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CONTRIBUTIONS TO THE
DATA ON THEORETICAL METALLURGY

I. THE ENTROPIES OF INORGANIC SUBSTANCES

BY

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FOREWORD

As part of its work to improve metallurgical processes the Bureau of Mines has undertaken a study of the fundamental thermodynamic constants of metallurgical materials and will publish from time to time summaries of its work and the data available in the literature on various phases of this study. Bureau of Mines Bulletin 296, *Iron Oxide Reduction Equilibria, a Critique from the Standpoint of the Phase Rule and Thermodynamics*, by O. C. Ralston, and Bulletin 324, *Zinc Smelting from a Chemical and Thermodynamic Viewpoint*, by C. G. Maier, have already appeared, summarizing the work in these two fields. The present paper, covering the entropies of metallurgically important substances, will be followed by others of similar nature. This work is being carried on under the direction of Charles G. Maier, supervising engineer and metallurgist of the Pacific Experiment Station of the Bureau of Mines at Berkeley, Calif.

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THE ENTROPIES OF INORGANIC SUBSTANCES¹

By K. K. KELLEY²

INTRODUCTION

The present trend in metallurgical research is toward application of the methods of thermodynamics to metallurgical reactions. Such methods have been used by the chemist for many years, but the metallurgist has been slower to appreciate their direct applicability to his problems and their exactness. Thermodynamic data on substances important in metallurgy are scattered throughout technical and scientific literature, and it is a primary function of the Pacific Experiment Station of the United States Bureau of Mines to collect and correlate these data and to systematically supply new data in cases where they are lacking or considered unsatisfactory. The present work is an attempt to collect all the available data referring to one important thermodynamic property and to supply sufficient discussion to make the results readily usable by metallurgists.

In the study of chemical or metallurgical reactions two factors have predominant importance—the free energy of reaction and the speed of reaction. The subject of this publication is so closely allied to the former that it may be well to consider briefly some of the uses to which free-energy data may be put.

USES OF FREE-ENERGY DATA

If one wishes to know whether or not an experimentally untested reaction is possible there is no surer, cheaper, or quicker means than the application of reliable free-energy data. For a possible reaction, or one that is well known, free-energy data definitely give the position of the reaction equilibrium under the various conditions required by experiment or industrial practice. Thus, it may readily be known without experiment (provided, of course, the necessary free-energy data are already available) whether a given chemical process is yielding the ratio of product to raw material that is thermodynamically possible. If the yield is smaller, means of improving the process may be indicated.

On the other hand, since free-energy data are concerned only with the initial and final conditions of the reacting system, no information is given as to the speed of reaction or the mechanism, except, that one is often able to eliminate mechanisms that were thought possible and thus to simplify the consideration of this phase of the problem. Reaction rates constitute a separate study and are best handled theoretically by statistical mechanics.

¹ Work on manuscript completed March, 1931.

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For an example of the application of thermodynamics and, in particular, of free-energy calculations to practical metallurgical problems the reader is referred to the recent bulletin of C. G. Maier³ on zinc smelting.

METHODS OF DETERMINING FREE-ENERGY DATA

Let us next consider the three general methods of determining free-energy changes for reactions: (1) The equilibrium may be studied, in which case the free-energy change is given by

$$\Delta F^\circ_T = -RT \ln K,$$

where ΔF°_T is the standard free-energy change at the absolute temperature T , and $\ln K$ is the natural logarithm of the equilibrium constant.⁴ (2) The reaction may be allowed to take place reversibly in a galvanic cell and the electromotive force measured.

Then

$$\Delta F^\circ_T = -nfE,$$

where ΔF°_T has the same meaning as before, n is the number of chemical equivalents involved in the reaction, f is Faraday's constant, and E is the electromotive force of the cell.⁵ (3) The free-energy change may be obtained from the well-known statement of the second law of thermodynamics

$$\Delta F_T = \Delta H - T\Delta S,$$

where ΔH is the heat of reaction and ΔS the entropy of reaction; that is, the difference in entropy between the products of reaction and the reactants.⁶

As the majority of reactions can not be made to take place reversibly in cells that are free from objection, and as most equilibrium measurements are either prohibited or made unreliable by experimental difficulties, method (3) is frequently the only available means for calculating free-energy changes. Consequently, the determination of the entropies of the elements and the compounds encountered in metallurgy is a problem of the utmost importance.

PURPOSE OF THIS PUBLICATION

It is the purpose of this publication, therefore, to give values of the entropies at 298.1° K. (25° C.) for those elements and common compounds, such as oxides and sulphides, for whose calculation the necessary data are at present available and to call attention to means of obtaining approximate values when data are lacking. Previous tables for the elements may be found in the textbook of Lewis and Randall⁷ and in the Treatise on Physical Chemistry edited by Taylor.⁸ Recent data, however, make it necessary to revise many

³ Maier, C. G., Zinc Smelting from a Chemical and Thermodynamic Viewpoint: Bull. 324, Bureau of Mines, 1930, 93 pp.

⁴ Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 294. Throughout this work the symbols of Lewis and Randall will be used, and references will be given to their textbook for derivations and explanations of thermodynamic formulas.

⁵ Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 167.

⁶ Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923, pp. 169-175.

⁷ Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 464.

⁸ Taylor, H. S., A Treatise on Physical Chemistry (vol. 2, ch. 17, by Rodebush, W. H.): D. van Nostrand Co., New York, 1925, p. 1161.

of their values. A table for compounds has been given by Miething,⁹ which was quite complete at the time of its publication, and more recently Rodebush and Rodebush¹⁰ have tabulated some of the available elements and compounds.

The final purpose of the present publication is not only to present recalculated figures in such form as to be readily usable by metallurgists but also to furnish a tabulation into which data that may become available in the future can consistently be inserted. The continuation of low-temperature measurements now in progress at the Pacific Experiment Station and elsewhere should result, within a few years, in the availability of at least moderately satisfactory entropy figures for all the elements and simpler compounds, such as oxides and sulphides, for the whole periodic system, except the rare earths and a few of the other very rare or costly materials.

METHODS OF CALCULATING ENTROPIES FROM EXPERIMENTAL DATA

CALCULATIONS FROM LOW-TEMPERATURE THERMAL DATA

In all but a comparatively few cases the calculation of entropies will be based upon the third law of thermodynamics, which Lewis and Gibson¹¹ have stated as follows: "If the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero, and the entropy of any other substance is greater than zero."

The change in entropy on heating a substance from the absolute zero to a temperature, T_1 , is, by definition¹²

$$\Delta S = S_{T_1} - S_0 = \int_0^{T_1} \frac{dQ}{T} \quad (1)$$

Here, S_{T_1} is the entropy of the substance at the temperature T_1 , S_0 the entropy at 0° K. and dQ the increment of heat absorbed at the temperature T . Now, if the substance is in a pure, crystalline state at 0° K., it follows from the third law of thermodynamics that S_0 is zero and equation (1) becomes

$$S_{T_1} = \int_0^{T_1} \frac{dQ}{T} \quad (2)$$

Consider first a pure, crystalline substance undergoing no change in state or modification in crystal form in the interval 0 to T_1° K. In such a case, $dQ = C_p dT$ or $dQ = C_v dT$, throughout this temperature range, depending on whether the substance is heated at constant pressure or at constant volume. The symbol C_p represents the true or "instantaneous" specific heat at constant pressure and C_v the true specific heat at constant volume. The integral in equation (2) gives either the entropy at constant pressure or constant volume,

⁹ Miething, —, *Abhand. Deut. Bunsen-Gesell.*, No. 9, 1920.

¹⁰ Rodebush, W. H., and Rodebush, E., *International Critical Tables*: Vol. 5, McGraw-Hill Book Co. (Inc.), New York, 1929, p. 84.

¹¹ Lewis, G. N., and Gibson, G. E., *The Third Law of Thermodynamics and the Entropy of Solutions and of Liquids*: *Jour. Am. Chem. Soc.*, vol. 42, 1920, p. 1529. See also Lewis, G. N., and Randall, M., *Thermodynamics and the Free Energy of Chemical Substances*: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 435.

