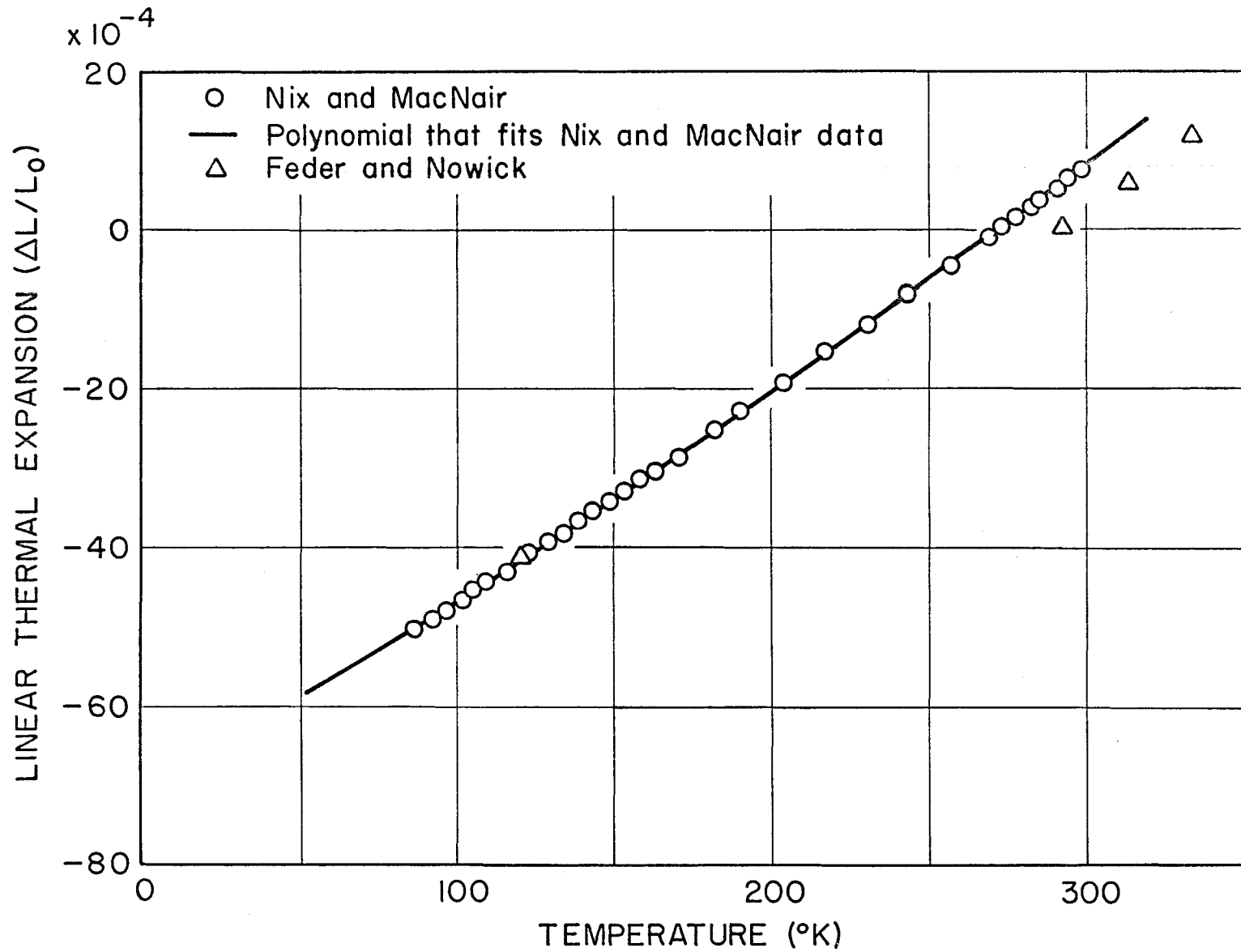
and T = temperature in degree Kelvin.

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.2×10^{-5} which represents a 0.2 per cent deviation at 300°K .

Figure 24 shows the low temperature $\Delta l/l_0$ values obtained by Nix and MacNair⁴³ and the polynomial used to fit their data. At around 300°K it is observed that a difference of 6.0×10^{-4} (75 per cent) exists between the data of Nix and MacNair⁴³ and those of Feder and Nowick⁴⁵. It should be emphasized that the per cent difference obtained is high due to very low Δl values at around 300°K , and, as it will be shown later, it produces only a very small difference in the α_v calculations.

Figure 25 shows the high temperature linear thermal expansion $\Delta l/l_0$ where, above 450°K , good agreement is obtained between the results of D'Heurle, Feder and Nowick⁴⁴ and Feder and Nowick⁴⁵ and the polynomials used to fit their data.

Figure 26 shows the results of the linear coefficient of thermal expansion α obtained in different investigations. Nix and MacNair⁴³ measured graphically the α values from their low temperature $\Delta l/l_0$ data. The polynomial calculated to fit their data is given by



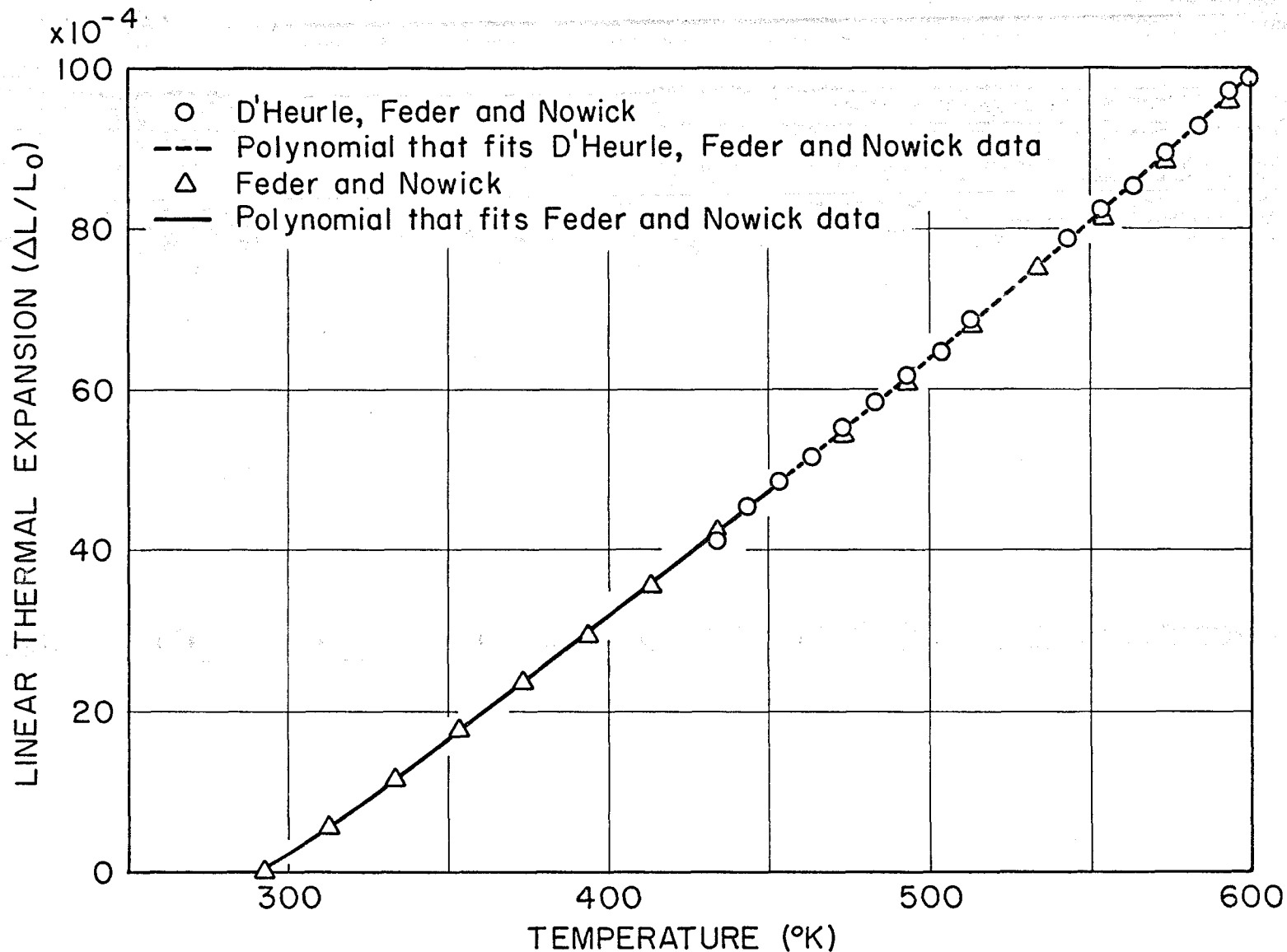


Figure 25. High temperature linear thermal expansion for lead.

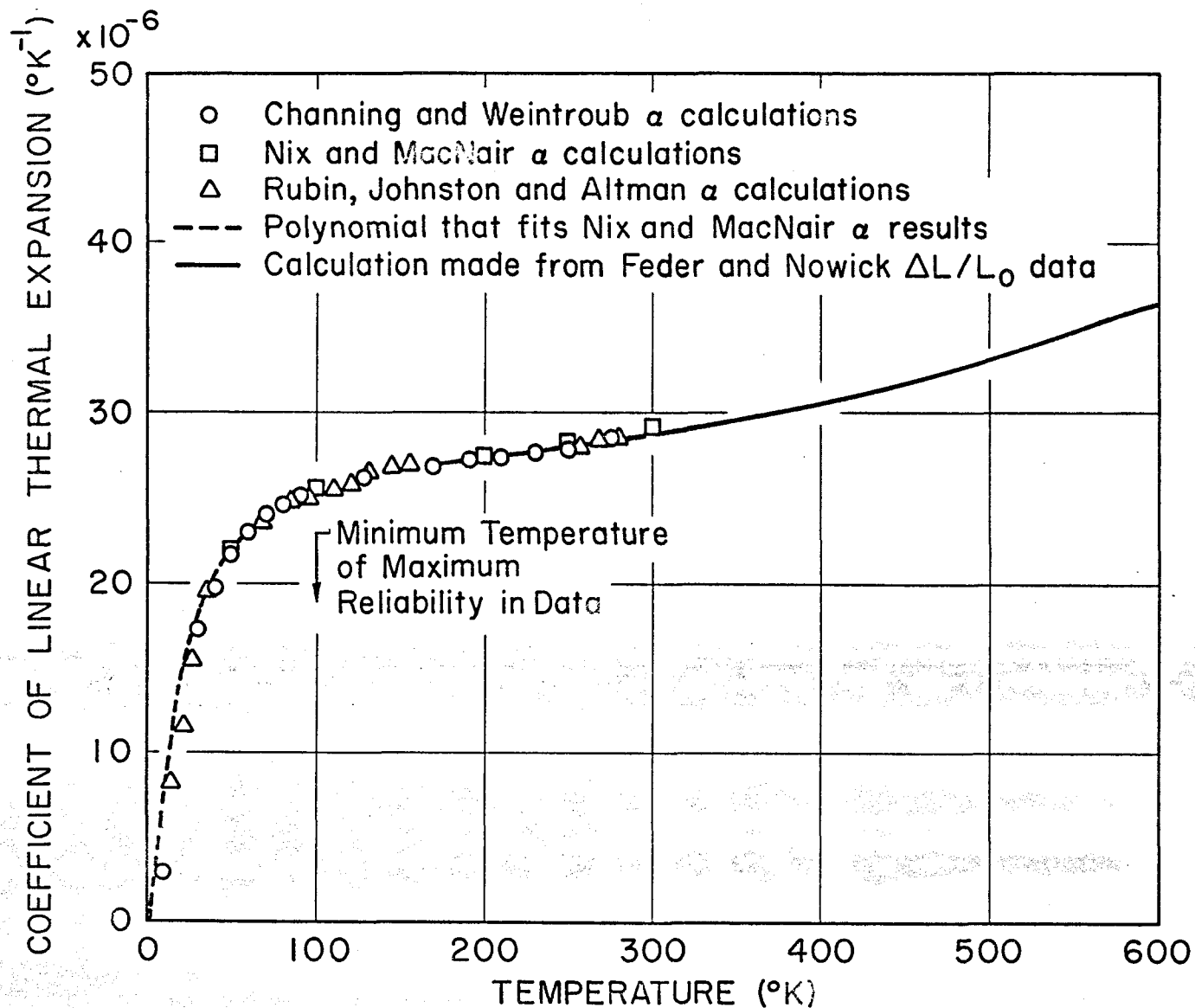


Figure 26. Coefficient of linear thermal expansion for lead.

$$\alpha = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 + c_6 T^5 \quad (29)$$

where, for α in $^{\circ}\text{K}^{-1}$,

$$c_1 = +79.25 \times 10^{-7},$$

$$c_2 = +48.76 \times 10^{-8},$$

$$c_3 = -54.40 \times 10^{-10},$$

$$c_4 = +30.72 \times 10^{-12},$$

$$c_5 = -84.00 \times 10^{-15},$$

$$c_6 = +88.67 \times 10^{-18},$$

and $T = +88.67 \times 10^{-18}$.

The standard deviation of the results of Nix and MacNair⁴³ with respect to the above polynomial is $0.4 \times 10^{-15} \text{ }^{\circ}\text{K}^{-1}$ which represents a deviation of 0.1×10^{-8} per cent at 300°K . Rubin, Johnston and Altman⁴⁶ and Channing and Weintroub⁴⁷ have reported α values at low temperature for lead ($T \leq 300^{\circ}\text{K}$); no length values were reported. Their results are also shown in Figure 26, and are within one per cent of those of Nix and MacNair⁴³. The α curve calculated from the polynomial used to fit the $\Delta l/l_0$ data of Feder and Nowick⁴⁵ (Equation 28), by using Equation (19), is also shown in Figure 26. Since the α curve calculated from Equation (28) by using the procedure summarized in Equation (19), was used for comparison and for future calculations, it was decided to represent the calculated α^* by a simpler polynomial, which is given by

*All calculations involving the use of Equation (19) were made for a temperature interval of ten degrees.

$$\alpha = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 \quad (30)$$

where, for α in $^{\circ}\text{K}^{-1}$,

$$c_1 = +21.50 \times 10^{-6},$$

$$c_2 = +51.08 \times 10^{-9},$$

$$c_3 = -15.98 \times 10^{-11},$$

$$c_4 = +28.08 \times 10^{-14},$$

$$c_5 = -14.46 \times 10^{-17},$$

and T = temperature in degrees Kelvin.

The standard deviation of the calculated α values obtained by using Equation (19) with respect to the above polynomial is $0.1 \times 10^{-10} \text{ }^{\circ}\text{K}^{-1}$ which represents a deviation of 0.3×10^{-4} per cent at 300°K ; this difference shows that the use of the polynomial instead of the calculated α did not produce any appreciable deviation in the α results.

The high temperature α values obtained from Equation (30) were 1.4 per cent below the Nix and MacNair polynomial at 300°K , and this difference decreased to zero at 160°K . The difference at low temperature between the polynomial given by Equation (30) and the α obtained from the work of Rubin, Johnston and Altman⁴⁶ and Channing and Weintroub⁴⁷ is 0.2 per cent.

The coefficient of linear thermal expansion given by Equation (30) and obtained from the polynomial that fits Feder and Nowick⁴⁵ $\Delta l/l_0$ data was used in the determination of the dilation term ($\alpha_v = 3\alpha$). Basically, all the different results were within one per cent for $T \leq 300^{\circ}\text{K}$; for

$T \geq 400^\circ\text{K}$ the α results obtained from the polynomials that fit the $1/l_0$ data of D'Heurle, Feder and Nowick⁴⁴ and Feder and Nowick⁴⁵ agreed within 0.8 per cent. For $300 < T < 400^\circ\text{K}$ no other α but that calculated from the polynomial that fits Feder and Nowick $\Delta 1/l_0$ data was available. It is expected that the maximum variation due to the use of Equation (30) is no greater than one per cent.

b. Molar Volume

As in the case of gold, the molar volume at 25°C was calculated from the lattice parameters given by Pearson⁴⁰ which was used as a reference to calculate the molar volume as a function of temperature by using Equation (21) and the constants C_1, C_2, C_3, C_4, C_5 and C_6 given in Equation (28). The V data points obtained every ten degrees were used to determine a simpler polynomial which was used in the calculation of the dilation term C^d . The polynomial, shown in Figure 27, is

$$V = C_1 + C_2T + C_3T^2 + C_4T^3 \quad (31)$$

where, for V in cubic centimeters per mole, the constants

C_1, C_2, C_3 and C_4 are given by

$$C_1 = +17.81 \times 10^{+0},$$

$$C_2 = +15.74 \times 10^{-4}$$

$$C_3 = -36.33 \times 10^{-6},$$

$$C_4 = +85.51 \times 10^{-9},$$

and T = temperature in degree Kelvin.

The standard deviation of the data points obtained by using

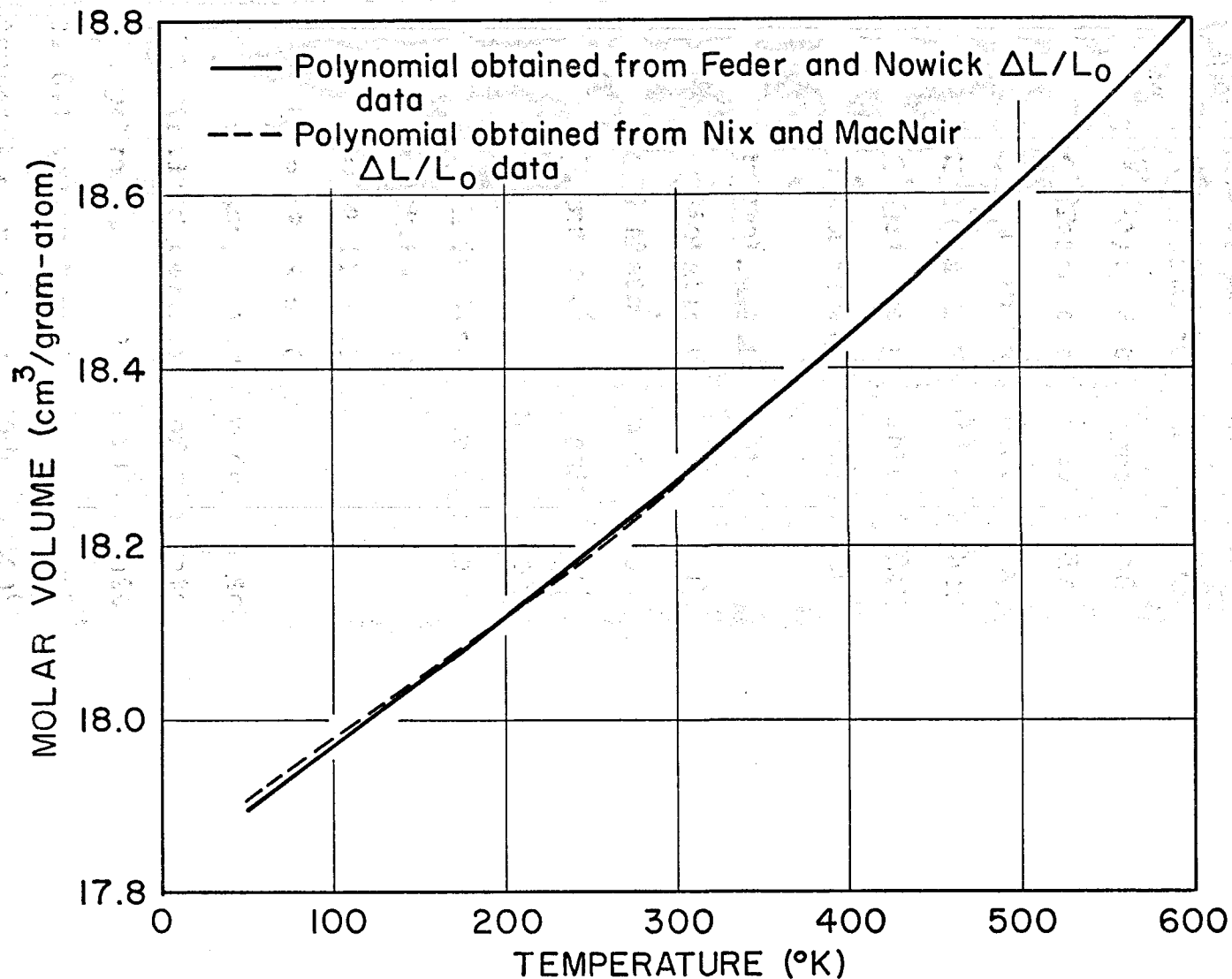


Figure 27. Molar volume for lead as a function of temperature.