¹² For a discussion of the concept of entropy the reader is again referred to Lewis, G. N., and Randall, M., *Thermodynamics and the Free Energy of Chemical Substances*: McGraw-Hill Book Co. (Inc.), New York, pp. 109-155.

depending on which specific heat is used. We shall here be concerned only with the calculation of entropies at a constant pressure of 1 atmosphere. Returning to equation (2) and inserting the value for dQ ,

$$S_{T_1} = \int_0^{T_1} \frac{C_p dT}{T}. \quad (3)$$

In such a simple case, specific-heat values down to very low temperatures are the only data required. Information as to the evaluation of this integral will be given later.

Suppose a more complicated state of affairs and assume a substance that changes from one crystalline form to another at some temperature, T' , melts at a temperature, T'' , and boils under 1 atmosphere pressure at T''' , the temperatures T' , T'' , and T''' lying in the range 0 to T_1° K. The integral in equation (2) will now consist of parts similar to equation (3), except for the limits of integration, and of parts due to the absorption of the heats of transition, fusion, and vaporization, each of which takes place at a constant temperature. Therefore,

$$S_{T_1} = \int_0^{T'} \frac{C_p(\text{crystals I}) dT}{T} + \frac{\Delta H'}{T'} + \int_{T'}^{T''} \frac{C_p(\text{crystals II}) dT}{T} + \frac{\Delta H''}{T''} \\ + \int_{T''}^{T'''} \frac{C_p(\text{liquid}) dT}{T} + \frac{\Delta H'''}{T'''} + \int_{T'''}^{T_1} \frac{C_p(\text{gas}) dT}{T}. \quad (4)$$

where $\Delta H'$, $\Delta H''$, and $\Delta H'''$ are respectively the heats of transition, fusion, and vaporization.

The integrals of equation (4), except the first, are readily evaluated by plotting C_p against $\ln T$, or $\frac{C_p}{T}$ against T , and mechanically computing the area under the resulting curve bounded by the curve, the $\ln T$ or T axis, and the two ordinates corresponding to the limits of integration.

The first integral of equation (4) and that of equation (3) need further consideration, as an extrapolation of the specific-heat curve between the lowest temperature at which measurements have been made and the absolute zero is required for their evaluation.

DEBYE SPECIFIC-HEAT FUNCTION

As a crystal is cooled to low temperatures the difference between the specific heat at constant pressure and that at constant volume gradually diminishes and is usually nearly negligible for inorganic crystals at approximately 50° K. Debye,¹³ assuming a monatomic solid to be an isotropic, elastic medium, deduces for the energy the relationship

$$E = 9NkT \left(\frac{kT}{h\nu_m} \right)^3 \int_0^{\frac{h\nu_m}{kT}} \frac{\left(\frac{h\nu}{kT} \right)^3 d\left(\frac{h\nu}{kT} \right)}{e^{\frac{h\nu}{kT}} - 1}. \quad (5)$$

¹³ Debye, P., Zur Theorie der spezifischen Wärmen: Ann. Physik., ser. 4, vol. 39, 1912, p. 789.

Differentiating with respect to the temperature at constant volume, one gets

$$C_v = 9Nk \left[4 \left(\frac{kT}{h\nu_m} \right)^3 \int_0^{h\nu_m} \frac{\left(\frac{h\nu}{kT} \right)^3 d \left(\frac{h\nu}{kT} \right)}{e^{\frac{h\nu}{kT}} - 1} - \frac{\frac{h\nu_m}{kT}}{e^{\frac{h\nu_m}{kT}} - 1} \right]. \quad (6)$$

In these equations

N = Avogadro's number,
 k = gas constant per molecule,
 h = Planck's constant,
 ν = frequency of vibration, and
 ν_m = limiting frequency of vibration.

By substituting $\frac{h\nu_m}{kT} = \frac{\theta_D}{T}$,

$$C_v = 9Nk \left[4 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} \frac{\left(\frac{h\nu}{kT} \right)^3 d \left(\frac{h\nu}{kT} \right)}{e^{\frac{h\nu}{kT}} - 1} - \frac{\frac{\theta_D}{T}}{e^{\frac{\theta_D}{T}} - 1} \right]. \quad (7)$$

θ_D is a characteristic constant for each substance and has the dimensions of temperature. Equation (7) expresses the fact that the specific heat at constant volume is a function of this characteristic constant divided by the absolute temperature.

T³ LAW FOR SPECIFIC HEATS

When T is large so that $\frac{h\nu}{kT}$ is small, $e^{\frac{h\nu}{kT}}$ may be approximated by $1 + \frac{h\nu}{kT}$ and equation (5) approaches

$$E = 3NkT, \quad (8)$$

and C_v approaches $3Nk = 3R$ where R equals gas constant per mole. The latter is the well-known rule of Dulong and Petit,¹⁴ which holds approximately for many elements around room temperature. When T is small, the upper limit of the integral in equation (5) may be taken as infinite and the integral evaluated as $\frac{\pi^4}{15}$. At low temperatures, then,

$$E = \frac{3\pi^4 Nk^4 T^4}{5h^3\nu_m^3}, \quad (9)$$

and

$$C_v = \frac{12\pi^4 Nk^4}{5h^3\nu_m^3} T^3 = aT^3, \quad (10)$$

where a is substituted for the complex constant multiplier.

Several substances have been studied at sufficiently low temperatures to check this T³ rule, and a great many have been investigated at low enough temperatures to show the adequacy of the general Debye equation. Consequently, if the substance whose entropy is

¹⁴ (a) Petit, —, and Dulong, —, Sur quelques points importants de la theorie de la chaleur: Ann. chim. phys., vol. 10, 1819, p. 395.

(b) Lewis, G. N., The Specific Heat of Solids at Constant Volume and the Law of Dulong and Petit: Jour. Am. Chem. Soc., vol. 29, 1907, p. 1165 and 1516.

to be calculated has had its specific-heat curve extended into the region where the Debye function or the T^3 rule holds, one may use these expressions for extrapolating to 0° K. The procedure will be to consider the first integral of equation (4) or the integral in equation (3) in two parts, the first of which accounts for the temperature range covered by the measured specific heats and is evaluated as are the other integrals in (4). The second part is entirely extrapolation. Tables for the specific heat at constant volume and the entropy for different values of $\frac{\theta_D}{T}$ for the Debye function may be found in several places,¹⁵ so that the labor of computation is minimized. When the T^3 rule is obeyed below a temperature, T , the entropy at T is simply $\frac{C_v}{3}$, for

$$S_T = \int_0^T \frac{C_p dT}{T} = \int_0^T aT^2 dT = \frac{aT^3}{3} = \frac{C_v}{3}. \quad (11)$$

The fact that the specific heats of some substances such as lead and mercury have been shown to follow a Debye curve of a particular θ_D over a considerable temperature range, then at lower temperatures depart from it, and finally at still lower temperatures come back on another Debye function of different θ_D , need not be considered here. Such fluctuations have great theoretical interest, but the known cases involve so little difference in entropy that they can be neglected from the standpoint of practical free-energy calculations.

EINSTEIN SPECIFIC-HEAT FUNCTION

Unfortunately, the Debye function alone will be of little aid for many of the substances considered here, since they are not monatomic solids and their specific-heat curves have been extended down only to liquid-air temperatures; that is, down to some point in the range 60° to 100° K., which is rarely low enough to coincide with a Debye function. Measured specific-heat curves rise above the expression given by Debye at higher temperatures, due to the interatomic vibrations picking up energy and to $C_p - C_v$ becoming appreciable. Assuming the atoms behave as harmonic oscillators one may assign, according to Einstein,¹⁶ the value

$$C_v = \frac{Nk e^{\frac{h\nu}{kT}} \left(\frac{h\nu}{kT}\right)^2}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2}, \quad (12)$$

as the specific-heat contribution of each vibrational degree of freedom. The symbols in this equation have the same meaning as in

¹⁵ (a) Landolt-Börnstein, —, *Physikalisch-chemische Tabellen: Erster Ergänzungsband*, Julius Springer, Berlin, 1927, pp. 702-707.

(b) Nernst, W., *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes*: 2d ed., Wilhelm Knapp, Halle, 1924, pp. 200-209.

(c) Nernst, W., *The New Heat Theorem*: E. P. Dutton & Co., New York, 1926, pp. 245-255.

(d) *Thermische Eigenschaften der Stoffe: Handbuch der Physik*, Julius Springer, Berlin, 1926, ch. 7, vol. 10, p. 350.