Equation (21) with respect to the above polynomial is 0.1×10^{-6} which represents a deviation of 0.6×10^{-5} per cent at 300°K .

Figure 27 also shows the polynomial that was obtained by using the data calculated from Equation (21) and Nix and MacNair⁴³ $\Delta l/l_0$ data represented by Equation (26). The maximum difference above 200°K is 0.04 per cent. The excellent agreement in the molar volume obtained from the $\Delta l/l_0$ data of Nix and MacNair⁴³ and those of Feder and Nowick⁴⁵ indicates that the probable maximum variation in the V results obtained from Equation (31) is no greater than one per cent.

c. Isothermal Compressibility

The adiabatic bulk modulus K for lead was determined by Waldorf and Alers⁴⁸ from elastic constants measurements between 0°K and 300°K . A polynomial that fits their data is

$$K = C_1 + C_2T + C_3T^2 \quad (32)$$

where, for K in dynes per square centimeter,

$$C_1 = +4.89 \times 10^{+12},$$

$$C_2 = -1.21 \times 10^{+9},$$

$$C_3 = -7.55 \times 10^{+5},$$

and T = temperature in degree Kelvin.

The standard deviation of the data points with respect to the polynomial is $0.6 \times 10^{+9}$, which represents a deviation of 0.1 per cent at 300°K . The polynomial was used for a temperature range of 200°K to 600°K , and it is shown in

Figure 28. Since for lead, bulk modulus data exist for temperatures below 300°K , the extrapolation of the polynomial used to represent the data for temperatures above 300°K is not expected to be greater than ± 1.6 per cent. The bulk modulus for lead decreases by around thirteen per cent in the extrapolated region ($300^{\circ} \leq T \leq 600^{\circ}\text{K}$), and an analysis on the decrease of the bulk modulus for zinc, by increasing temperature ($300^{\circ} \leq T \leq 600^{\circ}\text{K}$) shows a decrease of twelve per cent in the bulk modulus. (For zinc the available data was the adiabatic compressibility which is the reciprocal of the bulk modulus. See Section C-c-3). The above comparison give a slight indication that the assumed ± 1.6 per cent variation in the bulk modulus for lead could be a reasonable estimate. The estimated ± 1.6 variation in the bulk modulus was used to determine the effect of this variation in the isothermal compressibility β_v .

The calculation of the high temperature ($T > 300^{\circ}\text{K}$) isothermal compressibility β_v was made by using Equation (7), (30) and (31) in the present chapter, and the polynomial used to represent the present research C_p data of lead (Chapter III). The low temperature ($200^{\circ} \leq T \leq 300^{\circ}\text{K}$) calculation of β_v were made by using Equations (7), (30) and (31) in the present chapter and the low temperature C_p values given by Hultgreen et al.³⁵.

Polynomials were determined for the calculated β_v values for the low and high temperature data. The polynomial

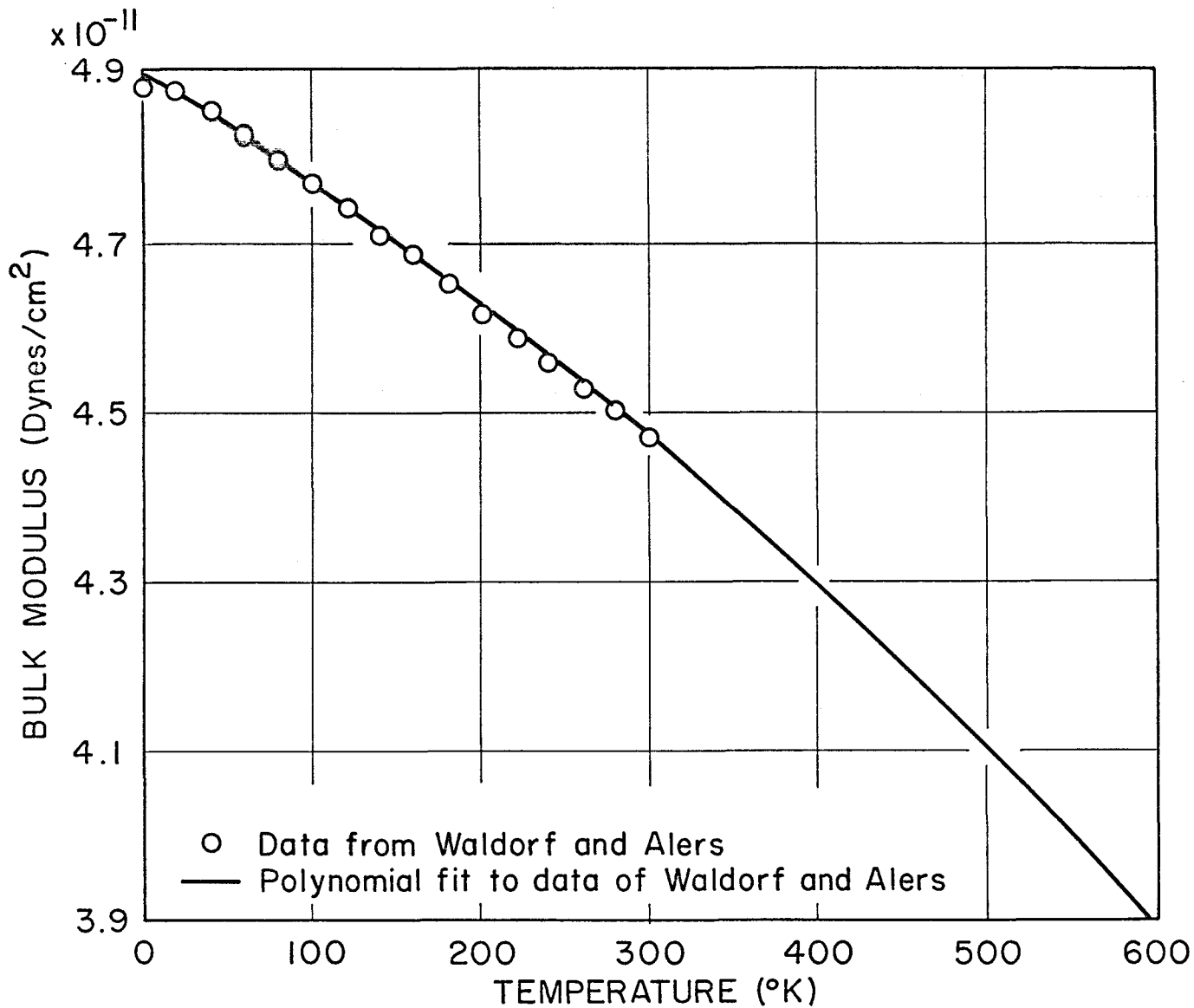


Figure 28. Bulk modulus for lead.

for the low temperature data is

$$\beta_v = c_1 + c_2 T + c_3 T^2 \quad (200 \leq T \leq 300^\circ \text{K}) \quad (33)$$

where, for β_v in square centimeters per degree,

$$c_1 = +20.48 \times 10^{-13},$$

$$c_2 = +83.14 \times 10^{-17},$$

$$c_3 = +10.83 \times 10^{-19},$$

and T = temperature in degree Kelvin.

The standard deviation of the calculated β_v with respect to the above polynomial is 0.1×10^{-24} which represents a deviation of 0.5×10^{-11} at 300°K .

The polynomial for the high temperature data is

$$\beta_v = c_1 + c_2 T + c_3 T^2 + c_4 T^3 \quad (300^\circ \leq T \leq 600^\circ \text{K}) \quad (34)$$

where, for β_v in square centimeters per degree,

$$c_1 = +20.58 \times 10^{-13},$$

$$c_2 = +94.60 \times 10^{-17},$$

$$c_3 = +10.44 \times 10^{-20},$$

$$c_4 = +16.55 \times 10^{-22},$$

and T = temperature in degree Kelvin.

The standard deviation of the calculated β_v with respect to the above polynomial is 0.5×10^{-16} which represents a deviation of 0.2×10^{-2} per cent at 300°K .

Figure 29 shows both the low and the high temperature polynomials used to represent the calculated isothermal compressibilities. Also shown in Figure 29 are the β_v data obtained by a combination of theoretical and experimental

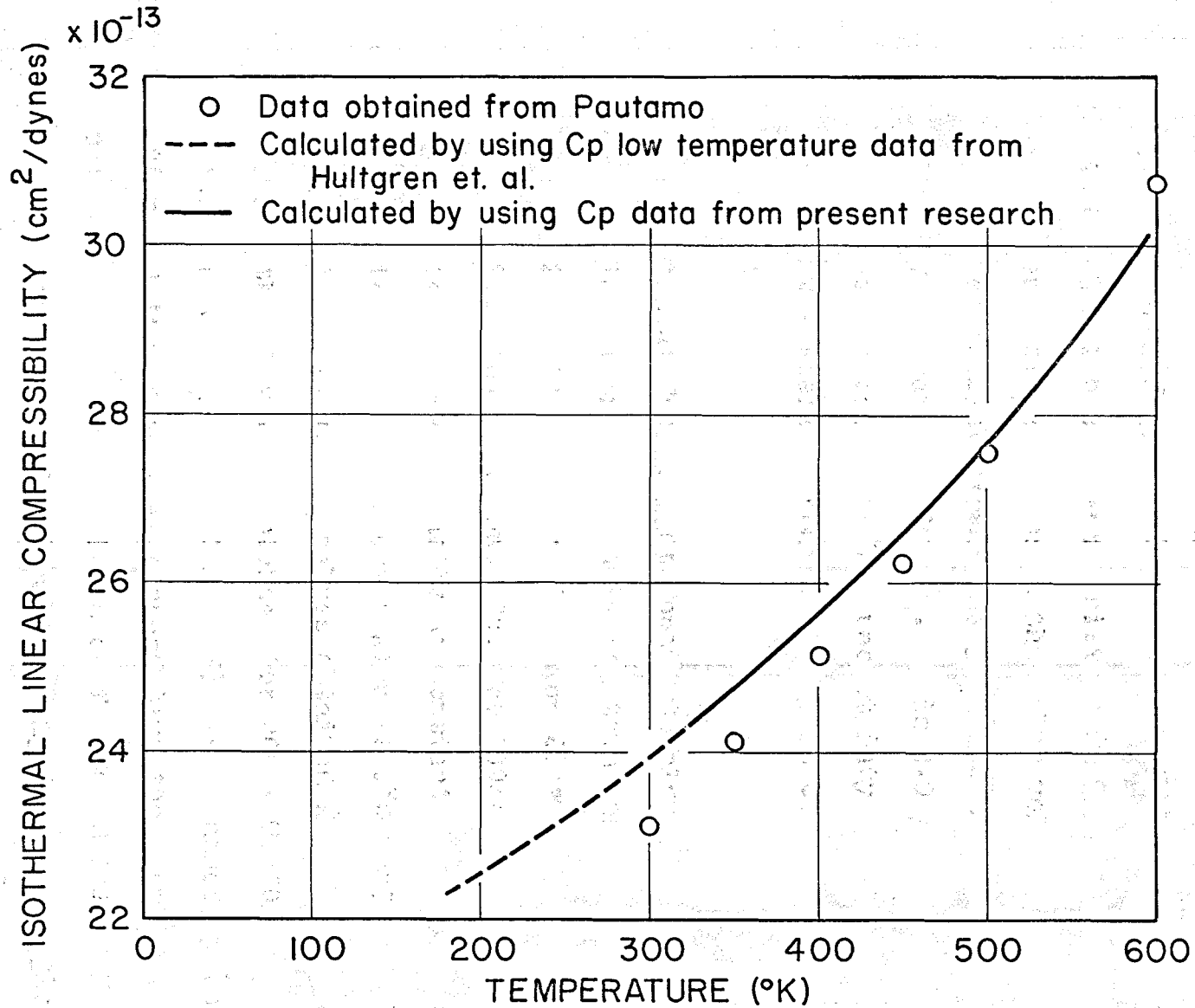


Figure 29. Isothermal compressibility for lead.

calculations made by Pautamo⁴⁹. The difference at low temperature between the polynomial and Pautamo's calculations is 3.3 per cent. The difference decreases at higher temperatures except for the melting point where a three per cent deviation is observed.

At 600°K a 1.6 per cent variation in the bulk modulus, and a one per cent variation in the molar volume, C_p and the coefficient of thermal expansion, produces a maximum uncertainty of two per cent in β_v . This 2.0 per cent variation was used to calculate the uncertainty in the dilation term C^d and the specific heat capacity at constant volume (Section B-e)

d. Specific Heat Capacity at Constant Volume

The calculation of the dilation term was made by using Equations (2), (30), (31) and (33) for $200 \leq T \leq 300^\circ\text{K}$, and Equations (2), (30), (31) and (34) for $300 \leq T \leq 600^\circ\text{K}$.

The specific heat capacity at constant volume was obtained for the low temperature region ($200^\circ \leq T \leq 300^\circ\text{K}$) by using Equation (1), the C_p values obtained from Hultgren et al.³⁵, and the C^d values obtained for $200^\circ \leq T \leq 300^\circ\text{K}$. The high temperature C_v ($300^\circ \leq T \leq 600^\circ\text{K}$) was obtained by using Equation (1) the polynomial representing the present research C_p data and the C^d value calculated for $300^\circ \leq T \leq 600^\circ\text{K}$.

The C_v results at low and high temperature are given in Table V, and are shown in Figure 30. At 300°K the difference between the low and high temperature calculation is 0.2 per cent.

TABLE V

SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME: LEAD

Low Temperature Data		High Temperature Data	
Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)	Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)
200	24.6518	310	24.7100
210	24.6679	320	24.7431
220	24.6824	330	24.7652
230	24.6953	340	24.7838
240	24.7056	350	24.7988
250	24.7162	360	24.8102
260	24.7242	370	24.8184
270	24.7305	380	24.8239
280	24.7353	390	24.8273
290	24.7384	400	24.8295
300	24.7353	410	24.8309
310	24.7397	420	24.8322
		430	24.8341
		440	24.8371
		450	24.8417
		460	24.8483
		470	24.8574
		480	24.8693
		490	24.8842
		500	24.9024
		510	24.9242
		520	24.9497
		530	24.9790
		540	25.0124
		550	25.0498
		560	25.0913
		570	25.1371
		580	25.1872
		590	25.2417
		600	25.3005

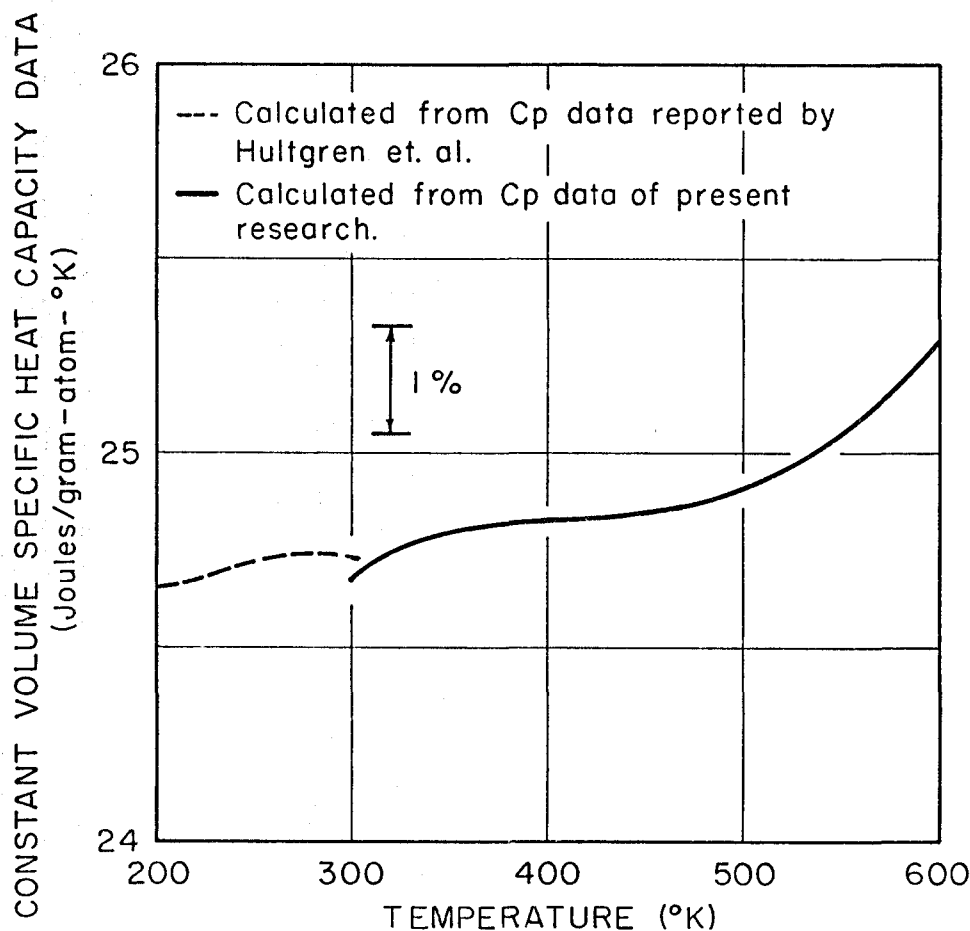


Figure 30. The specific heat capacity at constant volume for lead.

e. Probable Variation in C_V Due to Errors in the Chosen α_V , β_V , V and C_p

Due to the different uncertainties in the different terms involved in the calculation of the dilation term, an analysis was made on the effect of this uncertainties in the calculated C^d and the final C_V .

The analysis made on α_V ($\alpha_V = 3\alpha$), V and β_V (Sections B-a, B-b and B-c) indicated

- 1) that most α values, calculated and obtained from the literature, agreed within one per cent, so the maximum variation of the α_V used in the present research (calculated from the polynomial that fits Feder and Nowick⁴⁵ $\Delta 1/l_0$ data) was not greater than one per cent,
- 2) that a variation no greater than one per cent in the values of the molar volume is expected since the $\Delta 1/l_0$ data of Nix and MacNair⁴³, D'Heurle, Feder and Nowick⁴⁴ and Feder and Nowick⁴⁵ do not differ by more than one per cent, and
- 3) that the maximum variation in β_V calculated from the uncertainties in K , α_V , C_p and V is two per cent.

The above uncertainties, applied to Equation (9) at 600°K, indicated that the maximum variation in the dilation term is ± 0.25 Joules per gram-atom per degree (± 5.6 per cent),

which finally would give an error of one per cent in the calculated specific heat capacity at constant volume. A ± 1.0 per cent variation in C_p plus the ∓ 5.6 per cent variation in C^d will cause a maximum variation of ± 2.2 per cent in C_v . The variation of C_p and C^d , both with the same positive or negative sign will give a variation of ± 0.2 .

C. ZINC

a. Coefficient of Volume Thermal Expansion

The coefficient of volume thermal expansion for zinc was determined from the linear thermal expansion data (along the a and c axis) measured by Gilder and Wallmark⁵⁰ in 1969 from 300°K to 700°K. Since zinc has a hexagonal close-packed structure, the coefficient of volume thermal expansion has to be calculated by

i) determining, separately, the coefficient of linear thermal expansion α_a and α_c from the $\Delta l/l_0$ measurements along the a and c axis, respectively, of single crystals, and

ii) determining the coefficient of volume expansion by using the equation

$$\alpha_v = \frac{1}{V} \frac{dV}{dT} = 2\alpha_a + \alpha_c^* \quad (35)$$

*The derivation of this equation is presented in Appendix F.