¹⁶ Einstein, A., *Die plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme*: *Ann. Physik*, series 4, vol. 22, 1907, p. 180.

that of Debye. Tables of Einstein functions for different values of $\frac{\theta_E}{T} = \frac{h\nu}{kT}$ are also available.^{16a}

THE N-FORMULA

Lewis and Gibson¹⁷ have used an empirical method known usually as the n -formula for extrapolating heat-capacity curves to 0° K. Their method is useful in cases where the specific-heat data are meager, as only two good values, with certain restrictions, are required. For substances having a small number of atoms per molecule or per simplest chemical formula, it is quite satisfactory; however, it has been shown to lead to large errors in values for compounds of a more complicated nature, such as those of organic chemistry.¹⁸ The fact that it is based upon the average atom rather than on the molecule or the unit crystal (that is, the building block of the crystal lattice) also renders it theoretically unsound, except, of course, for monatomic solids. Consequently, this method is used only when necessary due to lack of data.

SPECIFIC-HEAT THEORY OF BORN AND VON KÁRMÁN

Born and Von Kármán,¹⁹ in a series of papers, have considered extensively the thermal vibrations in a crystal lattice, and Born²⁰ has summed up by stating that the heat content of a p -atomic crystal, which consists of n elementary parallelepipeds, may, to a close approximation, be considered as composed of two portions; the first part is given by the sum of 3 Debye functions of characteristic temperatures, θ_{D1} , θ_{D2} , and θ_{D3} , which are closely related to the elastic properties, and the second part consists of the sum of 3($p-1$) Einstein functions of θ_E 's, which may be found from a study of the infra-red dispersion of the crystal. In terms of specific heat this may be written

$$C_v = \frac{1}{3} \left[\sum_{i=1}^3 D\left(\frac{\theta_{D_i}}{T}\right) + \sum_{i=3}^{3(p-1)} E\left(\frac{\theta_{E_i}}{T}\right) \right], \quad (13)$$

where $D\left(\frac{\theta_{D_i}}{T}\right)$ and $E\left(\frac{\theta_{E_i}}{T}\right)$ represent respectively Debye and Einstein specific-heat functions. This equation gives the specific heat per chemical formula weight of the n unit parallelepipeds. The factor "3" occurs because generally crystals have different frequencies of vibration in different directions.

^{16a} See footnote 15, p. 6.

¹⁷ Lewis, G. N., and Gibson, G. E., *The Entropy of the Elements and the Third Law of Thermodynamics*: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554. See also *Thermodynamics and the Free Energy of Chemical Substances*: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 76.

¹⁸ Kelley, K. K., *The Heat Capacity of Methyl Alcohol from 16° K. to 298° K. and the Corresponding Entropy and Free Energy*: Jour. Am. Chem. Soc., vol. 51, 1929, p. 180; *The Heat Capacities of Ethyl and Hexyl Alcohols from 16° K. to 298° K. and the Corresponding Entropies and Free Energies*: Vol. 51, 1929, p. 779; *The Heat Capacities of Isopropyl Alcohol and Acetone from 16° to 298° K. and the Corresponding Entropies and Free Energies*: Vol. 51, 1929, p. 1145.

¹⁹ Born, M., and von Kármán, T., *Über Schwingungen in Raumgittern*: *Physikal. Ztschr.*, vol. 13, 1912, p. 297; *Zur Theorie der spezifischen Wärme*: vol. 14, 1913, p. 15; *Über die Verteilung der Eigenschwingungen von Punktgittern*: Vol. 14, 1913, p. 65.

²⁰ Born, M., *Dynamik der Kristallgitter*: Teubner, Leipzig and Berlin, 1915, p. 77.

METHOD OF EXTRAPOLATING SPECIFIC-HEAT CURVES

In only a few of the simpler cases are all the necessary data for applying equation (13) existent, so for the present purposes it must be modified somewhat. Since this paper is concerned only with a method of extrapolation of specific-heat curves to obtain a relatively small portion of the total entropy at 298° K., the approximations made should not be objectionable. First, let p mean the number of atoms in a molecule of the substance, if that is known, or else the number of atoms in the simplest chemical formula that may be written to represent the composition; also, instead of having 3 Debye functions and $3(p-1)$ Einstein functions, take 1 Debye function and $(p-1)$ Einstein functions and remove the factor, $\frac{1}{3}$, from equation (13) and write

$$C_p = D\left(\frac{\theta_D}{T}\right) + \sum_{i=1}^{p-1} E\left(\frac{\theta_{E_i}}{T}\right). \quad (14)$$

Each Debye and Einstein function now must be considered as being equivalent to one-third the sum of three it is replacing. In other words, their "θ's" and the corresponding frequencies are, in effect, "mean" values for three mutually perpendicular directions. For a crystal that is isotropic the theory immediately gives equation (14), except for the modification in the definition of p . Such an equation satisfactorily fits specific-heat curves for oxides, sulphides, chlorides, etc., up to temperatures where $C_p - C_v$ becomes appreciable.

The method of extrapolation by means of equation (14) is one of trial and may best be illustrated by taking bismuth trioxide as a typical example. The measured specific heats, extending down to 60° K., were plotted against $\log T$ and the curve extended smoothly into a Debye function. (It is convenient for this purpose to have Debye and Einstein functions accurately cut out of some rigid, transparent material such as a nitrocellulose derivative.) The Debye function is drawn in and extended up to room temperature. Then differences between the measured curve and the Debye are read off. In this case, if the formula for bismuth trioxide is written in the old-fashioned way, $O = Bi - O - Bi = O$, it seems reasonable from symmetry that the four Einstein functions required by the theory should consist of two pairs, the constituents of each pair having the same θ_E . Consequently, the differences mentioned above were divided by two and plotted on the same sheet against $\log T$. The Einstein curve was then fitted to the lower end of this difference plot and extended upward to room temperature. Next, a second set of differences was read—differences between this Einstein curve and the first difference plot. These also were plotted against $\log T$, and the resulting curve was examined to find whether it was an Einstein function. This examination showed the direction and indicated the amount the original Debye curve needed to be moved along the $\log T$ -axis. This shift was made, and the entire process as outlined was repeated with the result that the experimental specific-heat curve of bismuth trioxide was satisfactorily represented up to about 175° K. by the expression

$$C_{Bi_2O_3} = D\left(\frac{97}{T}\right) + 2E\left(\frac{225}{T}\right) + 2E\left(\frac{568}{T}\right).$$

The entropy at 60° K. was then found from the tables of Debye and Einstein functions and added to the result obtained by graphical integration between 60° and 298° K.

The extrapolations of a good many specific-heat curves for compounds, where experimental data extend down only to liquid-air temperatures, have been made by this method for incorporation in this publication. In very few cases has there been any reason to doubt the extrapolated values, and then only because the experimental data themselves were poor or because of questionable purity of the compounds. It should be remembered, however, that such curve fitting is largely empirical, since only those functions definitely given by measurement may be taken as certain. It would seem that the assumption of an error of about 10 per cent in that part of the entropy so obtained should be sufficient to account for the various difficulties. It is highly desirable to extend specific-heat measurements on all substances down at least to temperatures low enough for the Debye function to be followed, or, better still, down to the range of the T^3 law, thus making for much more reliable figures. For most calculations, however, the results obtained from the existing data are unusually satisfactory.

APPLICATION OF THIRD LAW OF THERMODYNAMICS

One point must be considered in connection with the third law of thermodynamics. The statement of Lewis and Gibson appears to be unquestionable so far as pure crystals are concerned, but doubt has sometimes arisen as to the method of applying it. Giauque²¹ has recently clarified matters by calling attention to the fact that the specific-heat measurements must be made under the condition of true equilibrium in "the distribution of energy between such energy states as are actually occupied by the system." This statement became necessary when it was discovered that ordinary hydrogen is a mixture of symmetrical and antisymmetrical molecules between which the attainment of equilibrium is so slow that specific-heat measurements at low temperatures, as ordinarily made, do not give the correct value for the entropy of hydrogen. A similar case was found in nitric oxide,²² and there are probably others. From the standpoint of metallurgical calculation, one should at present be skeptical of the entropy values for highly paramagnetic compounds, such as the derivatives of iron, cobalt, nickel, manganese, and chromium, although the entropies of these elements are probably beyond reproach.

CALCULATIONS FROM SACKUR EQUATION

The calculation of the entropy of an ideal, monatomic gas (or the translation entropy of any ideal gas) has been the subject of several

²¹ Giauque, W. F., and Johnston, H. L., Symmetrical and Antisymmetrical Hydrogen and the Third Law of Thermodynamics. *Thermal Equilibrium and the Triple Point Pressure*: Jour. Am. Chem. Soc., vol. 50, 1928, p. 3221.

²² Johnston, H. L., and Giauque, W. F., The Heat Capacity of Nitric Oxide from 14° K. to the Boiling Point and the Heat of Vaporization. *Vapor Pressures of Solid and Liquid Phases. The Entropy from Spectroscopic Data*: Jour. Am. Chem. Soc., vol. 51, 1929, p. 3194.

investigations,²³ with the result, first obtained by Sackur, that

$$S_o = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln V + \frac{5}{2} R + S_o. \quad (15)$$

Here M is the molecular weight of the gas, T the absolute temperature, V the molal volume, and R the gas constant per mole. S_o is a constant which was shown by Tetrode to have the value

$$S_o = R \ln \frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} = -16.024 \text{ calories per mole per degree,}$$

where k is the gas constant per molecule, h is Planck's constant and n is Avogadro's number.²⁴ Substituting the value for the molecular volume of an ideal gas at 298.1° K. and putting in the temperature gives

$$S^\circ_{298.1} = \frac{3}{2} R \ln M + 26.001. \quad (16)$$

Experimental data on argon and neon, which will be considered later, and the results of experiments and calculations by Giaque and his coworkers²⁵ on several gases have shown that equations (15) and (16) are very exact and have proved the correctness of Tetrode's constant. Equation (16) will be used to obtain the entropies of the rare gases, electron gas, and a few metallic gases in the ideal state at 298.1° K. In applying it outside the rare-gas group, considerable care should be used. It must be remembered that it gives the entropy of an ideal, monatomic gas and not the actual gas, where there is always some association and imperfection; also, this formula does not take into account any multiplicity in the lowest energy state of the molecule. Consequently, in calculating the entropies of lithium, sodium, potassium, copper, silver, and gold a correction of $R \ln 2$ must be added as these substances have a multiplicity of 2 in their lowest energy states. No such correction is needed for zinc, cadmium, and mercury. In all these cases a small correction to account for association and imperfection of gas is necessary before the Sackur values and those obtained by other means may be brought into complete agreement. In any case, examination of the spectroscopic data on the element involved is necessary before applying the

²³ (a) Sackur, O., Die Anwendung der kinetischen Theorie der Gase auf chemische Probleme: Ann. Physik, vol. 36, 1911, p. 958.

(b) Tetrode, H., Die chemische Konstante der Gase und das elementare Wirkungsquantum: Ann. Physik, vol. 38, 1912, p. 434.

(c) Stern, O., Zur kinetischen Theorie des Dampfdruckes einatomiger fester Stoffe und über die Entropiekonstante einatomiger Gase: Physikal. Ztscher., vol. 14, 1913, p. 629.

(d) Stern, O., Zusammenfassender Bericht über die Molekulartheorie des Dampfdruckes fester Stoffe und ihre Bedeutung für die Berechnung chemischer Konstanten: Ztschr. Electrochem., vol. 25, 1919, p. 66.

(e) Tolman, R. C., The Entropy of Gases: Jour. Am. Chem. Soc., vol. 42, 1920, p. 1185.

(f) Ehrenfest, —, and Trkal, —, Proc. Akad. Sci. Amsterdam, vol. 23, 1920, p. 162.

(g) Lewis, G. N., and Mayer, J. E., The Thermodynamics of Gases Which Show Degeneracy (Entartung): Proc. Nat. Acad. Sci., vol. 15, 1929, p. 208.

²⁴ Tetrode, H., Die chemische Konstante der Gase und das elementare Wirkungsquantum: Ann. Physik, vol. 38, 1912, p. 434.

²⁵ (a) Giaque, W. F., and Wiebe, R., The Entropy of Hydrogen Chloride. Heat Capacity from 16° K. to Boiling Point. Heat of Vaporization. Vapor Pressures of Solid and Liquid: Jour. Am. Chem. Soc., vol. 50, 1928, p. 101.

(b) Giaque, W. F., and Wiebe, R., The Heat Capacity of Hydrogen Bromide from 15° K. to its Boiling Point and its Heat of Vaporization. The Entropy from Spectroscopic Data: Vol. 50, 1928, p. 2193.

(c) Giaque, W. F., and Wiebe, R., The Heat Capacity of Hydrogen Iodide from 15° K. to its Boiling Point and its Heat of Vaporization. The Entropy from Spectroscopic Data: Vol. 51, 1929, p. 1441.

(d) Giaque, W. F., and Johnston, H. L., The Heat Capacity of Oxygen from 12° K. to its Boiling Point and the Heat of Vaporization. The Entropy from Spectroscopic Data: Vol. 51, 1929, p. 2300.

(e) Johnston, H. L., and Giaque, W. F., The Heat Capacity of Nitric Oxide from 14° K. to the Boiling Point and the Heat of Vaporization. Vapor Pressures of Solid and Liquid Phases. The Entropy from Spectroscopic Data: Jour. Am. Chem. Soc., vol. 51, 1929, p. 3194.

Sackur equation. No further discussion seems necessary here, as Professor Giauque of the University of California in a conversation with the author stated that he is planning a series of papers treating all of the metallic gases, for which he will calculate the entropies up to high temperatures from the actual energy levels of the atoms or molecules as determined spectroscopically.

CALCULATIONS FROM RESIDUAL-RAY FREQUENCIES

The infra-red absorption spectra of crystals is quite simple, and as Born has stated for a p -atomic crystal there should be at most 3 ($p-1$) characteristic vibration frequencies in the infra-red. The data of Rubens and coworkers, to which reference is made later, give the infra-red resonance frequencies of a number of salts. These frequencies have been identified with those in the Einstein equations and thus make possible the calculation of entropies. In accordance with Rodebush²⁶ the approximate expression, $\theta_E = 1.35 \theta_D$, will be used for the diatomic salts studied by Rubens. If the tables of Debye and Einstein functions are used, the entropies at constant volume at 298.1° K. may be calculated and the difference $S_p - S_v = \frac{1}{2}(C_p - C_v)$ added.²⁷ In anticipation of these calculations the following is given:

Comparison of values obtained from residual-ray frequencies and specific heats

Substance	S_{298} (residual rays)	S_{298} (specific heats)	Substance	S_{298} (residual rays)	S_{298} (specific heats)
NaCl.....	17.2	17.3±0.5	AgBr.....	26.1	25.6±0.1
KCl.....	19.5	19.8±.5	HgCl.....	24.7	23.0±.7
KBr.....	22.6	22.4±1.0	TlCl.....	23.7	25.9±.6
AgCl.....	22.4	23.0±.1			

Except for thallos chloride and mercurous chloride, very good agreement between the two methods of calculation is obtained.

CALCULATIONS FROM SPECTROSCOPIC DATA

Spectroscopic data (that is, the actual energy levels of a substance, when determined and interpreted correctly, together with the apriori probabilities) offer the most accurate method known of obtaining entropies of gases. The methods used have been described by Giauque²⁸ in considerable detail and need not be repeated as no new calculations of this kind are to be made here. The results so calculated for the hydrogen halides, nitric oxide, oxygen, hydrogen, and iodine will be used, however; and the reader will be referred to the literature on these substances when they are considered later.

²⁶ Taylor, H. S., A Treatise on Physical Chemistry (vol. 2, ch. 17, by Rodebush, W.H.): D. Van Nostrand Co., New York, 1925 p. 1157.

²⁷ This equation is an empirical approximation which may be used only for solids. Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923. p. 150.

²⁸ (a) See footnote 25, p. 10.

(b) Giauque, W. F., The Calculation of Free Energy from Spectroscopic Data: Jour. Am. Chem. Soc., vol. 52, 1930, p. 4808.

(c) Giauque, W. F., The Entropy of Hydrogen and the Third Law of Thermodynamics. The Free Energy and Dissociation of Hydrogen: Jour. Am. Chem. Soc., vol. 53, 1931, p. 507.