1. Coefficient of Linear Thermal Expansion Along the a-axis. The least square curve fitting method was used in the present research to determine the polynomial that fits Gilder and Wallmark⁵⁰ $\Delta l/l_0$ measurements along the a-axis $(\Delta l/l_0)_a$. The polynomial is

$$\left(\frac{\Delta l}{l_0}\right)_a = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 + c_6 T^5 \quad (36)$$

where

$$c_1 = -11.71 \times 10^{-3},$$

$$c_2 = +10.17 \times 10^{-5},$$

$$c_3 = -40.41 \times 10^{-8},$$

$$c_4 = +88.60 \times 10^{-11},$$

$$c_5 = -93.48 \times 10^{-14},$$

$$c_6 = +39.71 \times 10^{-17},$$

and T = temperature in degree Kelvin.

The standard deviation of the $\Delta l/l_0$ data with respect to the above polynomial is 0.6×10^{-5} which represents a 0.5 per cent deviation at 400°K .

Figure 31 shows the linear thermal expansion data for the a-axis $(\Delta l/l_0)_a$ obtained by Gilder and Wallmark⁵⁰, and the polynomial used to represent their data (Equation 36).

The coefficient of linear thermal expansion curve for the a-axis calculated by Gilder and Wallmark⁵⁰ from a graphical differentiation of their $(\Delta l/l_0)_a$ results is shown in Figure 32. They claimed an uncertainty in their

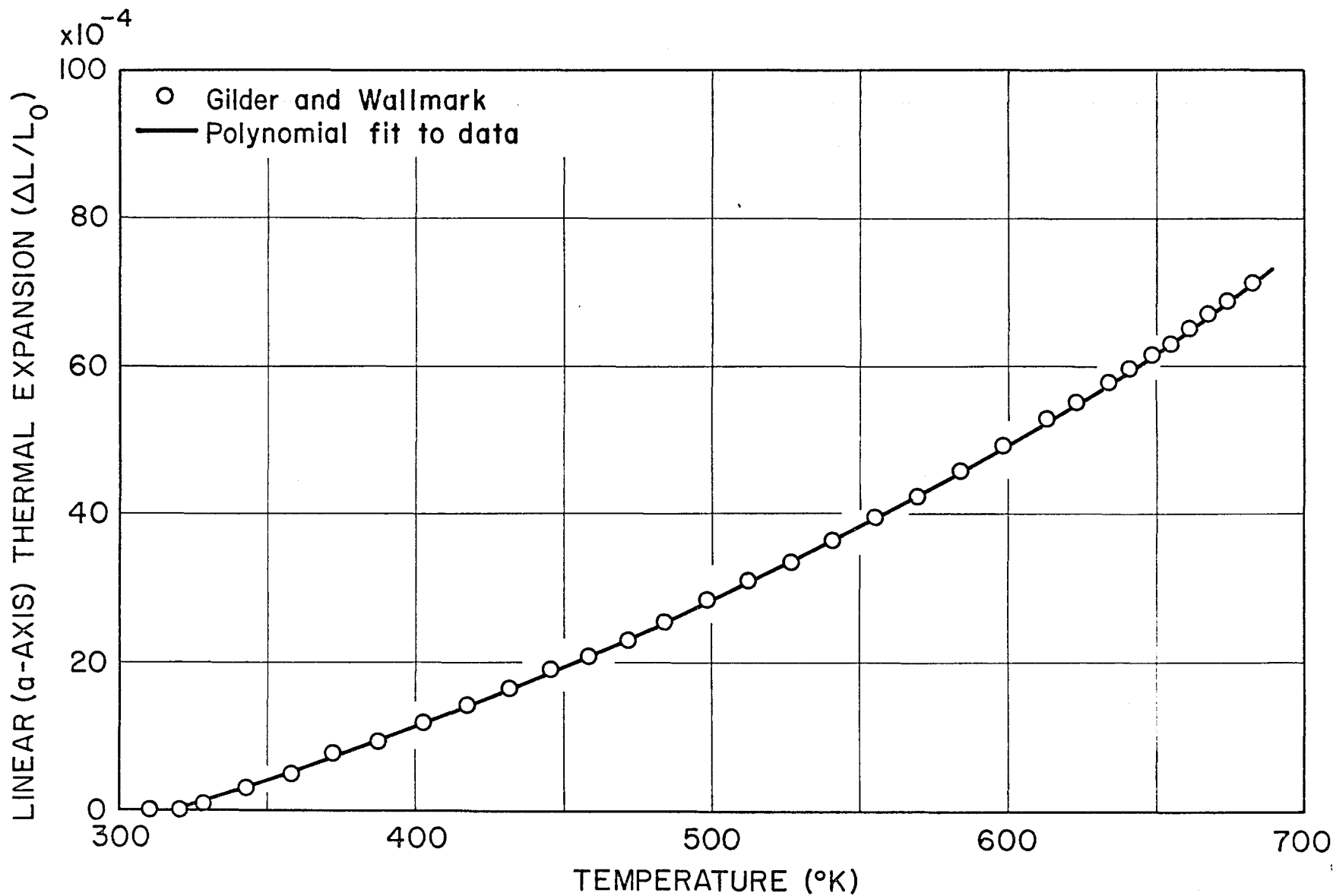


Figure 31. Linear thermal expansion for the a -axis in zinc.

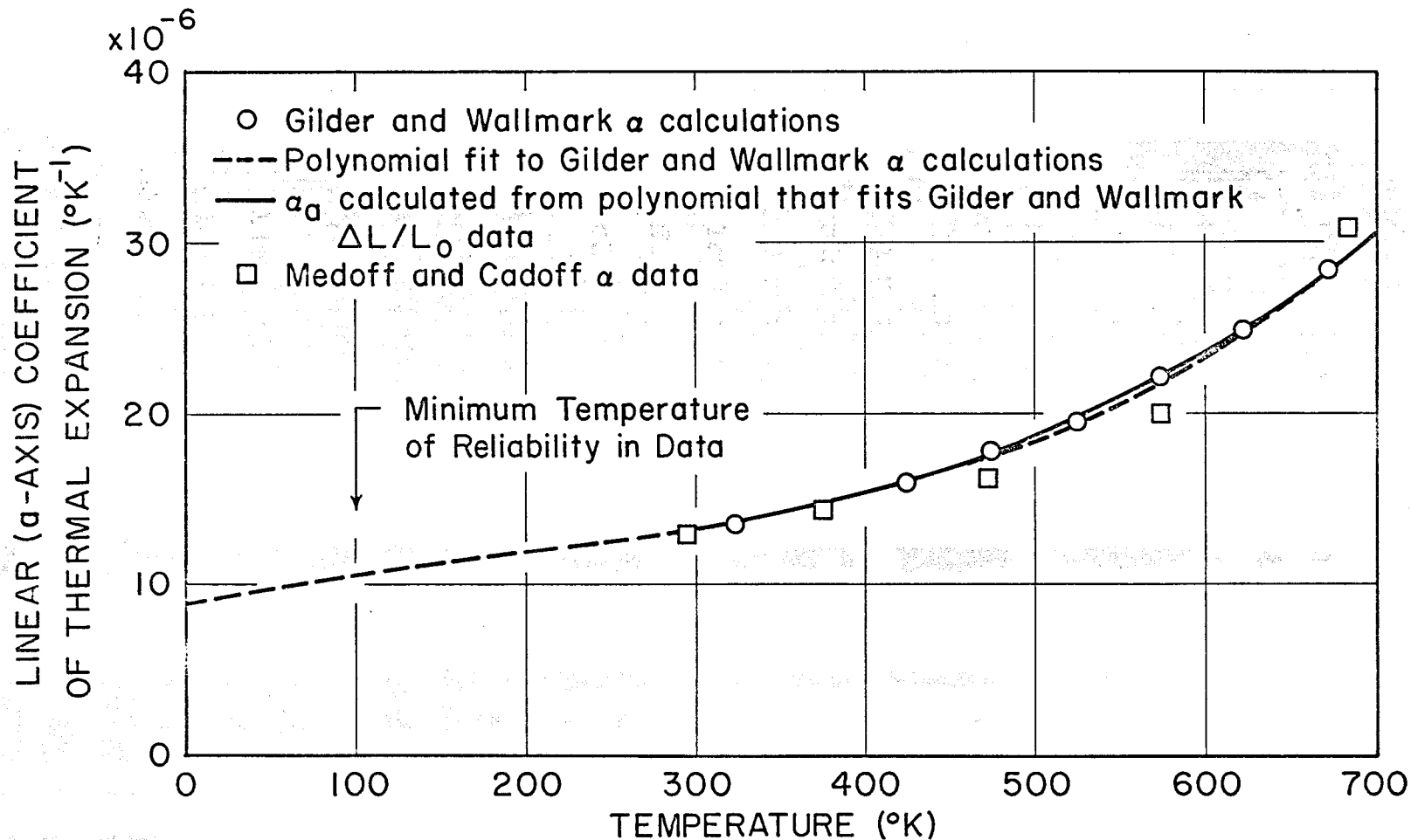


Figure 32. Coefficient of linear thermal expansion for the a-axis, zinc.

α_a results of one per cent. The α_a results obtained by Gilder and Wallmark⁵⁰ were used in the present research to determine a polynomial that could be used to represent their data. The polynomial shown in Figure 32 is given by

$$\alpha_a = C_1 + C_2T + C_3T^2 + C_4T^3$$

where, for α_a in $^{\circ}\text{K}^{-1}$,

$$C_1 = +89.32 \times 10^{-7},$$

$$C_2 = +18.68 \times 10^{-9},$$

$$C_3 = -39.48 \times 10^{-12},$$

$$C_4 = +81.64 \times 10^{-15},$$

and T = temperature in degree Kelvin.

The standard deviation of the α_a results of Gilder and Wallmark⁵⁰ with respect to the above polynomial is 0.2×10^{-6} , which is equivalent to a difference of around 0.2 per cent at 300°K . This difference decreases at higher temperatures.

Figure 32 also shows some α_a values obtained by Medoff and Cadoff⁵¹, who claimed an experimental uncertainty of five per cent in the calculated α_a results. At 573°K their results are ten per cent below those of Gilder and Wallmark⁵⁰, but exhibit closer agreement at other temperatures.

The α_a curve calculated from the polynomial that fits the data of Gilder and Wallmark⁵⁰ $(\alpha_l/l_o)_a$ (Equation (36)) by using Equation (19) is also shown in Figure 32. Since the α_a calculated from Equation (36) by using the procedure summarized in Equation (19) was used for comparison and for future calculations, it was decided to represent the calcu-

lated α_a^* by a simpler polynomial, given by

$$\alpha_a = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4 \quad (38)$$

where, for α_a $^{\circ}\text{K}^{-1}$,

$$C_1 = +10.08 \times 10^{-5},$$

$$C_2 = -80.00 \times 10^{-8},$$

$$C_3 = +26.30 \times 10^{-10},$$

$$C_4 = -36.98 \times 10^{-13},$$

$$C_5 = +19.62 \times 10^{-16},$$

and T = temperature in degree Kelvin.

The standard deviation between the calculated α_a obtained by using Equation (19) and the above polynomial is 0.2×10^{-8} , which produces a variation of 0.01 per cent at 300°K . The variation decreases as the temperature increases. The variations calculated above show that the use of the polynomial instead of the calculated α_a would not produce any appreciable variation in the α_a results. The result obtained by Equation (38) has a maximum variation of 1.4 per cent at 573°K with respect to the α_a calculations made by Gilder and Wallmark⁵⁰. The agreement is excellent at other temperatures. The polynomial given by Equation (38) is, at 573°K , seven per cent above the result obtained by Medoff and Cadoff⁵¹.

The coefficient of linear thermal expansion along the a -axis given by Equation (38) and obtained from the polynomial

*The calculation of the α_a values were made for a temperature interval of ten degrees.

that fits Gilder and Wallmark⁵⁰ ($\Delta l/l_0$) data was used in the determination of the coefficient of volume thermal expansion (Section C-a-3). The α_a results obtained from Equation (38) have a maximum deviation of 1.4 per cent with respect to the graphical determination of α_a made by Gilder and Wallmark⁵⁰. The expected maximum variation in the α_a values obtained from Equation (38) is 1.4 per cent. The per cent difference obtained between the results of Equation (38) and the α_a measured by Medoff and Cadoff⁵¹ was not considered in the chosen estimated error (1.4 per cent) since the latter claimed an uncertainty of five per cent in α_a .

2. Coefficient of Linear Thermal Expansion Along the c-axis. The polynomial determined by the present research to fit Gilder and Wallmark⁵⁰ ($\Delta l/l_0$) measurements along the c-axis ($\Delta l/l_0$)_c is shown in Figure 33 together with Gilder and Wallmark⁵⁰ measurements. The polynomial is given by

$$\left(\frac{\Delta l}{l_0}\right) = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5 \quad (39)$$

where

$$C_1 = -10.33 \times 10^{-3},$$

$$C_2 = -55.68 \times 10^{-6},$$

$$C_3 = + 55.93 \times 10^{-8},$$

$$C_4 = -12.99 \times 10^{-10},$$

$$C_5 = +14.98 \times 10^{-13},$$

$$C_6 = -69.23 \times 10^{-17},$$

and T = temperature in degree Kelvin.

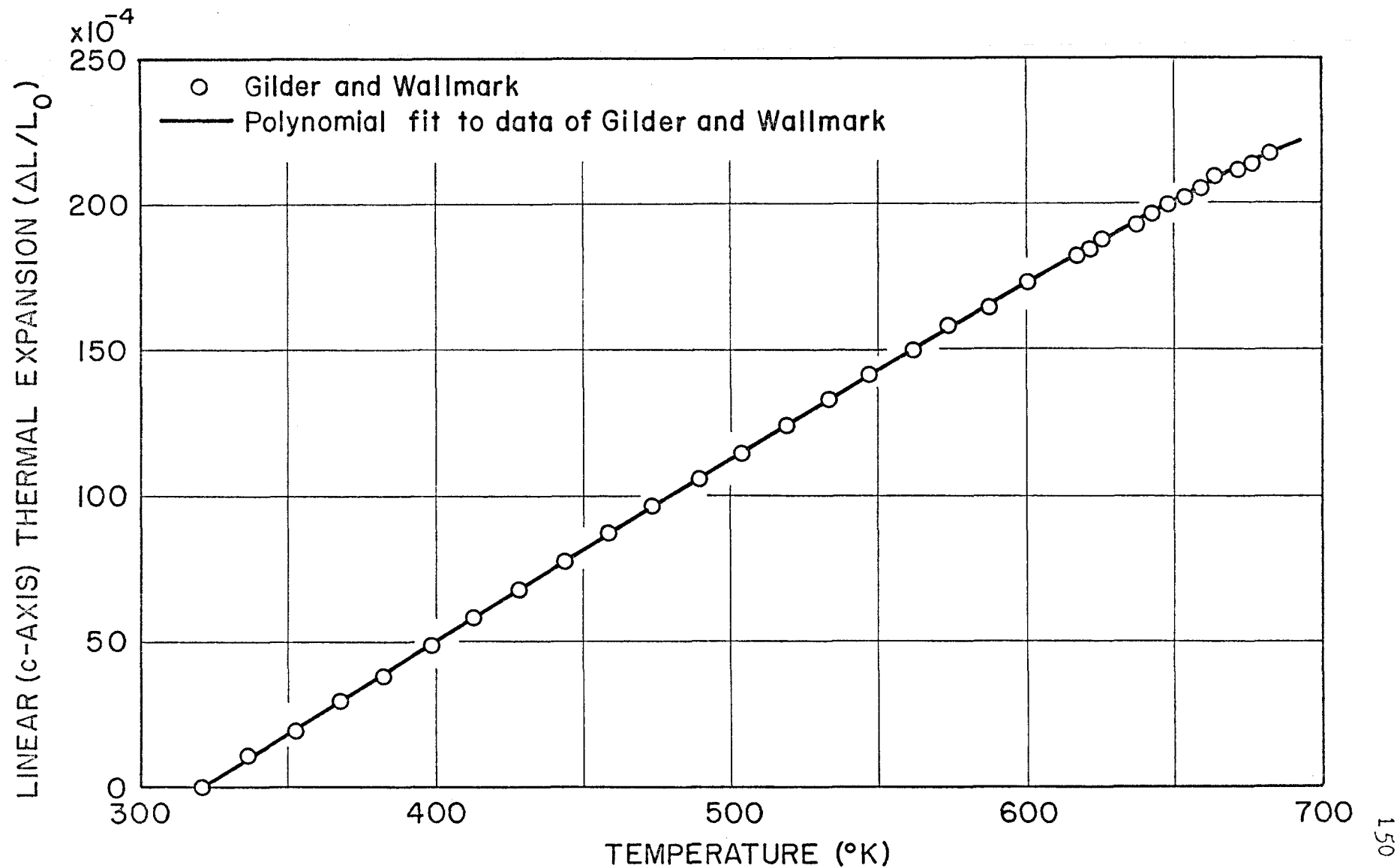


Figure 33. Linear thermal expansion for the c-axis in zinc.

The standard deviation of the $\Delta l/l_0$ data points with respect to the above polynomial is 0.4×10^{-8} which represent a deviation of 0.8×10^{-4} per cent at 400°K .

The coefficient of linear thermal expansion for the c -axis calculated by Gilder and Wallmark⁵⁰ from a graphical differentiation of their $(\Delta l/l_0)_c$ results is shown in Figure 34. The uncertainty claimed by Gilder and Wallmark⁵⁰ on the α_c results is one per cent.

Also shown in Figure 34 is the polynomial determined in this research to represent Gilder and Wallmark α_c results. The polynomial is given by

$$\alpha_c = c_1 + c_2T + c_3T^2 + c_4T^3 + c_5T^4 + c_6T^5 \quad (40)$$

where for, α_c in $^\circ\text{K}^{-1}$,

$$c_1 = +21.00 \times 10^{-3},$$

$$c_2 = -17.66 \times 10^{-5},$$

$$c_3 = +83.54 \times 10^{-8},$$

$$c_4 = -19.52 \times 10^{-10},$$

$$c_5 = +22.60 \times 10^{-13},$$

$$c_6 = -10.47 \times 10^{-15},$$

and T = temperature in degree Kelvin.

The standard deviation of the α_c data with respect to the above polynomial was 0.6×10^{-8} which produces a variation of 0.05 per cent at 300°K .