CALCULATIONS FROM MEASURED VALUES OF ΔH AND ΔF

To round out the table, some entropies will be calculated from measured heats of reaction and free energies of reaction as determined by cell and equilibrium measurements. The entropy of reaction is related to these data thermodynamically by

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

where ΔS is the difference in entropy between the products of reaction and the reactants at the temperature T .²⁹ Thus, if ΔS and the entropies of all the substances taking part or formed in the reaction except one are known, that one may be calculated.

ABSOLUTE ENTROPIES(?)

None of the entropies given here should be considered absolute; they should be looked upon merely as values which to the best of our present knowledge are the ones to be used in thermodynamic calculations. There are some forms of entropy that cancel out in chemical reactions, an equivalent effect being present in both reactants and products. For example, the entropy of mixing of the isotopes in a substance such as ordinary lead need not be considered, for other atoms, in reacting with lead, apparently recognize no difference in the various isotopes. This fact is not surprising, as the outer parts of these isotopic atoms, the parts which are important in chemical reactions, are the same or very nearly so. Gibson and Heitler³⁰ have shown that the contribution of nuclear spin to the entropy cancels out for reactions involving monatomic and diatomic reactants and products. Further comment of a similar nature has been made recently concerning hydrogen³¹ and iodine.³² Presumably, this cancellation would be found for polyatomic molecules also.

Some investigators may prefer to try to give absolute values of entropies so far as is possible—subject, of course, to the present concept of this property. However, the present trend is to omit those portions that are known to pass unchanged through chemical reaction, since to do so involves less modification of previous results.

ENTROPIES AT 298.1° K. FOR ELEMENTS AND COMPOUNDS
FROM EXPERIMENTAL DATA

METHOD OF ESTIMATING ACCURACY

In the following pages recalculated entropy values are given for the elements and compounds based upon experimental data. The elements are considered in alphabetical order, and in most cases the compounds are classified according to their more electropositive constituents. All values are for a constant pressure of 1 atmosphere and a temperature of 298.1° K. and are expressed in 15° gram-calories per gram-formula weight.

²⁹ Lewis G. N., and Randall, M., *Thermodynamics and the Free Energy of Chemical Substances*: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 169.

³⁰ Gibson, G. E., and Heitler, W., *Die chemische Konstante in der neuen Quantenstatistik*: Ztschr. Physik, vol. 49, 1928, p. 465.

³¹ Giauque, W. F., *The Entropy of Hydrogen and the Third Law of Thermodynamics*. *The Free Energy and Dissociation of Hydrogen*: Jour. Am. Chem. Soc., vol. 52, 1930, p. 4816.

³² Giauque, W. F., *Nuclear Spin and the Third Law of Thermodynamics*. *The Entropy of Iodine*: Jour. Am. Chem. Soc., vol. 53, 1931, p. 507.

An attempt has been made to give an estimate of the accuracy of each result. In many cases this estimate is largely a matter of judgment. For the values obtained from specific-heat measurements the general procedure followed has been to consider that part of the entropy given by actual measurement separately from the part that is entirely extrapolation. The assumed accuracy of the portion given by measurement depended partly on the estimated errors in the data as given by the investigator responsible and partly on the information obtained by comparing results of several workers. The error in the extrapolated portion was generally taken as about 10 per cent, which seemed a reasonable compromise since the uncertainty should increase with the magnitude of the extrapolation and since, for substances whose specific heats have been measured down to temperatures so low that the Debye function or T^3 law is obeyed, an error of this magnitude on the extrapolated part of the entropy is only a negligible portion of the total entropy at 298.1° K.

In some cases, the specific-heat values of several experimenters have been averaged, while in others the results of a single investigator have been used. All the calculations given here have been checked independently by Mrs. S. M. Kelley. The references in this section form a nearly complete (to April, 1931) bibliography of *true* specific-heat data on the elements and inorganic compounds at low temperatures. A table giving specific-heat values for the substances whose entropies have been calculated from the third law of thermodynamics is given on page 50). These figures were read from the curves plotted for calculating entropies and may be used as guides in case it is desired to recheck the calculations given here.

In view of the recent discoveries concerning hydrogen, nitric oxide, and carbon monoxide and the existing doubt concerning paramagnetic compounds one must expect that application of the third law to existing specific-heat data will in some cases give entropy values that will have to be modified as information on the subject increases. Consequently, the fact is emphasized that the estimate of errors in third-law calculations applies only to the existing specific-heat data and to the necessary extrapolations, the assumption being made that the systems dealt with are ones in which complete thermal equilibrium is established among the energy states actually present.

ALUMINUM AND ITS COMPOUNDS

Element.—The specific heat of aluminum metal has been measured by Nernst³³ between 30° and 90° K., by Nernst and Schwes³⁴ between 20° and 80° K., and at higher temperatures by Griffiths and Griffiths.³⁵ A smooth curve through these values results in 6.73 units for the entropy between 17.78° and 298.1° K., and the extrapolation below 17.78° K. is 0.02. Thus, for Al, $S_{298.1} = 6.75 \pm 0.1$.

Oxide.—Parks and Kelley³⁶ have determined the specific heat of a pure sample of Al_2O_3 in the form of sapphires down to 90° K. These

³³ Nernst, W., *Der Energieinhalt fester Stoffe*: Ann. Physik, vol. 36, 1911, p. 395. See also Nernst, W., and Lindemann, F. A., *Spezifische Wärme und Quantentheorie*: Ztschr. Electrochem., vol. 17, 1911, p. 817.

³⁴ Nernst, W., and Schwes, F., *Untersuchungen über die spezifische Wärme bei tiefen Temperaturen*: Sitzb. könig. preuss. Akad. Wiss., 1914, p. 355.

³⁵ Griffiths, E. H., and Griffiths, E., *The Capacity for Heat of Metals at Low Temperatures*: Proc. Roy. Soc. (London), vol. A 90, 1914, p. 557.

³⁶ Parks, G. S., and Kelley, K. K., *The Heat Capacities of Some Metallic Oxides*: Jour. Phys. Chem., vol. 30, 1926, p. 47.

measurements give 11.51 for the entropy between 89.12° and 298.1° K. The extrapolation below 89.12° is 1.09. Therefore, for Al_2O_3 (sapphires), $S_{298.1} = 12.6 \pm 0.2$.

Silicates.—The specific heats down to about 20° K. of three forms of aluminum silicate, disthen (or cyanite), andalusite, and sillimanite, have been studied by Simon and Zeidler.³⁷ The entropy values are as follows:

Substance	$S_{22.39}$ (extrapolated)	$S_{298.1} - S_{22.39}$ (measured)	$S_{298.1}$ per formula weight of Al_2SiO_5
Disthen.....	0.03	20.63	20.7±0.3
Andalusite.....	.13	26.90	27.0±.3
Sillimanite.....	.04	25.00	25.0±.3

ANTIMONY AND ITS COMPOUNDS

Element.—The specific heat of antimony has been measured down to 65° K. by Anderson.³⁸ His measurements give 2.34 for the entropy extrapolation below 63.10° K. and 8.17 for that between 63.10° and 298.1° K., making $S_{298.1} = 10.5 \pm 0.3$. The results of Günther³⁹ between 80° and 100° K. do not agree with those of Anderson and have been neglected as they cover such a small temperature range.

Oxides.—Anderson⁴⁰ has also studied Sb_2O_3 , Sb_2O_4 , and two samples of Sb_2O_5 , which contained some water and lower oxides. The resulting entropy values are:

Substance	$S_{66.23}$ (extrapolated)	$S_{298.1} - S_{66.23}$ (measured)	$S_{298.1}$
Sb_2O_3	4.09	25.35	29.4±0.6
Sb_2O_4	4.31	26.04	30.4±.7
Sb_2O_5	2.54	27.32	29.9±1.2

The entropy of Sb_2O_5 is the most uncertain due to the corrections for water and the lower oxides.

ARGON

Element.—Specific-heat measurements on solid and liquid argon down to 17° K. were made by Eucken,⁴¹ who also determined the melting point as 83° K. and the heat of fusion as 267.8 calories per mole (mean value). More recently Eucken and Hauck⁴² have found 83.6° K. for the melting point and 265.2 calories per mole for the heat of fusion. Eucken's values are used in this work, however, as errors in a heat of fusion measurement are often partly compensated by the

³⁷ Simon, F., and Zeidler, W., Untersuchungen über die spezifischen Wärmen bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 123, 1926, p. 383.

³⁸ Anderson, C. T., The Heat Capacities at Low Temperatures of Antimony, Antimony Trioxide, Antimony Tetroxide, and Antimony Pentoxide: Jour. Am. Chem. Soc., vol. 52, 1930, p. 2712.

³⁹ Günther, P., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, vol. 63, 1920, p. 476.

⁴⁰ See footnote 38.

⁴¹ Eucken, A., Über das thermische Verhalten einiger komprimierter und kondensierter Gase bei tiefen Temperaturen: Verh. Deut. phys. Gesell., vol. 18, 1916, p. 4.

⁴² Eucken, A., and Hauck, F., Die spezifischen Wärmen C_p und C_v einiger Stoffe im festen, flüssigen und hyperkritischen Gebiet zwischen 80° und 320° abs.: Ztschr. physikal. Chem., vol. 134, 1928, p. 161.

measured values of specific heat near the melting point. Born's⁴³ value for the heat of vaporization at the boiling point (760 mm. pressure) is 1,544 calories per mole. The boiling-point temperature is given as 87.3° K. by Henning.⁴⁴ Accordingly, for the crystals, $S_{17.8} = 1.13$ (extrapolation) and $S_{83.0} - S_{17.8} = 8.10$ (measured). The entropy of fusion is $\frac{267.8}{83.0} = 3.23$, the entropy change in heating the liquid from 83.8 to 87.3° K. is 0.53, and the entropy of vaporization is $\frac{1,544}{87.3} = 17.69$. Bringing the argon gas to 298.1° by means of the value 4.97 calories per mole for the specific heat of a monatomic gas results in an entropy change of 6.10 units; therefore, for argon, the value of $S_{298.1}$ is $1.13 + 8.10 + 3.23 + 0.53 + 17.69 + 6.10$, or 36.8 ± 0.2 units.

The entropy of argon calculated from the Sackur equation is 36.99, to which can be assigned only an entirely negligible error. The agreement between these two methods of obtaining the entropy is excellent. The latter value, however, is considered the better of the two.

ARSENIC AND ITS COMPOUNDS

Element.—The specific heat of arsenic has been studied down to about 55° K. by Anderson.⁴⁵ His values give $S_{56.2} = 1.20$ (extrapolation) and $S_{298.1} - S_{56.2} = 7.16$, resulting in $S_{298.1} = 8.4 \pm 0.2$.

Oxides.—The data of Anderson on As_2O_3 and As_2O_5 give the values: For As_2O_3 , $S_{56.2} = 3.54$ (extrapolation), $S_{298.1} - S_{56.2} = 22.04$, and $S_{298.1}$ is therefore 25.6 ± 0.5 ; and for As_2O_5 , $S_{63.1} = 1.94$ (extrapolation), $S_{298.1} - S_{63.1} = 23.30$, and $S_{298.1} = 25.2 \pm 0.4$.

BARIUM AND ITS COMPOUNDS

Nitrate.—The specific heat of barium nitrate between 15° and 298.1° K. was measured by Latimer and Ahlberg.⁴⁶ Their measurements give $S_{298.1} = 51.1 \pm 0.4$ per formula weight. This result involves an extrapolation of 0.56 below 15.8° K.

BERYLLIUM

Element.—Thermal data at low temperatures on beryllium and its compounds are extremely meager. The value, 0.125 calorie per gram-atom, is given as the mean specific heat of the metal between the boiling points of liquid nitrogen and liquid hydrogen by Dewar.⁴⁷ Lewis and Gibson⁴⁸ were able to utilize Dewar's mean values on a number of metals for entropy calculations. Their process consisted essentially of dividing his mean value by a factor, 1.085, and determining the θ_D for a Debye function from the resulting, single figure. For beryllium, however, they misplaced the decimal point in Dewar's

⁴³ Born, F., Über Dampfdruckmessungen an reinem Argon: Ann. Physik, vol. 69, 1922, p. 473.

⁴⁴ Henning, F., Grundlagen, Methoden, und Ergebnisse der Temperaturmessung: Friedr. Vieweg & Sohn, Braunschweig, 1915, p. 275.

⁴⁵ Anderson, C. T., The Heat Capacities of Arsenic, Arsenic Trioxide, and Arsenic Pentoxide at Low Temperatures: Jour. Am. Chem. Soc., vol. 52, 1930, p. 2296.

⁴⁶ Latimer, W. M., and Ahlberg, J. E., Die spezifische Wärme von Bariumnitrat von 15° bis 300° abs. Die Entropie des Nitrats: Ztschr. Physikal. Chem., Abt. A, vol. 148, 1930, p. 464.

⁴⁷ Dewar, J. D., Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Hydrogen I. The Mean Atomic Specific Heats at 50° Absolute of the Elements, a Periodic Function of the Atomic Weights: Proc. Roy. Soc. (London), vol. A 89, 1913, p. 158.

⁴⁸ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

specific-heat value and obtained an entropy that is much too high. Repetition of this calculation on the datum of Dewar gives $S_{298.1} = 3.3$ (θ_D being 776).

More recently Simon and Ruhemann,⁴⁹ from two measurements of the specific heat near 75° K., have given 1,035 for the value of θ_D for a sample of pure beryllium metal. The entropy at 298.1° K. corresponding to this value of θ_D is 2.1 ± 0.1 units (0.1 having been added for the difference $S_p - S_v$). This value is substantiated by the work of Lewis,⁵⁰ who has measured the specific heat of beryllium at room temperature, liquid-air temperature, and one intermediate point. His data give $S_{298.1} = 2.14 \pm 0.05$ for beryllium, with an extrapolation below 89.1° K. of only 0.09 unit. In view of the good agreement between the two latter results, it must be concluded that Dewar's measurement and the entropy value calculated therefrom are inaccurate; therefore, 2.14 ± 0.05 is adopted as the entropy of beryllium at 298.1° K.

Oxide.—Günther's⁵¹ specific-heat data on BeO between 75° and 85° are insufficient for an entropy calculation on this substance.

BISMUTH AND ITS COMPOUNDS

Element.—The heat capacity of bismuth metal has been determined by Keesom and van den Ende⁵² from about 4° to 20° K. and by Anderson⁵³ from 60° to 298° K. Merging these two sets of values, one obtains $S_{3.16} = 0.005$ (extrapolation) and $S_{298.1} - S_{3.16} = 13.76$ (from measurements); therefore, the entropy at 298.1° K. is 13.8 ± 0.6 . Anderson gives 12.4 ± 0.3 , based on his measurements only. The curve obtained by joining these two sets of results seems abnormally flat. These investigators may have studied two different crystalline modifications; however, for the present, the value 13.8 ± 0.6 is recommended.

Oxide.—Anderson's data on Bi_2O_3 lead to the values, $S_{56.2} = 6.22$ (extrapolation) and $S_{298.1} - S_{56.2} = 29.96$, making $S_{298.1} = 36.2 \pm 0.7$.

BROMINE

Element.—The specific heat of solid bromine has been studied down to 20° K. by Suhrmann and von Lüde⁵⁴ and down to 15° K. by Latimer and Hoenshel.⁵⁵ The results of the latter investigators will be relied on entirely in this paper, as the data of the former are extremely erratic. Weber⁵⁶ has given the melting point as 265.9° K. and Regnault,⁵⁷ the heat of fusion as 2,580 calories per mole. A mean specific

⁴⁹ Simon, F., and Ruhemann, M., Ein neuer Apparat zur schnellen Bestimmung von spezifischen Wärmen fester Körper bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 129, 1927, p. 321.

⁵⁰ Lewis, E. J., Some Thermal and Electrical Properties of Beryllium: Phys. Rev., vol. 34, 1929, p. 1575.
⁵¹ Günther, P., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 51, 1916, p. 828.

⁵² Keesom, W. H., and van den Ende, J. N., The Specific Heat of Solid Substances at the Temperatures Obtainable with the Aid of Liquid Helium. II. Measurement of the Atomic Heats of Lead and Bismuth: Proc. Acad. Sci. Amsterdam, vol. 33, 1930, p. 243.

⁵³ Anderson, C. T., The Heat Capacities of Bismuth and Bismuth Trioxide at Low Temperatures: Jour. Am. Chem. Soc., vol. 52, 1930, p. 2720.