The α_c values calculated by Medoff and Cadoff⁵¹, who claimed an uncertainty of five per cent, are also shown in Figure 34. Most of their α_c results, for temperatures below

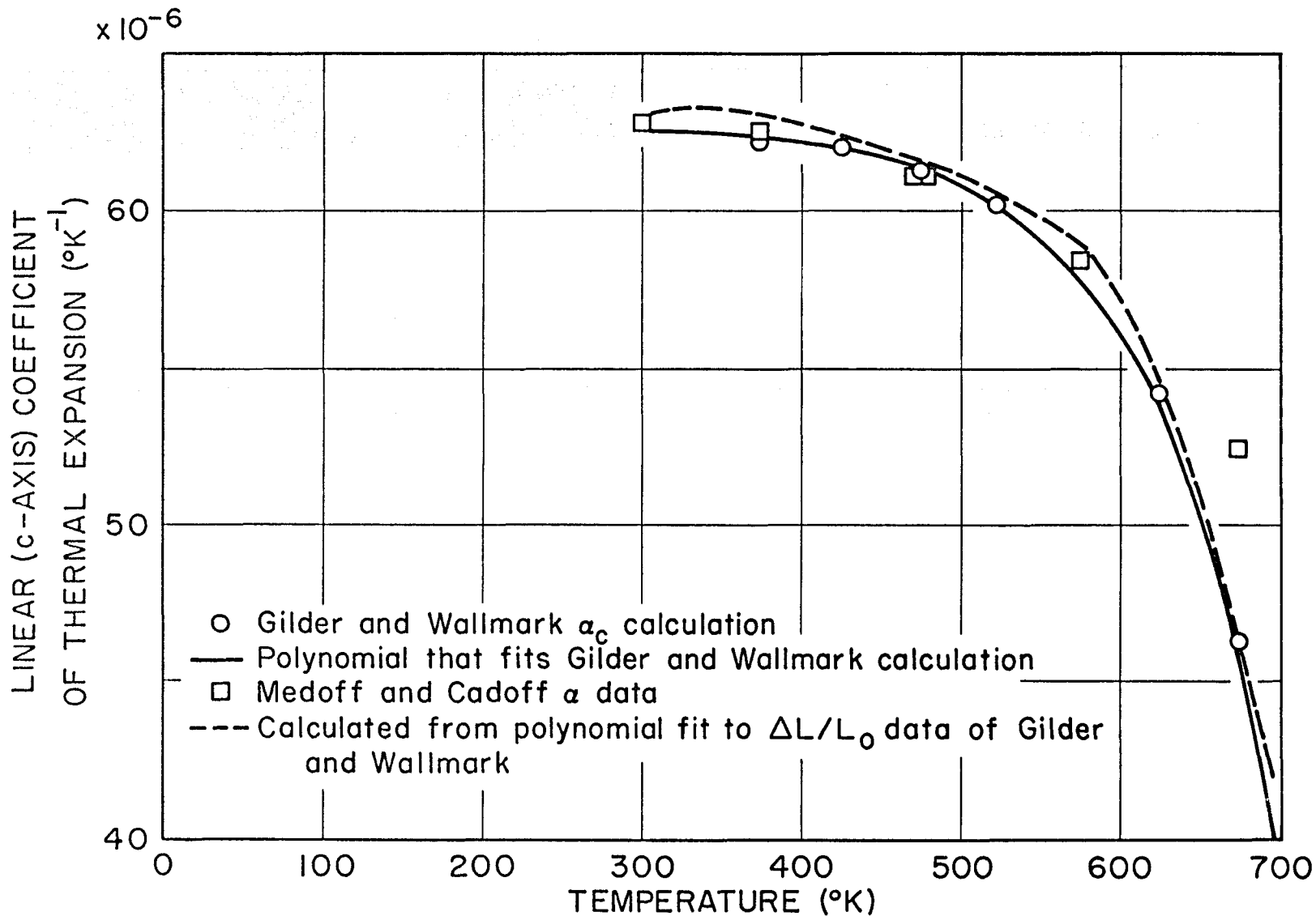


Figure 34. Coefficient of linear thermal expansion for the c-axis, zinc

600°K, are 1.4 per cent above the α_c determined by Gilder and Wallmark⁵⁰. Above 600°K the difference between both α_c results increases to around ten per cent.

The α_c calculated from the polynomial used to fit the data of Gilder and Wallmark⁵⁰ $(\Delta l/l_0)_c$ (Equation (39)), by using Equation (19), is also shown in Figure 34, where it is observed that a difference of 1.4 per cent exists with respect to the α_c graphical measurements made by Gilder and Wallmark⁵⁰, for temperatures below 680°K, and a difference of 3.4 per cent at 693°K.

Since the α_c calculated from Equation (39) by using the procedure summarized in Equation (19) was used for comparison and for future calculations, it was decided to represent the calculated α_c^* by a simpler polynomial which is given by

$$\alpha_c = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 \quad (41)$$

where for, α_c in °K⁻¹,

$$C_1 = -50.71 \times 10^{-6},$$

$$C_2 = +10.80 \times 10^{-7},$$

$$C_3 = -37.74 \times 10^{-10},$$

$$C_4 = +58.07 \times 10^{-13},$$

$$C_5 = -33.52 \times 10^{-16},$$

and T = absolute temperature in degree Kelvin.

The standard deviation of the calculated α_c by using Equa-

*The α_c calculations were made for a ten degrees temperature interval.

tion (19) and the above polynomial is 0.4×10^{-10} which at 690°K produces a variation equal to zero within three decimal places. This indicates that the use of the polynomial given by Equation (41) instead of the calculated α_c does not produce any appreciable deviation in the α_c results. The maximum deviation expected by using Equation (41) in the calculation of the coefficient of thermal expansion (Section C-a-3) is 3.4 per cent, which represent the maximum deviation of Equation (38) with respect to the graphical measurements of α_c made by Gilder and Wallmark⁵⁰. The deviation between Equation (38) and α_c results of Medoff and Cadoff was not considered in the chosen estimated error (3.4 per cent), since the latter claimed an uncertainty of five per cent in α_c .

3. Coefficient of Volume Thermal Expansion. The coefficient of volume thermal expansion was determined by substituting Equations (38) and (41) in Equation (35); the average coefficient of thermal expansion, shown in Figure 35, is equal to one third of the α_v calculated by using Equation (35).

Also shown in Figure 35 are the $\alpha_v/3$ results obtained from the α_a and α_c calculations of Gilder and Wallmark⁵⁰ and those of Medoff and Cadoff⁵¹. The difference between Gilder and Wallmark⁵⁰ α_a and α_c results (obtained by graphical differentiation) and the present research calculations (made by using the polynomial that fits Gilder and

$\times 10^{-6}$

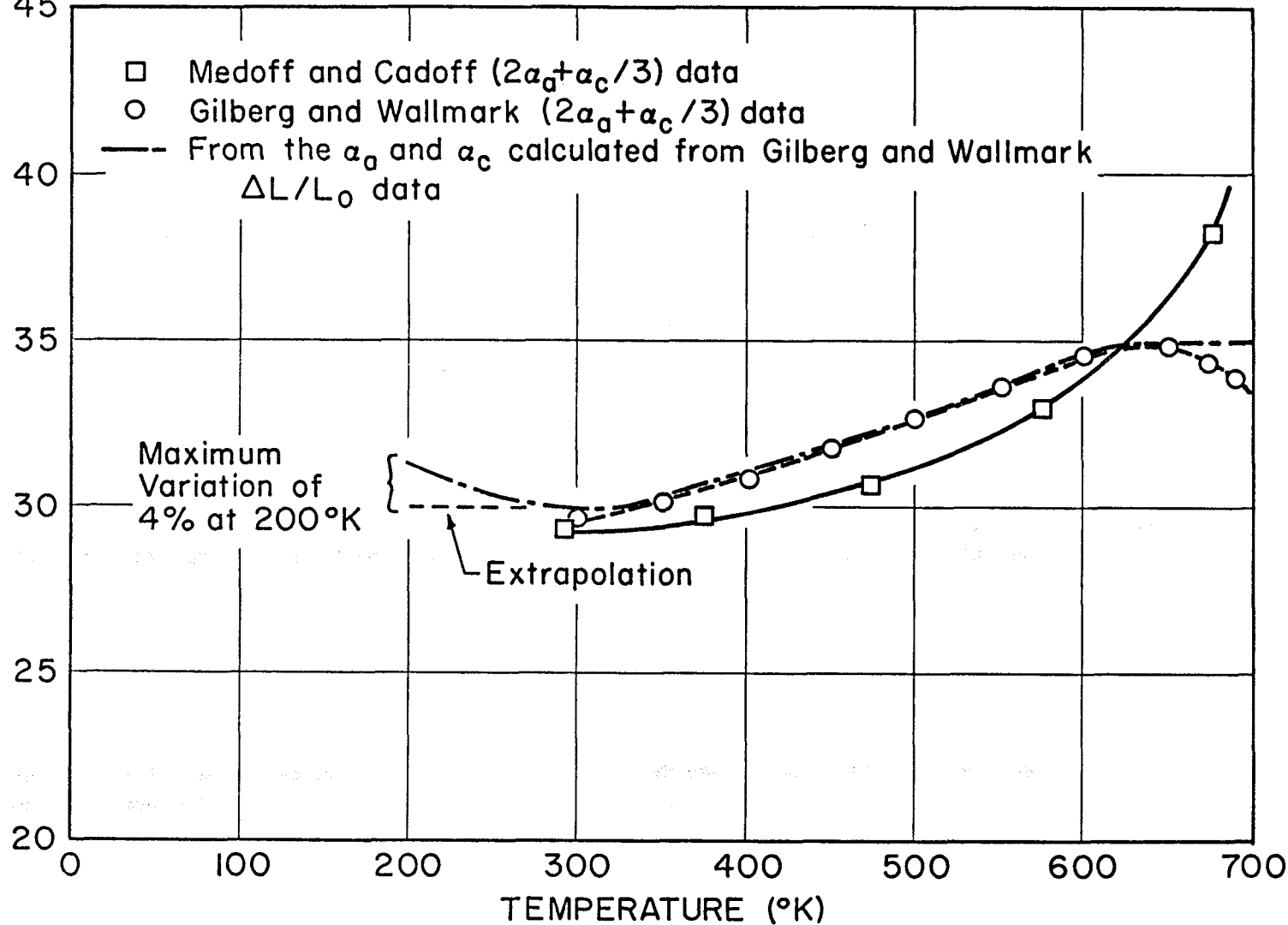


Figure 35. Average coefficient of linear thermal expansion for zinc.

Wallmark $(\Delta l/l_0)_a$ and $(\Delta l/l_0)_c$ measurements) is around one per cent for temperatures below 660°K; at the melting point the difference is around three per cent.

The results obtained from the α_a and α_c results of Medoff and Cadoff⁵¹ are five per cent below the present research calculations for temperatures below 600°K, and at the melting point, their data are around ten per cent above this research calculations.

The 1.4 and 3.4 per cent variation estimated for α_a and α_c will produce a maximum variation of two per cent in the coefficient of volume thermal expansion.

b. Molar Volume

The molar volume at 25°C was calculated from the lattice parameter data given by Pearson⁴⁰ at 25°C, and was used as a reference to calculate the molar volume as a function of temperature. The calculation was made by using the polynomials that fit Gilder and Wallmark⁵⁰ $(\Delta l/l_0)_a$ and $(\Delta l/l_0)_c$ measurements and the following equation

$$V = V_{298} \frac{(l_a)^2 l_c}{(l_a)_R^2 (l_c)_R} \quad (42)$$

where l_a and l_c are obtained by substituting the constants of Equation (36) and (39), respectively, into Equation (17); $(l_a)_R$ and $(l_c)_R$ are obtained by substituting the constants of Equations (36) and (39), respectively in Equation (17) for T equal to 298°K (25°C). The data points obtained by using

Equation (42) were represented in a simpler polynomial (shown in Figure 36) given by

$$V = C_1 + C_2T + C_3T^2 + C_4T^3 \quad (43)$$

where, for V in cubic centimeters per mole,

$$C_1 = +89.77 \times 10^{-1},$$

$$C_2 = +55.31 \times 10^{-5},$$

$$C_3 = +47.98 \times 10^{-8},$$

$$C_4 = -14.59 \times 10^{-11},$$

and T = temperature in degree Kelvin.

The standard deviation of the V calculated by using Equation (42) with respect to the above polynomial is 0.2×10^{-3} which represents a variation of 0.002 per cent at 300°K .

Figure 36 also shows a polynomial representing Owen and Yates⁵² V calculations; the maximum difference is 0.5 per cent at 500°K . The agreement between Owen and Yates⁵² results and those obtained in the present research indicates that the deviation obtained by using Equation (43) to calculate C^d should not be greater than one per cent.

c. Isothermal Compressibility

The adiabatic linear compressibility had been calculated by Alers and Neighbours⁵³ from measurements of elastic constants for temperatures between 4.2°K and 670°K . Polynomials were calculated in order to represent the results of Alers and Neighbours⁵³ along the a and c axis.

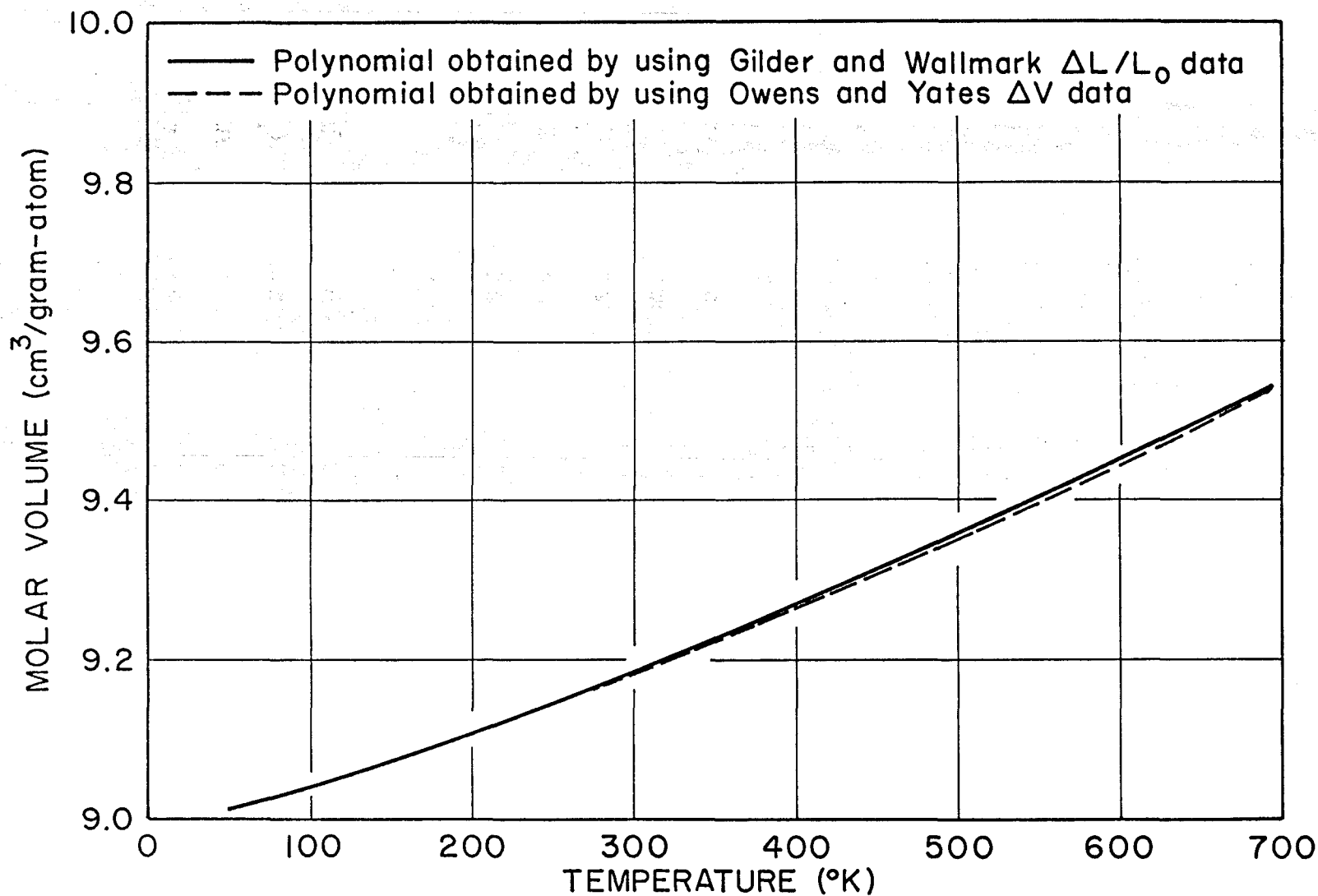


Figure 36. Molar volume for zinc.

1. Adiabatic Linear Compressibility Along the a-axis

$(\beta_A)_a$. The polynomial calculated to represent Alers and Neighbours⁵³ $(\beta_A)_a$ data is

$$(\beta_A)_a = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4 + C_6T^5 \quad (44)$$

where, for $(\beta_A)_a$ in square centimeters per degree Kelvin,

$$C_1 = +15.33 \times 10^{-14},$$

$$C_2 = -27.30 \times 10^{-18},$$

$$C_3 = -81.68 \times 10^{-20},$$

$$C_4 = +50.95 \times 10^{-22},$$

$$C_5 = -90.35 \times 10^{-25},$$

$$C_6 = +48.31 \times 10^{-28},$$

and T = temperature in degree Kelvin.

Figure 37 shows Alers and Neighbours⁵³ data and the above polynomial used to represent their data. The standard deviation of the data obtained by Alers and Neighbours⁵³ with respect to the polynomial given by Equation (44) is 0.6×10^{-15} which, at 300°K , gives a variation of 0.4 per cent.

It is expected that the use of Equation (44) to give the $(\beta_A)_a$, results in a maximum variation of one per cent. This value is used in a subsequent calculation of the uncertainty in the adiabatic volume compressibility.

2. Adiabatic Linear Compressibility Along the c-axis

$(\beta_A)_c$. The polynomial calculated to represent Alers and Neighbours⁵³ $(\beta_A)_a$ data is shown in Figure 38 together with

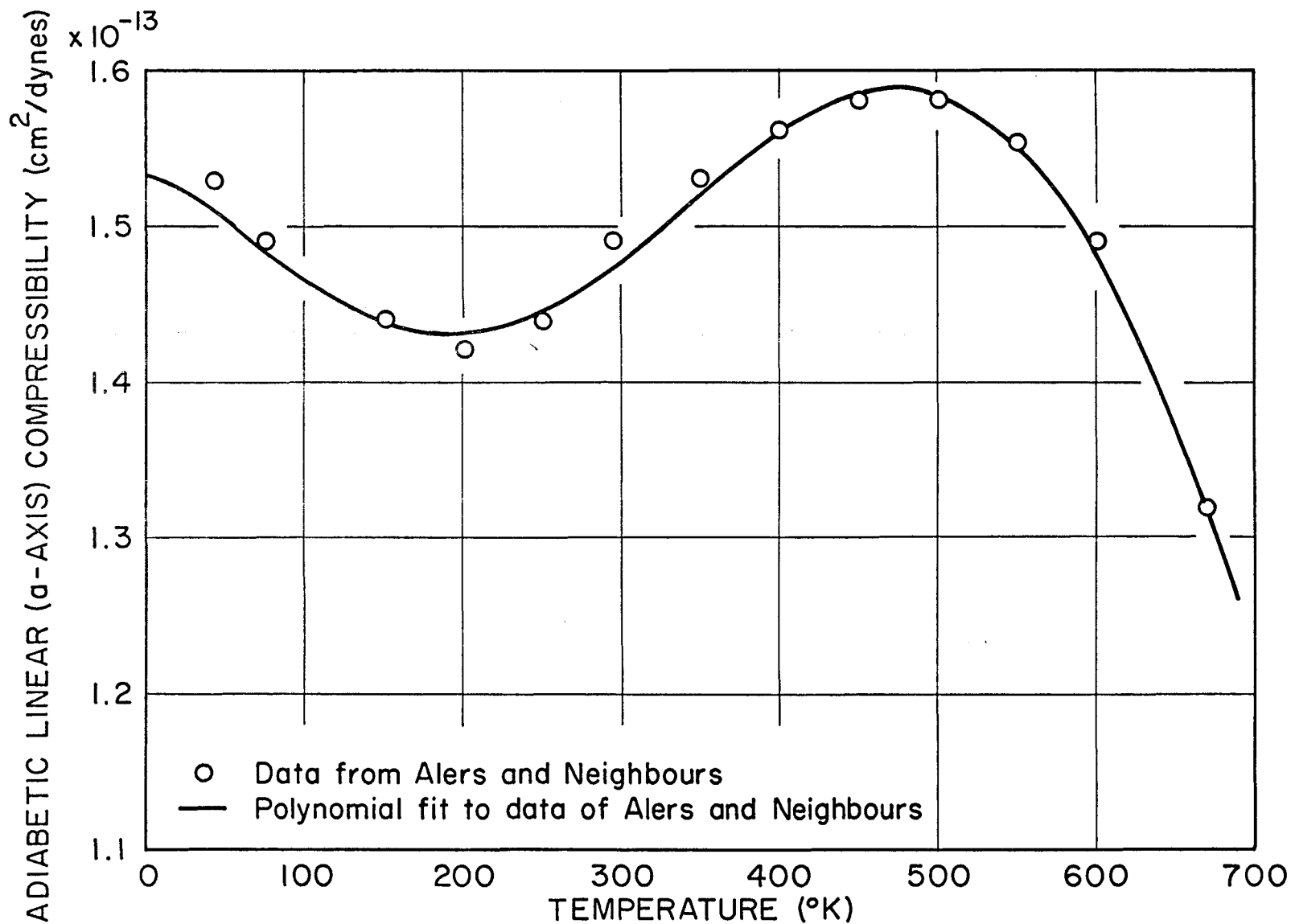


Figure 37. Adiabatic linear compressibility along the a-axis for zinc.