⁵⁴ Suhrmann, R., und von Lüde, K., Die spezifische Wärme des Broms bei tiefen Temperaturen und seine chemische Konstante: Ztschr. Physik, vol. 29, 1924, p. 71.

⁵⁵ Latimer, W. M., and Hoenshel, H. D., The Heat Capacity and Entropy of Lead Bromide and Bromine: Jour. Am. Chem. Soc., vol. 48, 1926, p. 19.

⁵⁶ Weber, H. C. P., The Atomic Weight of Bromine: U. S. Bureau of Standards Bull., vol. 9, 1913, p. 131.

⁵⁷ Regnault, V., Sur la chaleur spécifique, et la chaleur latente de fusion du brome, et sur la chaleur spécifique du mercure solide: Ann. chim. phys., series 3, vol. 26, 1849, p. 268.

heat of liquid bromine was measured near room temperature by Andrews.⁵⁸

The data of Latimer and Hoenshel lead to the values $S_{14.1} = 0.68$ (extrapolation) and $S_{265.9} - S_{14.1} = 24.32$ (from measurements), making the value for bromine crystals at the melting point $S_{269.5} = 25.00$. The entropy of fusion, $\frac{2,580}{265.9}$, is 9.70, and the entropy change in heating the liquid from the melting point to 298.1° K. is 1.94; therefore, for liquid bromine per mole (Br_2), $S_{298.1} = 25.00 + 9.70 + 1.94 = 36.6 \pm 0.5$.

CADMIUM AND ITS COMPOUNDS

Element.—The heat capacity of metallic cadmium has been measured down to 70° K. by Rodebush⁵⁹ and down to 10° K. by Lange and Simon.⁶⁰ A few values are also given by Griffiths and Griffiths.⁶¹ The work of Lange and Simon has been given the most weight. Their table of smoothed values extending from 10° to 600° K. seems to be satisfactory; therefore, their calculations are used, from which $S_{10.0} = 0.07$ for the extrapolated portion and $S_{298.1} - S_{10.0} = 12.27$ for the part given by measurement. The result is $S_{298.1} = 12.3 \pm 0.1$.

Oxide.—The specific-heat data of Millar⁶² on CdO extending down to 70° K. lead to the values, $S_{70.8} = 2.16$ (extrapolation) and $S_{298.1} - S_{70.8} = 10.94$ (measured); therefore, $S_{298.1} = 13.1 \pm 0.3$.

CÆSIUM

Element.—Data for the calculation of the entropy of solid cæsium do not exist, but the Sackur equation with $R \ln 2$ added gives $S_{298.1} = 41.95$ for the gas.

CALCIUM AND ITS COMPOUNDS

Element.—Günther⁶³ has measured the specific heat of calcium metal between 20° and 60° K., Eastman and Rodebush⁶⁴ have studied an impure sample down to 67° K., and recently Clusius and Vaughen⁶⁵ have made measurements down to 10° K. Relying almost entirely on the data of the latter investigators, the entropy values are $S_{10.0} = 0.013$ (extrapolation), $S_{298.1} - S_{10.0} = 9.94$, and $S_{298.1} = 9.95 \pm 0.1$.

Oxide.—Parks and Kelley⁶⁶ have studied the specific heat of a sample of CaO down to 87° K. Their results extrapolate smoothly into the lower-temperature portion of the data of Nernst and Schwers.⁶⁷ The

⁵⁸ Andrews, T., On the Specific Heat of Bromine: *Quart. Jour. Chem. Soc. (London)*, vol. 1, 1849, p. 18; Über die spezifische Wärme des Broms: *Poggendorf's Ann.*, vol. 75, 1848, p. 335.

⁵⁹ Rodebush, W. H., The Atomic Heats of Cadmium and Tin at Low Temperatures: *Jour. Am. Chem. Soc.*, vol. 45, 1923, p. 1413.

⁶⁰ Lange, F., and Simon, F., Spezifische Wärme and chemische Konstante des Cadmiums: *Ztschr., physical Chem.*, vol. 134, 1928, p. 374.

⁶¹ Griffiths, E. H., and Griffiths, E., The Capacity for Heat of Metals at Low Temperatures: *Proc. Royal Soc. (London)*, vol. A90, 1914, p. 557.

⁶² Millar, R. W., The Heat Capacity at Low Temperatures of Zinc Oxide and of Cadmium Oxide: *Jour. Am. Chem. Soc.*, vol. 50, 1928, p. 2653.

⁶³ Günther, P., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: *Ann. Physik*, series 4, vol. 51, 1916, p. 828.

⁶⁴ Eastman, E. D., and Rodebush, W. H., The Specific Heats at Low Temperatures of Sodium, Potassium, Magnesium and Calcium Metals, and of Lead Sulphide: *Jour. Am. Chem. Soc.*, vol. 40, 1918, p. 489.

⁶⁵ Clusius, K., and Vaughen, J. V., I. The Specific Heats of Thallium, Calcium and Magnesium Measured to 10° Absolute. II. The Entropy and Chemical Constants of Magnesium from Spectroscopic Data: *Jour. Am. Chem. Soc.*, vol. 52, 1930, p. 4686.

⁶⁶ Parks, G. S., and Kelley, K. K., The Heat Capacities of Some Metallic Oxides: *Jour. Phys. Chem.*, vol. 30, 1926, p. 47.

⁶⁷ Nernst, W., and Schwers, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: *Sitzb. könig. preuss. Akad. Wiss.*, 1914, p. 355.

resulting entropy values are $S_{28.2} = 0.04$ (extrapolation), $S_{298.1} - S_{28.2} = 9.46$, and $S_{298.1} = 9.5 \pm 0.2$.

Sulphide.—Anderson's⁶⁵ specific-heat measurements on CaS down to 58° K. result in the following entropy values: $S_{56.2} = 1.32$ (extrapolation), $S_{298.1} - S_{56.2} = 12.21$, and $S_{298.1} = 13.5 \pm 0.3$.

Fluoride.—The specific heats of CaF₂ (fluorspar) down to 17° K. have been measured by Eucken and Schwers.⁶⁶ The extrapolated portion of the entropy is $S_{17.8} = 0.02$ and the measured part is $S_{298.1} - S_{17.8} = 16.38$. The entropy at 298.1° K. is therefore $S_{298.1} = 16.4 \pm 0.4$.

Carbonates.—The data of Günther⁷⁰ on aragonite down to 23° K. lead to the values $S_{22.4} = 0.07$ (extrapolation), $S_{298.1} - S_{22.4} = 18.80$ (measured), and $S_{298.1} = 19.9 \pm 0.5$.

The data of Nernst and Schwers⁷¹ on calcite extend down to about 22° K. The entropy extrapolated below 22.4° K. amounts to 0.76 and that from the measurements to 22.21, making $S_{298.1} = 23.0 \pm 2.0$. More recently, Bäckström⁷² has studied the transition between calcite and aragonite by thermodynamic methods and arrives at the figure 0.74 ± 0.2 for the entropy of transition at 298.1° K. Consequently, the value $19.9 \pm 0.5 + 0.74 \pm 0.2 = 20.6 \pm 0.7$ is preferable for the entropy of calcite at 298.1° K.

Silicate.—A pure, synthetic sample of CaSiO₃ in the form pseudowollastonite was studied by Parks and Kelley⁷³ down to 88° K. Their measurements lead to the values $S_{89.1} = 5.17$ (extrapolation), $S_{298.1} - S_{89.1} = 17.01$, and $S_{298.1} = 22.2 \pm 0.7$.

Hydride.—Günther⁷⁴ has made specific-heat measurements on CaH₂ between 70° and 86° K. Applying the n -formula of Lewis and Gibson⁷⁵ to his results, the value $S_{298.1} = 9.9 \pm 1.0$ is obtained. This result is in disagreement with dissociation pressure data on CaH₂.⁷⁶

Hydroxide.—The n -formula applied to the results of Nernst and Schwers⁷⁷ on Ca(OH)₂ between 20° and 90° K. leads to the result, $S_{298.1} = 17.4 \pm 1.0$.