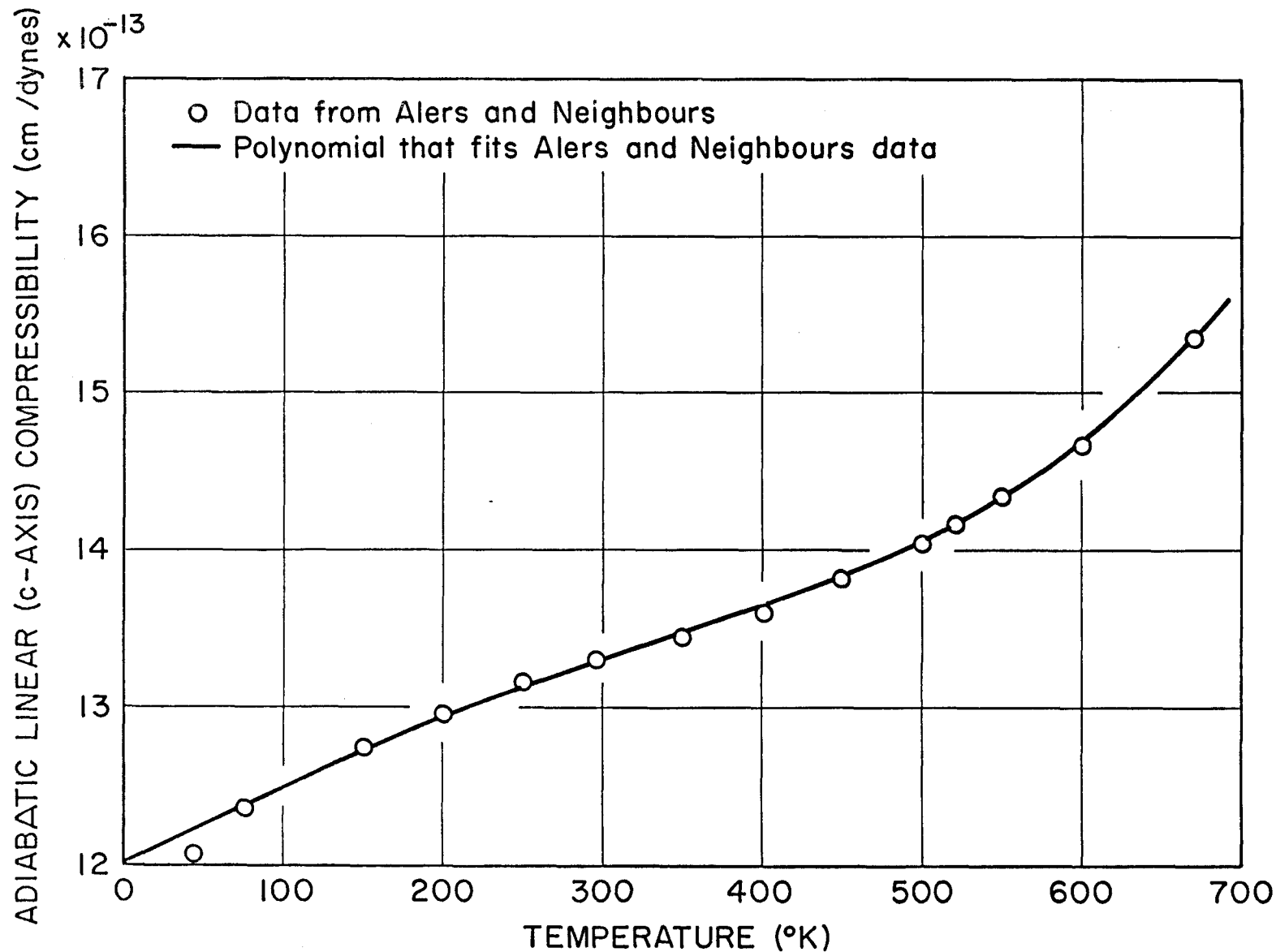


Figure 38. Adiabatic linear compressibility along the c-axis for zinc.

their data. The polynomial is

$$(\beta_A)_c = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4 \quad (45)$$

where, for $(\beta_A)_c$ in square centimeters for dyne,

$$C_1 = +12.03 \times 10^{-13},$$

$$C_2 = +45.03 \times 10^{-17},$$

$$C_3 = +25.73 \times 10^{-20},$$

$$C_4 = -19.94 \times 10^{-22},$$

$$C_5 = +25.33 \times 10^{-25},$$

and T = temperature in degree Kelvin.

The standard deviation of the data obtained by Alers and Neighbours⁵³ $(\beta_A)_c$ with respect to the above polynomial is 0.2×10^{-14} which, at 300°K , would produce a variation of 0.1 per cent.

It is expected that the use of Equation (45) to give the $(\beta_A)_c$, results in a maximum variation of one per cent. This calculation is used in a subsequent calculation of the uncertainty in the adiabatic compressibility.

3. Adiabatic Volume Compressibility. β_A . The adiabatic compressibility is given by

$$\beta_A = 2(\beta_A)_a + (\beta_A)_c^* \quad (46)$$

where $(\beta_A)_a$ and $(\beta_A)_c$ are the results obtained by using Equations (44) and (45), respectively. Figure 39 shows the β_A results.

*The derivation of this equation is similar to that of Equation (35).

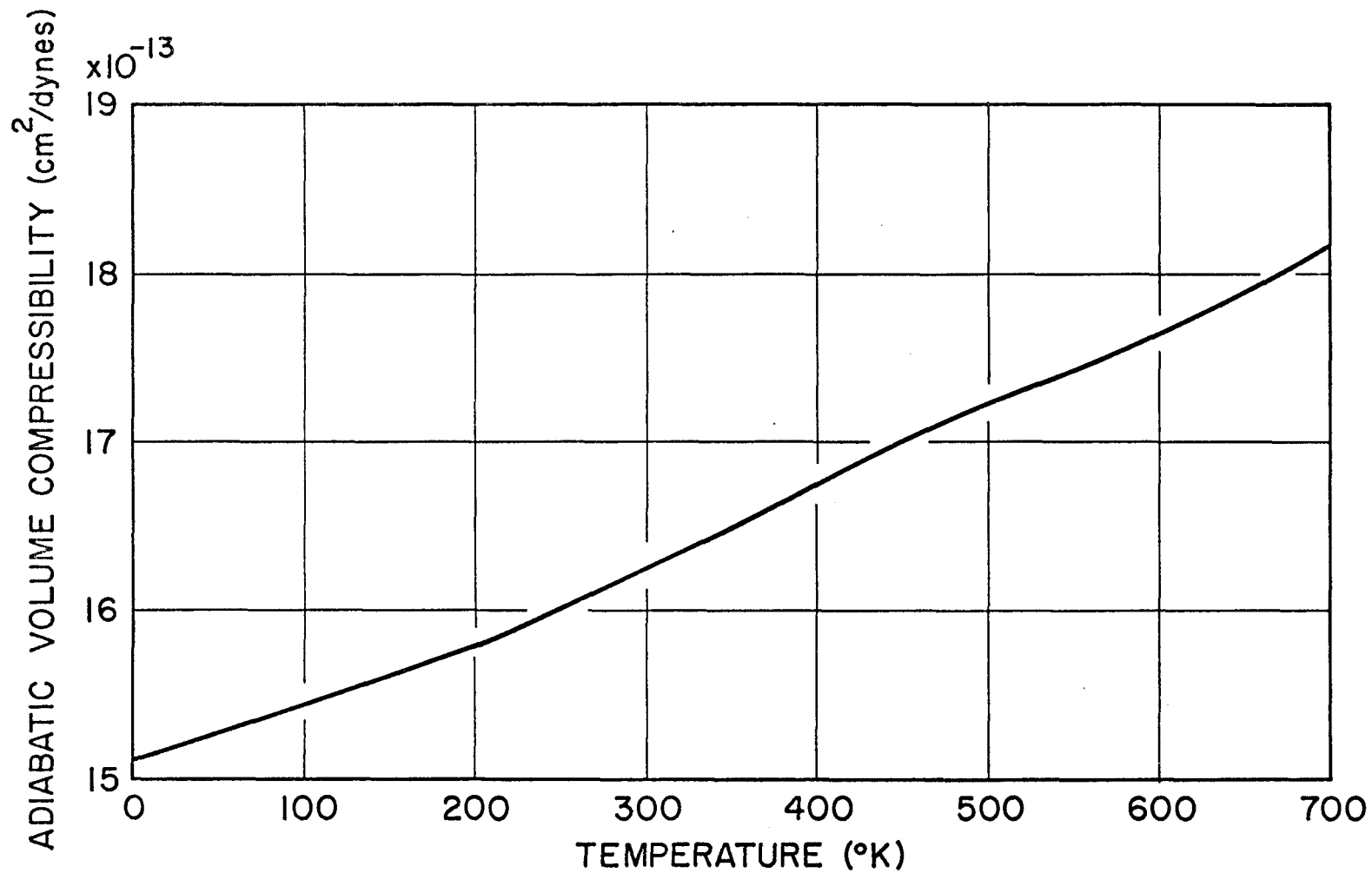


Figure 39. Adiabatic volume compressibility for zinc.

The estimated one per cent variation in $(\beta_A)_a$ and $(\beta_A)_c$ will produce a variation of one per cent in the β_A results.

4. Isothermal Volume Compressibility. The isothermal volume compressibility β_V for zinc was calculated at low temperature ($200^\circ \leq T \leq 300^\circ \text{K}$) by using Equation (7) and the low temperature C_p data of Schimpft⁵⁴. A polynomial was calculated to represent these β_V data and it is

$$\beta_V = C_1 + C_2T + C_3T^2, \quad 200^\circ \leq T \leq 300^\circ \text{K} \quad (47)$$

where, for β_V in square centimeters per degree,

$$C_1 = +15.90 \times 10^{-13},$$

$$C_2 = +54.84 \times 10^{-18},$$

$$C_3 = +11.79 \times 10^{-19},$$

and T = temperature in degree Kelvin.

The standard deviation of the data calculated by using Equation (47) with respect to the above polynomial is 0.8×10^{-18} which produces a variation of 0.5×10^{-4} per cent at 300°K .

The high temperature ($300^\circ \leq T \leq 693^\circ \text{K}$) isothermal volume compressibility β_V was calculated by using Equation (7) in the present chapter and the polynomial used to represent the C_p data of the present research (Chapter III). The result was then used to obtain a polynomial to represent the high temperature β_V as a function of temperature. This polynomial is given by

$$\beta_V = C_1 + C_2T + C_3T^2 + C_4T^3, \quad 300^\circ \leq T \leq 693^\circ \text{K} \quad (48)$$

where, for β_v in cubic centimeters per degree,

$$C_1 = +15.41 \times 10^{-13},$$

$$C_2 = +24.64 \times 10^{-17},$$

$$C_3 = +13.67 \times 10^{-19},$$

$$C_4 = -96.47 \times 10^{-23},$$

and T = temperature in degree Kelvin.

The standard deviation of the β_v data obtained from Equation (47) with respect to the above polynomial is 0.9×10^{-15} , which at 300°K would give a variation of 0.05 per cent. This variation decreases with increasing temperature. The low and high temperature β_v results are shown in Figure 40. At 320°K a difference of 0.2 per cent exists between the β_v calculated from the low temperature polynomial and the β_v calculated from the high temperature polynomial.

The estimated one per cent variation in β_A , v , a_v and C_p will produce a maximum uncertainty of two per cent in β_v at 690°K .

d. The Specific Heat Capacity at Constant Volume

The calculation of the dilation term C^d at low temperature ($200^\circ \leq T \leq 300^\circ\text{K}$) was made by using Equations (2), (35)*, (43) and (47); the C^d at high temperature ($300^\circ \leq T \leq 693^\circ\text{K}$) was obtained by using Equation (2), (35)*, (43) and (48).

The specific heat capacity at constant volume was ob-

* a_a and a_c in Equation (35) are substituted by Equation (38) and (41), respectively.

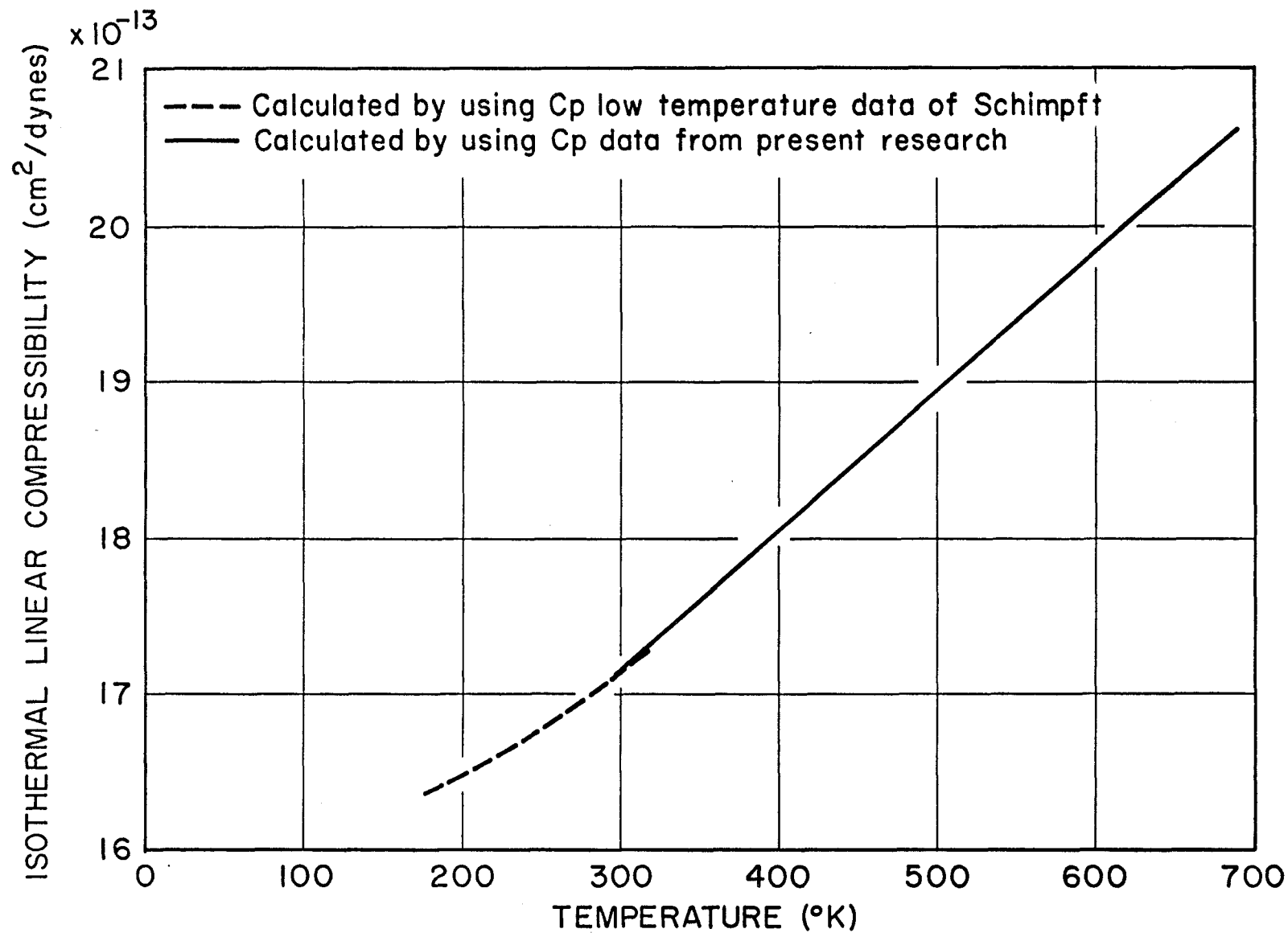


Figure 40. Isothermal volume compressibility for zinc.

tained for the low temperature region ($200^{\circ} \leq T \leq 300^{\circ} \text{K}$) by using Equation (1) in the present chapter, the C_p values obtained by Schimpft⁵⁴ and the C^d values obtained for $200 \leq T \leq 300^{\circ} \text{K}$. The high temperature C_v ($300^{\circ} \text{K} \leq T \leq 693^{\circ} \text{K}$) was obtained by using Equation (1), the polynomial representing the C_p data obtained in the present research and the C^d values obtained for $300^{\circ} \leq T \leq 693^{\circ} \text{K}$.

The results in the low and high temperature ranges are given in Table VI, and are shown in Figure 41. At 320°K the low temperature C_v results obtained from the Schimpft⁵⁴ C_p data are one per cent higher than the value calculated from the C_p determined in the present research.

e. Probable Variations in C_v Due to Errors in the Chosen α_v , β_v , V and C_p

Due to the different uncertainties in the different terms involved in the calculation of the dilation term, an analysis was made on the effect of this uncertainties in the calculated C^d and the final C_v .

The analysis made on α_v , V and β_v (Section C-a, C-b and C-c) indicated

- 1) that the variation in α_v due to a variation of 1.4 and 3.4 per cent in α_a and α_c was two per cent,
- 2) that a variation no greater than one per cent is expected in the molar volume, and
- 3) that the maximum variation in β_v due to a one per cent variation in C_p , V and β_A and a two per cent

TABLE VI

SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME: ZINC

Low Temperature Data		High Temperature Data	
Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)	Temperature (degree Kelvin)	C_v (Joules/gram- atom/degree Kelvin)
200	22.1980	320	23.8248
210	22.4747	330	23.9350
220	22.7301	340	24.0614
230	22.9645	350	24.1911
240	23.1779	360	24.3157
250	23.3705	370	24.4299
260	23.5425	380	24.5310
270	23.6939	390	24.6178
280	23.8250	400	24.6902
290	23.9357	410	24.7491
300	24.0264	420	24.7957
310	24.0971	430	24.8317
		440	24.8591
		450	24.8798
		460	24.8958
		470	24.9091
		480	24.9217
		490	24.9354
		500	24.9520
		510	24.9730
		520	25.0001
		530	25.0346
		540	25.0778
		550	25.1309
		560	25.1950
		570	25.2710
		580	25.3600
		590	25.4626
		600	25.5796
		610	25.7116
		620	25.8593
		630	26.0230
		640	26.2032
		650	26.4004
		660	26.6148
		670	26.8466
		680	27.0962
		690	27.3637

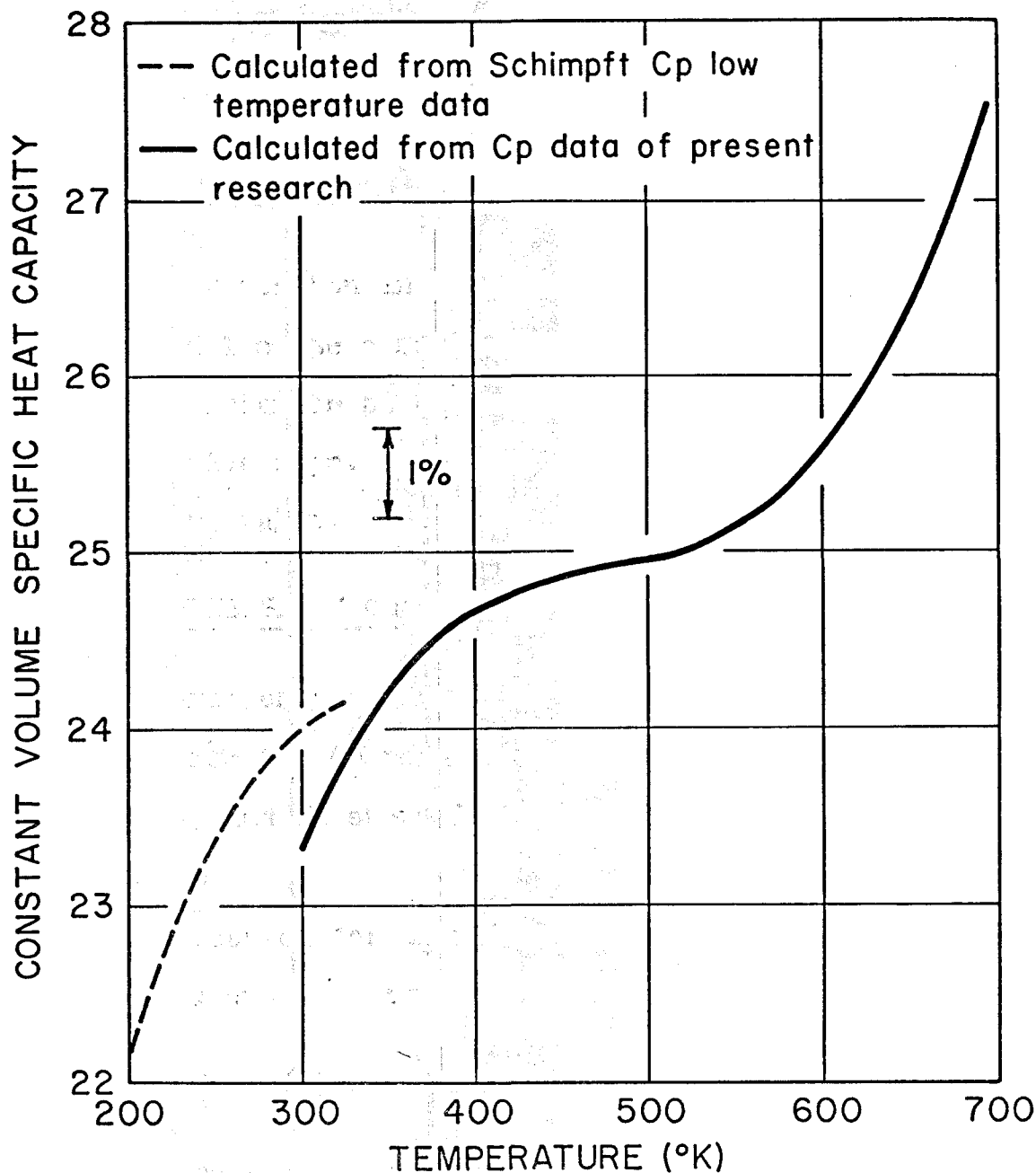


Figure 41. The specific heat capacity at constant volume for zinc.

variation in α_v was two per cent.

The above uncertainties, applied in Equation (9) at 690°K , indicated that the maximum variation in the dilation term is 0.25 Joules per gram-atom per degree Kelvin (7.3 per cent) which finally would give an error of 0.9 per cent in the calculated C_v .

A ± 1.0 variation in C_p plus the ± 7.3 per cent variation in C^d will cause a maximum variation of ± 2.0 per cent in C_v . The variation of C_p and C^d , both with the same positive or negative sign, will give a variation of ± 0.9 per cent in the C_v value.

D. GRUNEISEN'S CONSTANT Γ : EFFECT ON C_v

The Gruneisen's constant for gold, lead and zinc was calculated from the C_v results obtained in parts A, B, and C respectively, and is shown in Figure 42 as a function of temperature.

The expression for C_v using Gruneisen's constant, from Equations (1) and (3), is

$$C_v = \frac{C_p}{1 + \frac{\Gamma \alpha_v T}{C_p}} \quad (49)$$

The terms used to calculate Γ are all available at 300°K , so by assuming Γ to be constant, the C_v as a function of temperature can be calculated. As is observed in Figure 42, Γ changes considerably with temperature, so by assuming it to be constant, an error is made in the approximation.

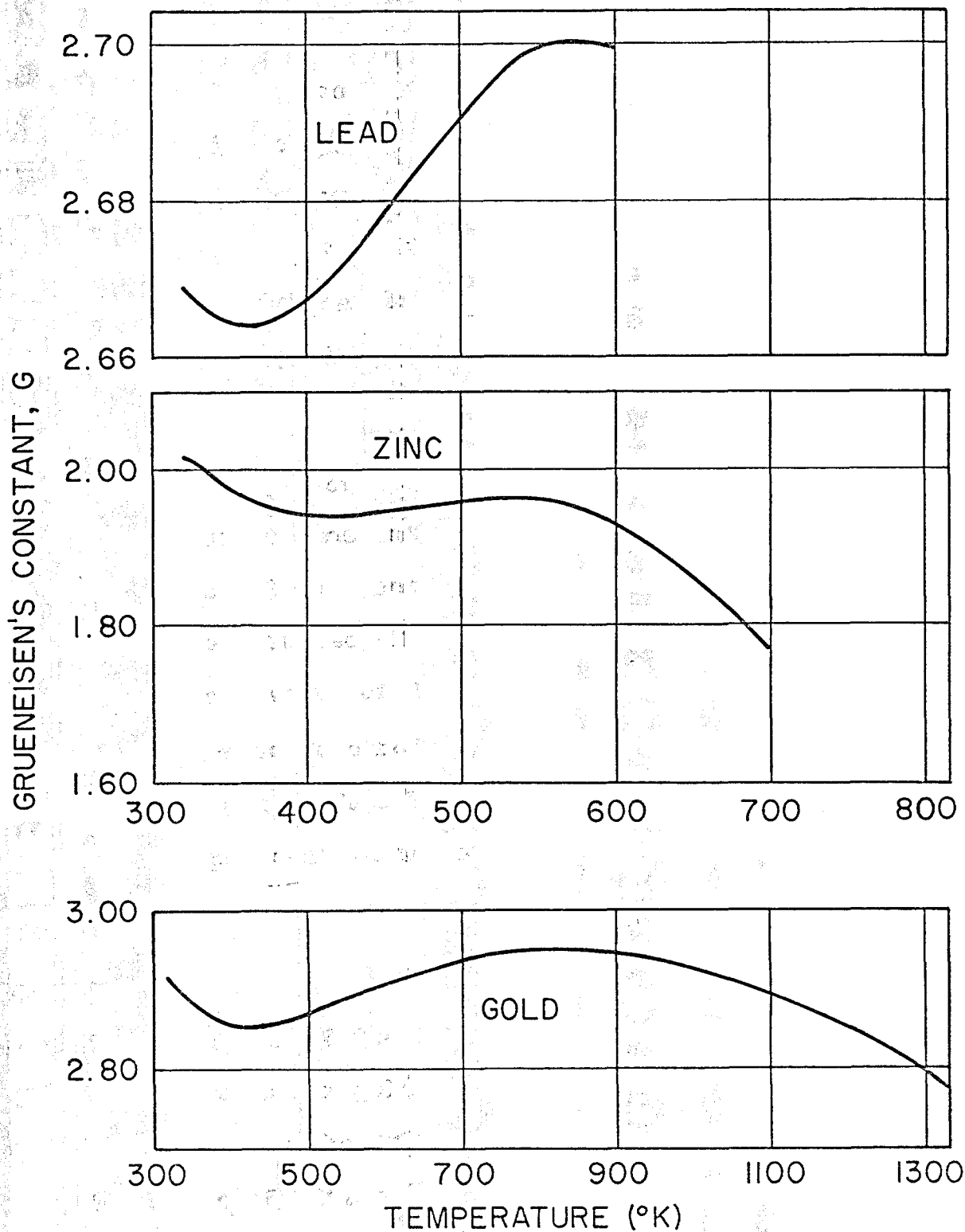


Figure 42. The Gruneisen's constant as a function of Temperature for gold, lead and zinc.

a. Gold

The use of the Gruneisen's constant at 300°K to calculate C_v at 1330°K gives a value of 26.60 Joules per gram-atom per degree, which compared to the value 26.96 Joules per gram-atom per degree in Table IV (Page 121) gives an error of around 1.3 per cent in the specific heat capacity at constant volume. Note that between 320°K and 1330°K ., Gruneisen's constant, varies by five per cent.

b. Lead

For lead, it is observed that a smaller variation exists in the Gruneisen's constant with temperature than for gold. At 600°K Γ is 1.1 per cent lower than the value of 300°K . The use of the Gruneisen's constant at 300°K to calculate C_v at 600°K gives a value of 25.43^* Joules per gram-atom per degree, which when compared to the value 25.30 Joules per gram-atom per degree from Table V (Page 140), gives an error of 0.5 per cent in the specific heat capacity at constant volume.

c. Zinc

The variation of the Gruneisen's constant for zinc is even greater than for gold or lead. At 693°K Γ is 12.0 per cent less than the value at 320°K .

The use of Equation (49) to determine the specific heat

*The calculation was made by using Equation (49).

capacity at constant volume at 690°K by using the Γ value at 320°K gives a result of 27.35 Joules per gram-atom per degree, which when compared to the value 27.36 Joules per gram-atom per degree from Table VI (Page 168), gives an error of 1.1 per cent in the specific heat Capacity C_v .

E. THE EFFECT OF THE USE OF THE NERNST-LINDEMANN

APPROXIMATION ON C_v

Another approximation which could have been used to calculate C_v is the Nernst-Lindemann approximation given by Equation (6). The use of this constant A would have been possible since data of α_v , $V C_p$ and β_v exist around 300°K to allow its calculation.

Figure 43 shows the variation of the constant A as a function of temperature, as calculated from the C_v obtained in part A, B and C for gold, lead and zinc, respectively.

a. Gold

For gold the use of the Nernst-Lindemann approximation to calculate C_v at high temperature would have caused a high value of C_v due to the sharp increase in A around 320°K. A maximum variation of 17 per cent exists in the A value given by Equation (6) (Figure 43).

If the A value at 320°K were used to calculate C_v at 1330°K, the error in C_v would be around two per cent. This approximation is obviously better for gold than the use of the Gruneisen's constant.

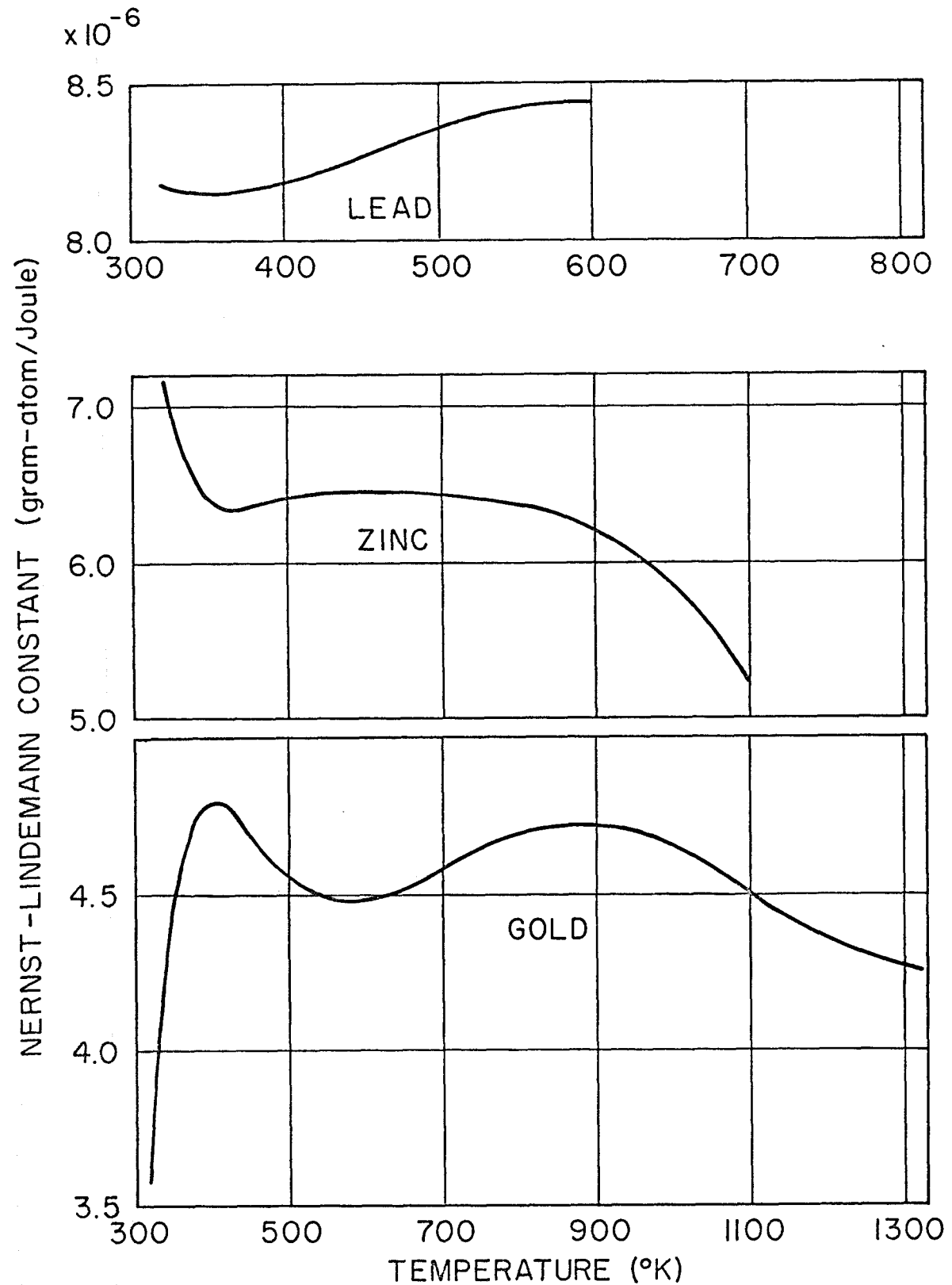


Figure 43. The Nernst-Lindemann constant as a function of temperature, for gold, lead and zinc.

b. Lead

For lead, the maximum variation of the A value given by Equation (6) is four per cent (Figure 43). The use of A at 320°K to calculate C_v at 600°K produces an error of around one per cent in the specific heat capacity at constant volume. This approximation works reasonably well for lead, as it did for gold.

c. Zinc

A variation of 28.0 per cent exists in A for zinc (Figure 43). The calculation of the specific heat capacity at constant volume by using the A value at 320°K produces an error of four per cent in C_v at 690°K .

THEORETICAL CONTRIBUTIONS TO THE SPECIFIC HEAT CAPACITY
AT CONSTANT VOLUME: RESULTS AND CONCLUSIONS

For gold, lead and zinc the different theoretical contributions to the specific heat capacity (discussed in detail in Chapter I) were determined after the necessary parameters (Debye temperature Θ_D , electronic heat capacity constant γ , formation energies of monovacancies and divacancies, Δh_{1v} and Δh_{2v} respectively, and the entropy change due to the formation of monovacancies and divacancies, ΔS_{1v} and ΔS_{2v} , respectively) were obtained from the literature. The analysis was made assuming all contributions to C_v lattice, electronic, formation of imperfections (monovacancies and divacancies) to be independent from each other. Then the anharmonic contribution was obtained by subtracting the theoretical contributions from the experimental C_v , which was calculated from the experimental C_p .

The formula that relates $(C_v)_{\text{experimental}}$ to all the different contributions is

$$(C_v)_{\text{experimental}} = (C_L)_v + (C_E)_v + (C_{1v})_v + (C_{2v})_v + (C_{\text{anharmonic}})_v \quad (1)$$

or

$$(C_{\text{anharmonic}})_v = (C_v)_{\text{experimental}} - (C_L)_v - (C_E)_v - (C_{1v})_v - (C_{2v})_v \quad (2)$$

The lattice contribution is

$$(C_L)_v = 3Nk \left[3 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{e^x x^4 dx}{(e^x - 1)^2} \right]^* \quad (3)$$

where N = Avogadro's number,

k = Boltzman's constant,

and T = temperature in degree Kelvin

The electronic contribution is

$$(C_E)_v = \gamma T \left[1 - \frac{3\pi^2}{10} \left(\frac{kT}{\zeta_0} \right)^2 \right] \quad (4)$$

where

$$\gamma = \frac{1}{2} \pi^2 R^k \frac{\zeta_0}{\zeta_0} Z,$$

ζ_0 = Fermi Energy,

and Z = number of free electrons per atom.

The contribution due to the formation of monovacancies is

$$(C_{1v})_v = (N e^{\Delta S_{1v}/k}) \left(\frac{\Delta h_{1v}^2}{kT^2} \right) e^{-\Delta h_{1v}/kT} \quad (5)$$

and the contribution due to the formation of divacancies is

$$(C_{2v})_v = (N \frac{Z}{2} e^{\Delta S_{ev}/k}) \left(\frac{\Delta h_{2v}^2}{kT^2} \right) e^{-\Delta h_{2v}/kT}, \quad (6)$$

*The computer program that was used⁷³ to calculate the integral is able to perform numerical integration of any analytic function by sixteen point Gaussian quadrature. The integrals are broken into two regions and the limits of integration for a desired integral are given as two arguments of a subroutine call statement.

where

$$\Delta h_{2v} = 2\Delta h_{1v} - B,$$

B = binding energy for two vacancies,

z = coordination number

and T = temperature in degree Kelvin.

At relatively low temperature ($T < 400^\circ\text{K}$) $(C_{1v})_v$ and $(C_{2v})_v$ are negligible. Further, in the present treatment $(C_{\text{anharmonic}})_v$ is assumed to be very small at low temperature. Then, for these temperatures, Equation (2) becomes

$$C_v)_{\text{experimental}} = (C_L)_v + (C_E)_v \quad (7)$$

Due to the wide range of values given in the literature for θ_D and γ^* , these parameters were chosen to give values for $[(C_L)_v + (C_E)_v]$ that were the closest to the experimental C_v obtained in this research, for temperatures close to 300°K . For all three metals studied during this investigation, around 300°K the sum of the lattice and electronic contributions to the specific heat capacity was closest to the experimental C_v when the θ_D value used was the highest and the γ value used was the lowest. An examination was then made of the effect of the variation of θ_D and γ on the total theoretical lattice and electronic contributions to C_v , and on the difference ΔC_v obtained between the theoretical specific heat capacity at constant volume and the $(C_v)_{\text{experimental}}$. The effect of the variation in θ_D and

* The γ is determined experimentally at low temperatures and the present treatment assumes that no appreciable varia-

on γC_v was examined at two or three different temperatures.

It is emphasized that the variation of θ_D is due to the different temperatures at which its determination has been made (its variation being especially large for temperatures around 0°K), and to the method employed for its determination. It will be shown, for gold, lead and zinc, that above 300°K the variation in θ_D and γ does not affect appreciably the lattice plus electronic contributions to C_v . Analyses of the variation of θ_D with temperature and method employed for its determination have been made by Gschneidner⁵⁶, Herbstein⁵⁷ and Kelly and MacDonald⁵⁸.

In the present treatment the θ_D and γ values were obtained from a compilation of data and analysis made by Gschneidner⁵⁶.

The contribution to C_v due to the formation of monovacancies was determined by using one of the Δh_{1v} and ΔS_{1v} values given in the literature for a given metal; the effect on C_v due to a variation in these Δh_{1v} and ΔS_{1v} values was then analyzed. The contribution to C_v due to the formation of divacancies was obtained by assuming the binding energy B for two vacancies to be within the limit $\Delta h_{1v}/6$ and $E_c/6^*$, as explained by Bartlett and Dienes⁵⁵. The rea-

tion exists when this experimental γ result is assumed to be constant, independent of volume changes produced by increasing temperature.

* E_c is the lattice cohesive energy.

son for this choice of B will be explained during the analysis of the $(C_{2v})_v$ contribution for gold.

A. RESULTS

a. Gold

1. Lattice and Electronic Contributions to C_v . θ_D
 values for gold have been obtained by specific heat capacity, elastic constants, electrical resistivity and thermal expansion measurements⁵⁶; the values range from 156°K (calculated from elastic constants measurements at 298°K) to 203°K (calculated from electrical resistivity measurements at 100°K). The relatively closest $(C_L)_v$ value to the experimental C_v results were obtained with a θ_D equal to 203°K; the theoretical $(C_L)_v$ result being at 320°K 0.3 Joules per gram-atom per degree Kelvin above the present research $(C_v)_{\text{experimental}}$. Any other θ_D smaller than 203°K will increase that difference. The use of a θ_D value equal to 156°K produces a $(C_L)_v$ result that, when compared to those obtained with θ_D equal to 203°K, is higher by 0.23 Joules per gram-atom per degree Kelvin at 300°K (0.94 per cent), 0.13 at 400°K (0.53 per cent), 0.08 at 500°K (0.32 per cent), and 0.01 at 1330°K (0.04 per cent). The $(C_L)_v$ results with θ_D equal to 203°K are listed in Table VII. The difference between $(C_v)_{\text{experimental}}$ and $(C_L)_v$ is increased when the electronic contributions $(C_E)_v$ is added to

TABLE VII

LATTICE AND ELECTRONIC CONTRIBUTIONS TO THE SPECIFIC HEAT
CAPACITY AT CONSTANT VOLUME: GOLD

Temperature (Degree Kelvin)	$(C_L)_v$ *	$(C_E)_v$ **	$(C_L)_v + (C_E)_v$
200	23.7014	0.1470	23.8484
220	23.9100	0.1617	24.0717
240	24.0704	0.1764	24.2468
260	24.1963	0.1911	24.3874
280	24.2969	0.2058	24.5027
300	24.3785	0.2205	24.5990
320	24.4455	0.2352	24.6807
340	24.5013	0.2499	24.7512
360	24.5482	0.2646	24.8128
380	24.5880	0.2793	24.8673
400	24.6220	0.2940	24.9160
420	24.6514	0.3087	24.9601
440	24.6768	0.3234	25.0002
460	24.6991	0.3381	25.0372
480	24.7186	0.3528	25.0714
500	24.7359	0.3675	25.1034
520	24.7512	0.3822	25.1334
540	24.7649	0.3969	25.1618
560	24.7772	0.4116	25.1888
580	24.7882	0.4263	25.2145
600	24.7981	0.4410	25.2391
620	24.8071	0.4557	25.2628
640	24.8153	0.4704	25.2857
660	24.8227	0.4801	25.3078
680	24.8295	0.4998	25.3293
700	24.8357	0.5145	25.3502
720	24.8414	0.5292	25.3706
740	24.8467	0.5439	25.3906
760	24.8515	0.5586	25.4101
780	24.8560	0.5733	25.4293
800	24.8602	0.5880	25.4482
820	24.8640	0.6027	25.4667
840	24.8676	0.6174	25.4850
860	24.8709	0.6323	25.5030
880	24.8740	0.6468	25.5208
900	24.8769	0.6615	25.5384
920	24.8797	0.6762	25.5559
940	24.8822	0.6909	25.5731

TABLE VII (continued)

Temperature (Degree Kelvin)	$(C_L)_v^*$	$(C_E)_v^{**}$	$(C_L)_v + (C_E)_v$
960	24.8846	0.7056	25.5902
980	24.8868	0.7203	25.6071
1000	24.8890	0.7350	25.6240
1020	24.8910	0.7497	25.6406
1040	24.8928	0.7644	25.6572
1060	24.8946	0.7791	25.6737
1080	24.8963	0.7938	25.6901
1100	24.8978	0.8085	25.7063
1120	24.8993	0.8232	25.7225
1140	24.9008	0.8379	25.7387
1160	24.9021	0.8526	25.7547
1180	24.9034	0.8673	25.7707
1200	24.9046	0.8820	25.7866
1220	24.9058	0.8967	25.8025
1240	24.9069	0.9114	25.8183
1260	24.9079	0.9261	25.8340
1280	24.9089	0.9408	25.8497
1300	24.9099	0.9555	25.8654
1320	24.9108	0.9702	25.8810
1330	24.9113	0.9776	25.8888

*The calculation of $(C_L)_v$ was made with Θ_D equal to 203°K. $(C_L)_v$ is given in Joules per gram-atom per degree Kelvin.

**The calculation of $(C_E)_v$ was made with γ equal to 0.735×10^{-3} Joules per gram atom per degree Kelvin squared. $(C_E)_v$ is given in Joules per gram-atom per degree Kelvin.

$(C_L)_v$ in order to obtain the total theoretical specific heat capacity at constant volume (see next paragraph).

The γ values obtained from Gschneidner⁵⁶ range from 0.735×10^{-3} to 0.761×10^{-3} Joules per gram-atom per degree Kelvin squared. The lowest value, 0.735×10^{-3} , was chosen in this research since, as observed above, the electronic contribution will increase the difference between the theoretical and experimental C_v in the temperature range (temperature close to 300°K) where the theoretical and experimental values should be very close to each other. The $(C_E)_v$ results obtained with γ equal to 0.735×10^{-3} Joules per gram-atom per degree Kelvin squared are shown in Table VII together with the $(C_L)_v$ and $[(C_L)_v + (C_E)_v]$ results.

The difference between the $[(C_L)_v + (C_E)_v]$ results obtained when the γ value is changed from 0.735×10^{-3} (Table VII) to 0.761×10^{-3} Joules per gram-atom per degree Kelvin squared (θ_D remaining equal to 203°K) is 0.03 Joules per gram atom per degree Kelvin (0.11 per cent) at 1330°K . The difference in the $[(C_L)_v + (C_E)_v]$ results obtained with the two different γ values decreases with decrease in temperature.

The calculation of $(C_E)_v$ was made by neglecting the least term in Equation (4)* since, by assuming the effective valence to be one, this last term becomes, at 1330°K , 0.13

$$\frac{*3\pi^2}{10} \quad \frac{kT^2}{\zeta_0}$$

per cent of the $(C_E)_V$ term $\left(0.005 \text{ per cent of } [(C_E)_V + (C_L)_V] \right)$.

Figure 44 shows the comparison of the $(C_V)_{\text{experimental}}$ with the $[(C_E)_V + (C_L)_V]$ obtained with γ and θ_D equal to 0.735×10^{-3} Joules per gram-atom per degree Kelvin squared and 203°K , respectively.

2. Excess Specific Heat Capacity at Constant Volume.

The difference (ΔC_V) between $(C_V)_{\text{experimental}}$ and the theoretical $[(C_L)_V + (C_E)_V]$ contributions to C_V is shown in Table VIII and Figure 45. This excess specific heat capacity ΔC_V can be associated with the formation of lattice defects (monovacancies and divacancies) and/or anharmonic lattice vibrations.

i) Contributions due to the formation of equilibrium lattice defects.

The excess energy is very dependent on the type of model used to calculate the theoretical contributions to the specific heat capacity at constant volume, and any variation in the C_V results obtained by using different models, has a tremendously great influence on the type of mechanisms to which the excess ΔC_V could be attributed. It was shown in Chapter IV that an uncertainty of 2.8 per cent exists for $(C_V)_{\text{experimental}}$. It was also emphasized in the analysis of the theoretical contribution that a variation of 0.32 per cent could exist at 500°K due to the use of a θ_D different by 23 per cent from the one used to calculate the $(C_L)_V$ contribution (Page 181) and that this variation

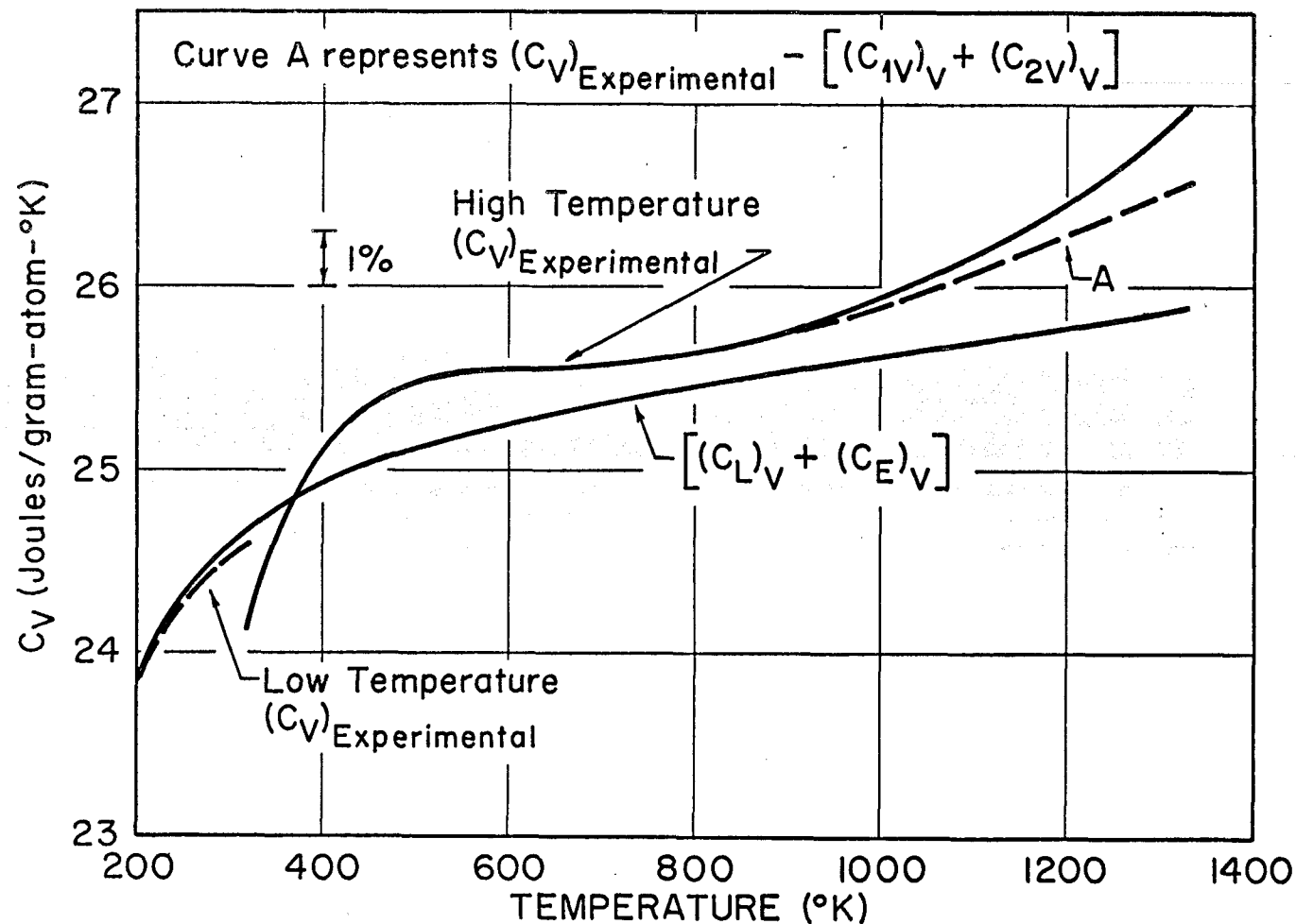


Figure 44. Specific heat capacity at constant volume for gold : theoretical and experimental.

TABLE VIII
EXCESS SPECIFIC HEAT CAPACITY AT
CONSTANT VOLUME: GOLD

Temperature (Degree Kelvin)	Excess C_v^*	
	ΔC_v	$(\Delta C_v)_A^{**}$
380	0.096	0.096
400	0.208	0.208
420	0.285	0.285
440	0.335	0.335
460	0.365	0.365
480	0.379	0.379
500	0.381	0.381
520	0.374	0.374
540	0.362	0.362
560	0.344	0.344
580	0.325	0.325
600	0.304	0.304
620	0.284	0.284
640	0.263	0.263
660	0.244	0.244
680	0.227	0.227
700	0.212	0.211
720	0.199	0.198
740	0.188	0.186
760	0.181	0.179
780	0.177	0.174
800	0.175	0.171
820	0.175	0.169
840	0.180	0.172
860	0.187	0.177
880	0.196	0.183
900	0.210	0.195
920	0.225	0.205
940	0.243	0.218
960	0.264	0.233
980	0.288	0.251
1000	0.314	0.269
1020	0.343	0.289
1040	0.375	0.311
1060	0.408	0.332
1080	0.445	0.356
1100	0.484	0.380

TABLE VIII (continued)

Temperature (Degree Kelvin)	Excess C_v *	
	ΔC_v	$(\Delta C_v)_A$ **
1120	0.524	0.404
1140	0.567	0.429
1160	0.612	0.454
1180	0.659	0.477
1200	0.708	0.502
1220	0.760	0.528
1240	0.813	0.553
1260	0.867	0.566
1280	0.923	0.598
1300	0.983	0.622
1320	1.042	0.640
1330	1.073	0.653

*The units are Joules per gram-atom per degree Kelvin.

** $(\Delta C_v)_A = \Delta C_v - (C_{1v})_v - (C_{2v})_v$. $(C_{1v})_v$ was calculated by using Δh_{1v} equal to 0.97 e.v. and ΔS_{1v} equal to 1.2k; $(C_{2v})_v$ was calculated by using Δh_{1v} equal to 1.84 e.v. and ΔS_{2v} equal to 1.5k.

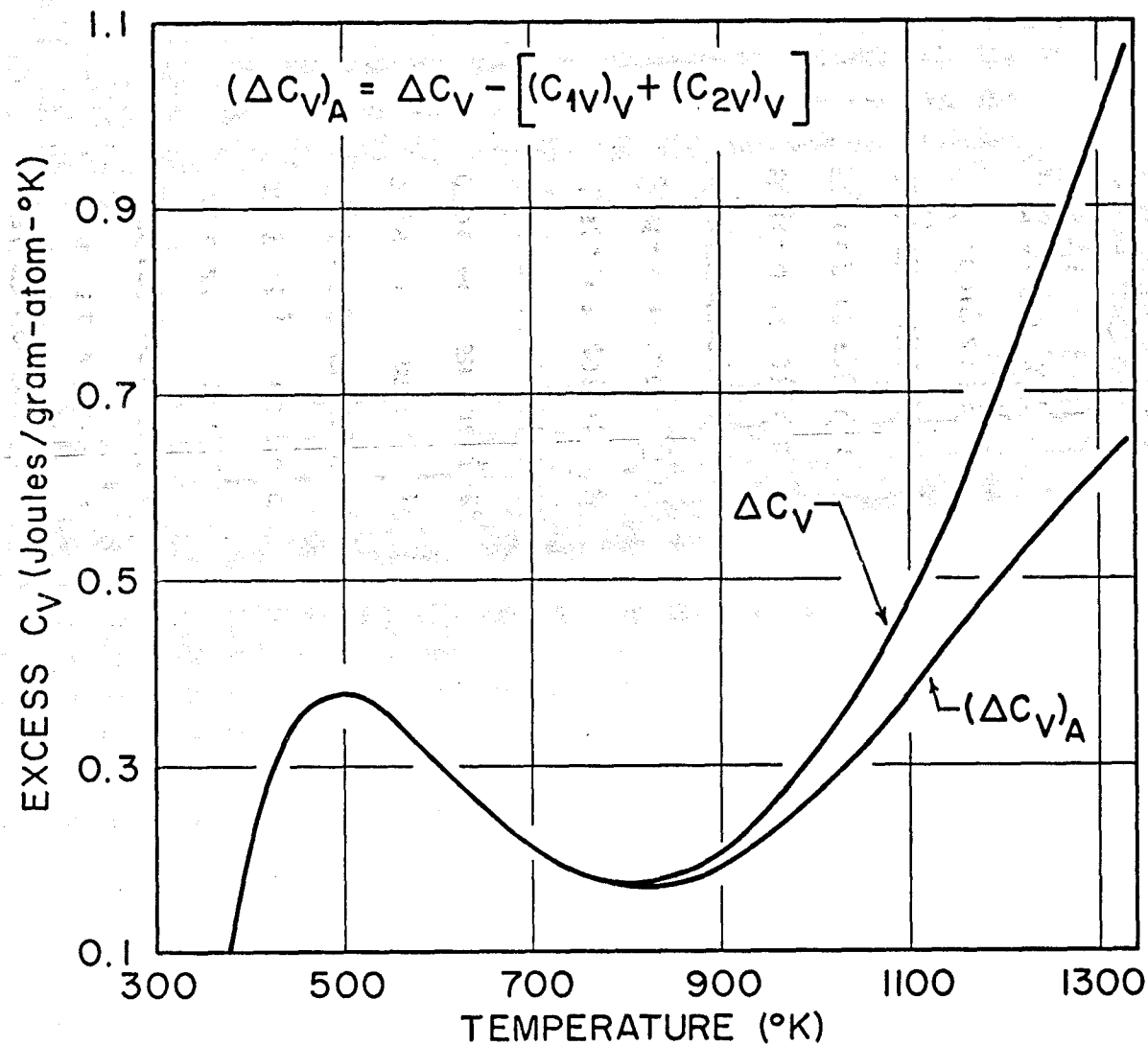


Figure 45. Excess specific heat capacity C_V : gold.

in $(C_L)_V$ increased for lower temperatures. Due to the above considerations, and because of the small ΔC_V values obtained for temperatures below 800°K , no attempt was made to try to justify the low temperature results of a plot of $\log_e (\Delta C_V)T^2$ versus $1/T^*$ (discussed below). It is emphasized that the following analysis made on the high temperature ΔC_V results is also affected considerably by the variations of the different terms in the theoretical model used for the calculation of the excess C_V . The effect of these variations is discussed in detail later.

If it is assumed that the excess specific heat capacity at constant volume ΔC_V is due only to one type of equilibrium lattice defect (i.e. monovacancies), a plot of $\log_e (\Delta C_V)T^2$ versus $1/T$ will be linear. The energy Δh_{1V} for monovacancies can be determined from the slope of the plot in the temperature region where only the one defect contribution is significant. Figure 46 shows this plot and above around 1040°K the formation of one defect is characterized by the more or less straight line which identifies the monovacancies in gold; the slope of the line gives 67,500 Joules per gram-atom (0.7 e.v.), and the variation involved in the graphical measurement of this slope is ± 14.0 per cent. No other type of defect at high temperature is observed from the plot of $\log_e (\Delta C_V)T^2$ versus $1/T$. It is

*A detailed analysis of the uncertainties in ΔC_V is made later in this section and the section dealing with the anharmonic contributions to C_V .

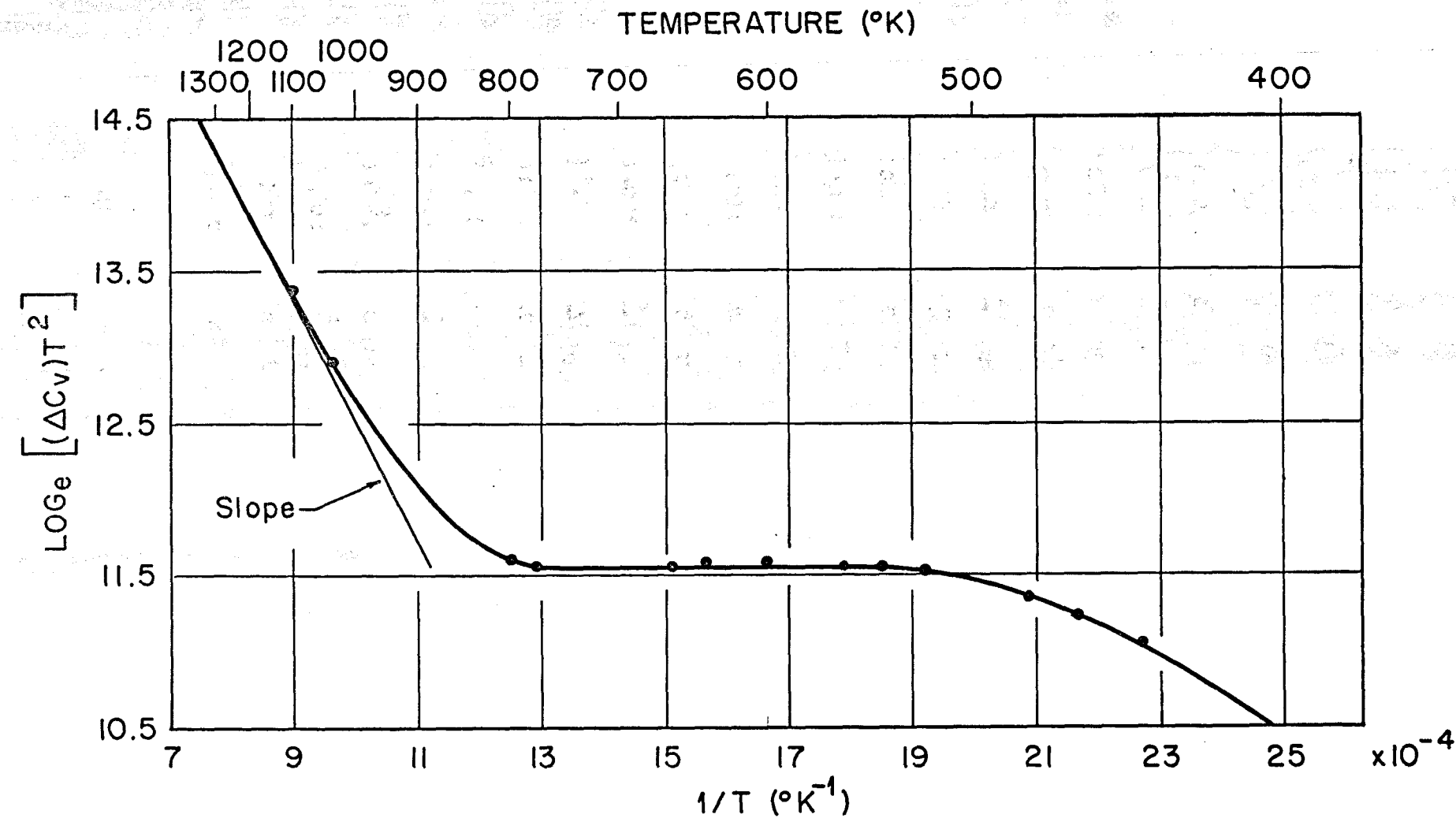


Figure 46. Logarithm of $(\Delta C_v)T^2$ versus $1/T$ for gold.

emphasized that this Δh_{1v} value calculated from the slope of the plot of the $\log_e(\Delta C_v)T^2$ versus $1/T$ is not recommended since considerable error is involved every time a set of data is transformed into logarithmic values, which have a tendency to give straight lines for any given set of data that do not differ appreciably in magnitude; further, as was stated at the beginning of this section, the variations in the calculated ΔC_v increases considerably the uncertainties in the Δh_{1v} calculated above. The measured 0.7 e.v. is 14.0 to 33.0 per cent below the Δh_{1v} values obtained from different more reliable techniques used to determine the energy of formation of point defects.

Since other experimental techniques give much more precise Δh_{1v} values, the analysis of the contributions of monovacancies was made using the Δh_{1v} and ΔS_{1v} values measured by Simmons⁵⁹ ($\Delta h_{1v} = 0.97 \pm 0.04$ e.v., $\Delta S_{1v} = 1.2 \pm 0.2k$)*. The Δh_{1v} values of other investigations are: 0.95 e.v. by Bradshaw and Pearson⁶⁰, 0.96 e.v. by Baverle and Koeler⁶¹, 0.97 ± 0.1 e.v. by De Sorbo⁶², 0.94 e.v. by Simmons and Balluffi³⁹, 0.95 to 1.03 e.v. by Mori, Meshii and Kauffman⁶³, 0.8 e.v. by Misek and Polak⁶⁴, 0.96 e.v. by De Jong and Koehler⁶⁵, and 0.85 to 0.88 e.v. by Seeger and Mehrer⁶⁶. Simmons and Balluffi³⁹ suggested from their results a ΔS_{1v} value of 1.0k, and Seeger and Mehrer⁶⁶ a value

* k is the Boltzmann constant.

of 1.0k, and Seeger and Mehrer⁶⁶ a value of 0.5 k.

The selection of Δh_{2v} was more difficult since the binding energy B^* for two vacancies as determined in different investigations gives values for B that range from 0.1 to 0.4 e.v. The determination of B in the different investigations was based on:

i-i) an analysis on the conservation of the total amount of vacancies made on quenched samples (Koehler, Seitz and Bauerle⁶⁷, where B is between 0.1 and 0.2 e.v.);

i-ii) an analysis of the clustering vacancies made on the recovery of the electrical resistivity of quenched samples after annealing (Mori, Meshii and Kauffman^{68, 69}, where B is greater than 0.3 e.v.);

i-iii) an analysis of the decrease in quenched-in resistivity observed during the transient process in which single vacancies and divacancies come into equilibrium with one another (De Jong and Koehler⁶⁵, where $B = 0.1 \pm 0.03$ e.v.); and

i-iv) an analysis of self diffusion and quenching studies in gold (Stoebe and Dawson⁷⁰, where $B = 0.3$ e.v., Seeger and Mehrer⁶⁶, where $B = 0.16$ e.v., and Wang, Seidman and Balluffi⁷¹, where $B = 0.4$ e.v.).

An analysis of the limit values for B, similar to that made for copper by Bartlett and Dienes⁵⁵ where

$$^* \Delta h_{2v} = 2 \Delta h_{1v} - B$$

$\Delta h_{1v}/6 \leq B \leq E_c/6^*$, gives for gold the limit values 0.16 and 0.56 e.v. Since the experimental results concerning divacancies can not yet give an specific value for B which could be compared with theoretical calculations, it was not necessary to go into very complicated calculations in order to determine the binding energy of the vacancies to form divacancies. For the divacancy contribution the value of 0.1 e.v. was chosen and an analysis was made concerning the effect of a variation of B on $(C_{2v})_v$ and ΔC_v .

The value 1.5k for ΔS_{2v} was chosen from the work of Seeger and Mehrer⁶⁶ since it was the value used during the determination of their B value ($B \leq 0.16$ e.v.). Table VIII (Page 186) and Figure 46 (Page 190) show the $(\Delta C_v)_A$ remaining after the contributions due to monovacancies and divacancies were subtracted from ΔC_v . Figure 44 (Page 185) shows the effect of monovacancies and divacancies on the $(C_v)_{\text{experimental}}$. The calculations for the contributions due to the monovacancies and divacancies were then made by using

$$\Delta h_{1v} = 0.97 \text{ e.v.}, \quad \Delta S_{1v} = 1.2k \quad (8a)$$

$$\Delta h_{2v} = 2(0.97) - 0.1 = 1.84, \quad \Delta S_{2v} = 1.5k \quad (8b)$$

The contributions due to the formation of monovacancies started being noticeable (within three decimal places) at 700°K and the contributions due to the formation of divacancies at 1180°K.

* E_c is the cohesive energy (sublimation energy).

In order to observe the effect of a different Δh_{1v} value on the $(C_{1v})_v$ contribution to the specific heat capacity, a Δh_{1v} value of 0.85 e.v. (determined by Seeger and Mehrer⁶⁶) was used to calculate at 1330°K the $(C_{1v})_v$ contribution. The ΔS_{1v} value was not change for this new calculation ($\Delta S_{1v} = 1.2k$). The use of Δh_{1v} equal to 0.85 e.v. will increase, at 1330°K, the contribution due to monovacancies by 0.495 Joules per gram-atom per degree Kelvin, above the value calculated when using the Δh_{1v} value given in Equation (8a). The above increase is 118.0 per cent of the total value of the contributions due to monovacancies and divacancies as calculated by using Δh_{1v} equal to 0.97 e.v., and it decreases the calculated $(\Delta C_v)_A$ value at 1330°K by 76.0 per cent, to a new value of 0.158 Joules per gram-atom per degree Kelvin. Furthermore, an increase of the ΔS_{1v} by 0.2k together with the use of Δh_{1v} equal to 0.85 e.v. will increase the contributions due to monovacancies by 0.645 Joules per gram-atom per degree Kelvin (155.0 per cent); this increase in $(C_{1v})_v$ produces a decrease in $(\Delta C_v)_A$ to 0.011 Joules per gram-atom per degree Kelvin (99.0 per cent).

At 1330°K the contribution of divacancies, by using the values in Equation (8b), is 0.003 Joules per gram-atom per degree Kelvin which represents 0.7 per cent of the total contributions due to both monovacancies and divacancies (0.420 Joules per gram-atom per degree Kelvin). The use of a binding energy B equal to 0.4 e.v. increases the contribu-

tions due to divacancies by 0.024 Joules per gram-atom per degree Kelvin. This increment in $(C_{2v})_v$ together with the use of Δh_{1v} equal to 0.85 e.v. and ΔS_{1v} equal to 1.4 will decrease $(\Delta C_v)_A$ to zero which means that within the uncertainty of the Δh_{1v} , ΔS_{1v} , B and ΔS_{2v} , the excess ΔC_v can be attributed to the formation of lattice defects. It is emphasized that an increase in Δh_{1v} and a decrease in B, ΔS_{1v} and ΔS_{2v} with respect to the values used (Equations (8a) and (8b)) will increase the $(\Delta C_v)_A$.

ii) Anharmonic contributions.

In Chapter IV it was stated that a variation of ± 2.8 per cent in the calculated $(C_v)_{\text{experimental}}$ could be expected due to the ± 1.0 per cent absolute error of C_p and to variations in the different terms used in the dilation term. This 2.8 per cent variation in C_v , if negative, reduces ΔC_v from 1.073 to 0.319 Joules per gram-atom per degree Kelvin at 1330°K. This new value is easily surpassed by the contributions due to imperfections in the lattice, which means that, within these uncertainties, $(\Delta C_v)_A$ could be negative.

The variations in the $(C_v)_{\text{experimental}}$ and $[(C_{1v})_v + (C_{2v})_v]$ gives a range in the calculated $(\Delta C_v)_A$ of ± 1.4 Joules per gram-atom per degree at 1330°K. The variation decreases with decreasing temperature and at 700°K the variation in $(\Delta C_v)_A$ is ± 0.8 Joules per gram-atom per degree Kelvin.

For temperatures around 700°K a decrease of 1.5 per

cent in the $(C_v)_{\text{experimental}}$ or an increment by the same percentage in $(C_L)_v + (C_E)_v$ will decrease to zero the ΔC_v and $(\Delta C_v)_A$ values at this temperature. The variation in $(C_v)_{\text{experimental}}$ and/or $[(C_L)_v + (C_E)_v]$ needed to decrease to zero the $(\Delta C_v)_A$ value, is less than 1.5 per cent for temperatures below 700°K .

For gold, the $(\Delta C_v)_A$ results obtained in this research (Table VIII in Page 186) could be attributed to anharmonic contributions, but due to the high uncertainties involved in the $(\Delta C_v)_A$ calculations it is difficult to predict with assurance the veracity of such a statement.

b. Lead

1. Lattice and Electronic Contributions to C_v . The characteristic Debye temperature for lead had been calculated from specific heat capacity, elastic constants, electrical resistivity, thermal expansion and X-ray intensity measurements⁵⁶, at temperatures ranging from 0° to 298°K . The θ_D values range from 670°K (calculated from X-ray intensity data at 298°K) to 107°K (calculated from specific heat measurements at 0°K). The relatively closest $(C_L)_v$ values to the experimental results were obtained with a θ_D equal to 107°K , the theoretical $(C_L)_v$ result being at 300°K 0.1 Joules per gram-atom per degree Kelvin above the present research $(C_v)_{\text{experimental}}$. Any θ_D smaller than 107°K will increase the above difference. The use of θ_D value equal to

67°K produces a $(C_L)_V$ result which, when compared to that obtained with Θ_D equal to 107°K, is higher by 0.1 Joules per gram-atom per degree Kelvin at 300°K (0.39 per cent), 0.05 at 400°K (0.22 per cent), 0.04 at 500°K (0.14 per cent) and 0.02 at 600°K (0.1 per cent). The $(C_L)_V$ results with Θ_D equal to 108°K are shown in Table IX. The 0.1 Joules per gram-atom per degree Kelvin difference between $(C_V)_{\text{experimental}}$ and $(C_L)_V$ was increased when the electronic contribution $(C_E)_V$ was added to $(C_L)_V$ in order to obtain the total theoretical specific heat capacity at constant volume.

The γ values given by Gschneidner⁵⁶ range from 2.99×10^{-3} to 3.29×10^{-3} Joules per gram-atom per degree Kelvin squared. The value chosen in this research was 2.99×10^{-3} Joules per gram-atom per square degree Kelvin, since as observed above, the electronic contributions will increase the difference between the theoretical and experimental C_V in the temperature range (temperatures close to 300°K) where the theoretical and experimental values should be very close to each other. The $(C_E)_V$ results obtained with γ equal to 2.99×10^{-3} Joules per gram-atom per degree Kelvin squared are shown in Table IX together with the $(C_L)_V$ and $[(C_L)_V + (C_E)_V]$ results.

The difference between the $(C_L)_V + (C_E)_V$ results obtained when the γ value is changed from 2.99×10^{-3} (Table IX) 3.29×10^{-3} Joules per gram atom per degree Kelvin squared (Θ_D remaining equal to 107°K) is 0.18 Joules per gram-atom

TABLE IX

LATTICE AND ELECTRONIC CONTRIBUTIONS TO THE SPECIFIC
HEAT CAPACITY AT CONSTANT VOLUME: LEAD

Temperature Degree Kelvin	$(C_L)_v^*$	$(C_E)_v^{**}$	$(C_L)_v + (C_E)_v$
200	24.5870	0.5980	25.1850
220	24.6478	0.6578	25.3056
240	24.6941	0.7176	25.4117
260	24.7303	0.7774	25.5077
280	24.7591	0.8372	25.5963
300	24.7823	0.8970	25.6793
320	24.8014	0.9568	25.7582
340	24.8172	1.0166	25.8338
360	24.8304	1.0764	25.9068
380	24.8417	1.1362	25.9779
400	24.8513	1.1960	26.0473
420	24.8595	1.2558	26.1153
440	24.8667	1.3156	26.1823
460	24.8729	1.3754	26.2483
480	24.8784	1.4352	26.3136
500	24.8832	1.4950	26.3783
520	24.8875	1.5548	26.4423
540	24.8914	1.6146	26.5060
560	24.8948	1.6744	26.5692
580	24.8979	1.7342	26.6321
600	24.9007	1.7940	26.6947

*The calculation of $(C_L)_v$ was made with Θ_D equal to 107°K. $(C_L)_v$ is given in Joules per gram atom per degree Kelvin.

**The calculation of $(C_E)_v$ was made with γ equal to 2.99×10^{-3} Joules per gram-atom per degree Kelvin squared. $(C_E)_v$ is given in Joules per gram-atom per degree Kelvin.

per degree Kelvin (0.67 per cent) at 600°K . The difference in the $[(C_L)_v + (C_E)_v]$ results obtained with the two different γ values decreases with a decrease in temperature.

The calculation of $(C_E)_v$ was made by neglecting the last term in Equation (3)* since, by assuming the effective valence for lead to be two, this last term becomes at 600°K , 0.02 per cent of the $(C_E)_v$ term $[0.8 \times 10^{-5}$ per cent of $(C_E)_v + (C_L)_v]$.

Figure 47 shows the comparison of the $(C_v)_{\text{experimental}}$ with the $(C_E)_v + (C_L)_v$ obtained with γ and θ_D equal to 2.99×10^{-3} Joules per gram-atom per degree Kelvin squared. and 107°K respectively.

2. Excess Specific Heat Capacity at Constant Volume.

The difference (ΔC_v) between $(C_v)_{\text{experimental}}$ and the theoretical $(C_L)_v + (C_E)_v$ contributions to C_v is shown in Table X and Figure 48. This excess specific heat capacity ΔC_v is negative for lead and the contributions due to the formation of monovacancies and divacancies increase this difference for temperatures above 360°K , indicating a probable negative anharmonic contribution.

i) Contributions due to the formation of equilibrium lattice defects.

As it was stated in the analysis made of the contribu-

* $\frac{3\pi^2}{10} \frac{KT^2}{\zeta_0}$

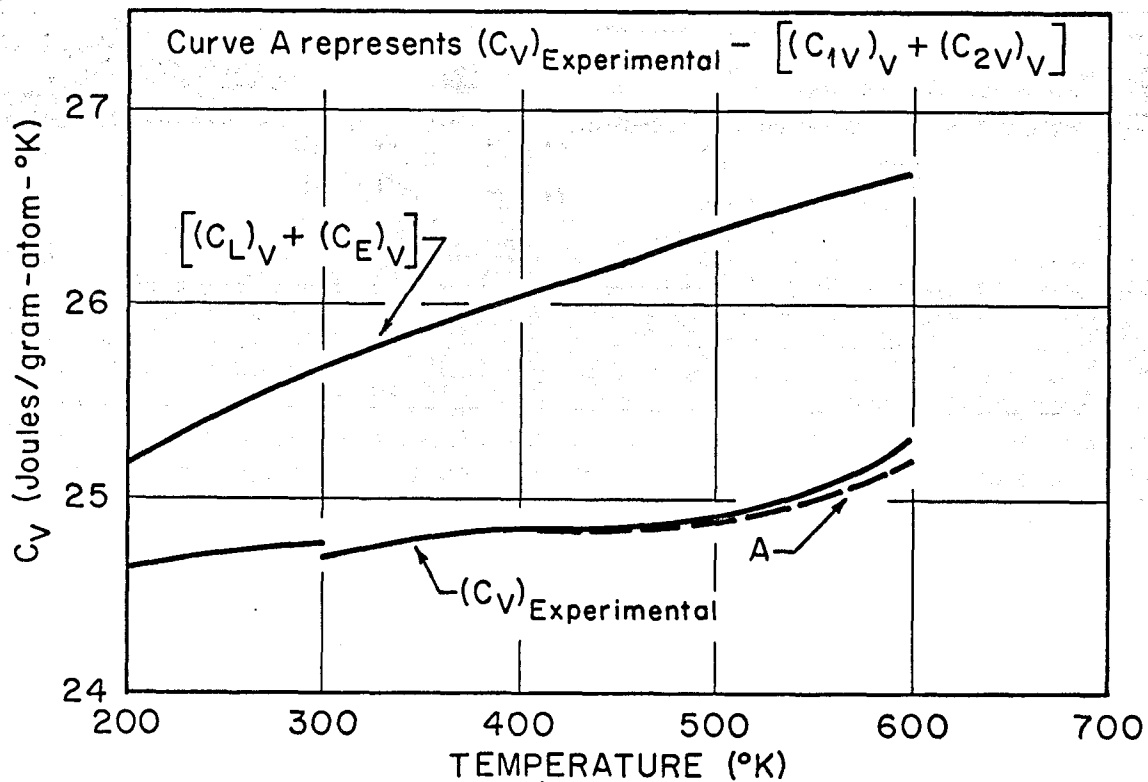


Figure 47. Specific heat capacity at constant volume for lead: theoretical and experimental.