CARBON AND ITS COMPOUNDS

Element.—Nernst⁷⁸ has studied the heat capacity of diamonds down to 30° K. and finds that at about 50° K. the specific heat of this modification is practically zero (to three significant figures). He has also studied β graphite down to 29° K. where its specific heat is 0.06 calorie per gram-atom. As there are no newer data to consider, the entropy values are $S_{298.1} = 0.6$ for diamond and $S_{298.1} = 1.3$ for β graphite. The extrapolations involved are negligible, being zero (within the limits

⁶⁵ Anderson, C. T., The Heat Capacities at Low Temperatures of Manganese Sulphide, Ferrous Sulphide, and Calcium Sulphide: Jour. Am. Chem. Soc., vol. 53, 1931, p. 476.

⁶⁶ Eucken, A., and Schwers, F., Eine experimentelle Prüfung des T³ Gesetzes für den Verlauf der spezifischen Wärme fester Körper bei tiefen Temperaturen: Ber. Deut. phys. Gessell., vol. 15, 1913, p. 578.

⁷⁰ Günther, P., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 51, 1916, p. 823.

⁷¹ Nernst, W., and Schwers, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Sitzb. könig. preuss. Akad. Wiss., 1914, p. 355.

⁷² Bäckström, H. L. J., The Thermodynamic Properties of Calcite and Aragonite: Jour. Am. Chem. Soc., vol. 47, 1925, p. 2432.

⁷³ Parks, G. S., and Kelley, K. K., The Heat Capacity of Calcium Silicate: Jour. Phys. Chem., vol. 30, 1926, p. 1175.

⁷⁴ Günther, P., Untersuchungen über die spezifischen Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 51, 1916, p. 823.

⁷⁵ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2564.

⁷⁶ Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 473.

⁷⁷ Nernst, W., and Schwers, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Sitzb. könig. preuss. Akad. Wiss., 1914, p. 355.

⁷⁸ Nernst, W., Der Energieinhalt fester Stoffe: Ann. Physik, vol. 36, 1911, p. 395. See also Nernst, W., and Lindemann, F. A., Spezifische Wärme und Quantentheorie: Ztschr. Electrochem., vol. 17, 1911, p. 817.

of experimental error) for diamond and about 0.02 for β graphite. Thus, from the standpoint of thermodynamic calculations, since the entropies are so small, the values at 298.1° K. also contain only negligible errors. The form of elementary carbon, which has been adopted as the standard for free-energy calculations, is β graphite.⁷⁹

Carbon monoxide.—The specific heats of solid and liquid CO have been measured down to 17° K. by Eucken⁸⁰ and, more recently, down to 12° K. by Clusius.⁸¹ Both investigators also determined the temperature and heat of fusion and the temperature and heat of transition between two crystalline modifications. Olszewski⁸² has determined the boiling point (760 mm. pressure) as 83.1° K. from vapor-pressure measurements, and Eucken has obtained 1,414 calories per mole for the heat of vaporization.

The specific heat of the gas at 93° K. and 291° K. was measured by Scheel and Heuse.⁸³

From these measurements, $S_{11.2} = 0.41$ (extrapolation), which, added to the entropy obtained graphically up to the transition point (61.5° K. by Clusius), gives $S_{61.5} = 10.10$ for the entropy of the low-temperature crystal form. The entropy of transition is $\frac{151.2}{61.5} = 2.46$ (using the data of Clusius), and the entropy change involved in heating the high-temperature form to the melting point (68.2° K.) is 1.26.

The entropy of fusion, $\frac{201.5}{68.2}$, is 2.95. To heat the liquid from 68.2° to 83.1° K. the addition of 2.86 units of entropy is required. For vaporization the entropy change is $\frac{1,414}{83.1}$, or 17.02. An increment of 9.12 units is necessary to warm the gas to 298.1° K.; therefore, $S_{298.1} = 10.10 + 2.46 + 1.26 + 2.95 + 2.86 + 17.02 + 9.12 = 45.8$.

The free-energy equation of Lewis and Randall⁸⁴ gives $\Delta F_{298}^{\circ} = -32,510$ calories and $\Delta H_{298} = -26,150$ calories, making the entropy of formation of CO equal to 21.3 units. Using the entropy for β graphite (1.3) and the value for oxygen to be listed later (49.0 per mole), the entropy of CO at 298.1° K. is 47.1.

Eastman⁸⁵ has recently reviewed the data on CO and obtained a free-energy equation in conformity with $\Delta F_{298}^{\circ} = -32,265$ calories and $\Delta H_{298} = -26,320$ calories. These figures result in $S_{298.1} = 45.7$.

Recently, in a conversation with the author, W. F. Giaque stated that he had obtained $S_{298.1} = 47.3 \pm 0.1$ for the entropy of carbon monoxide from spectroscopic data. This value agrees with Lewis and Randall's⁸⁶ free-energy equation and will be adopted here. The value from specific heats would previously have been thought entirely satisfactory. Just what causes the difference is at present unknown.

⁷⁹ Lewis, G. N., and Randall, M., *Thermodynamics and the Free Energy of Chemical Substances*: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 569.

⁸⁰ Eucken, A., Über das thermische Verhalten einiger komprimierter und kondensierter Gase bei tiefen Temperaturen: *Verh. Deut. phys. Gessell.*, vol. 18., 1916, p. 4.

⁸¹ Clusius, K., Über die spezifische Wärme einiger kondensierter Gase zwischen 10° abs. und ihrem Tripelpunkt: *Ztschr. physikal. Chem.*, Abt. B, vol. 3, 1929, p. 41.

⁸² Olszewski, V., Relation entre les températures et les pressions du protoxyde de carbone liquide: *Compt. rend.*, vol. 99, 1884, p. 706.

⁸³ Scheel, K., and Heuse, W., Die spezifische Wärme von Helium und einiger zweiatomigen Gasen: *Ann. Physik*, series 4, vol. 40, 1913, p. 473.

⁸⁴ Lewis, G. N., and Randall, M., *Thermodynamics and the Free Energy of Chemical Substances*: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 576.

⁸⁵ Eastman, E. D., *The Free Energy of Water, Carbon Monoxide, and Carbon Dioxide*: *Inf. Circ.* 6125, Bureau of Mines, 1929, 15 pp.

⁸⁶ See footnote 84.

The magnitude, however, is so near to $R \ln 2$ that an entropy of mixing two components in equal portions is indicated.

Carbon dioxide.—Specific-heat measurements on solid CO_2 have been made by Eucken⁸⁷ down to 19°K . and by Eucken and Hauck⁸⁸ down to 80°K . Henning and Stock⁸⁹ have determined the sublimation point (760 mm. pressure) as 194.6°K ., and Andrews⁹⁰ has measured the heat of sublimation as 6,210 calories per mole. From the sublimation pressure data of several investigators,⁹¹ 6,240 calories per mole was calculated for the heat of sublimation, from the equation $\frac{dR \ln P}{dT} = -\Delta H$. A mean value of 6,220 calories per mole may be taken.

Heuse⁹² gives two specific-heat values for CO_2 gas.

In the calculation of entropy, $S_{17.8} = 0.32$ by extrapolation and $S_{194.6} = 16.80$ for the solid. The entropy of sublimation, $\frac{6,220}{194.6}$, is 31.96, and the entropy change on heating the gas from 194.6° to 298.1°K . is 3.61; therefore, $S_{298.1} = 16.80 + 31.96 + 3.61 = 52.4$ units.

Eastman's⁹³ free-energy equation for the formation of CO_2 gas from the elements puts $\Delta F_{298}^\circ = -93,647$ calories and $\Delta H_{298} = -94,270$ calories. The ΔS of reaction corresponding to these figures is -2.1 , from which $S_{298.1} = 48.2$ for CO_2 , which disagrees with the third-law value.

The free-energy equation of Lewis and Randall⁹⁴ results in the value, 50.4, while Bäckström⁹⁵ has calculated the value as 50.8 and 49.2 depending on the entropy value used for calcite. It thus appears that the third-law value may be considerably too high, but the reason is by no means obvious. The specific-heat data of Eucken on the other condensed gases studied give reasonably accurate entropy values. The heats of sublimation as obtained by two different methods are also in agreement, and the contribution of the gas amounts to only 3.61 entropy units which can not be greatly in error. If the third law had resulted in too low a value an explanation might be found more readily. Perhaps the best that can be done at present is to take the value 50 ± 2 units for the entropy of CO_2 gas at 298.1°K . In using the free-energy equation of Eastman, or Lewis and Randall, however, the value for the entropy employed should be the one that is consistent. It is unfortunate that the entropy of such an important substance as CO_2 has not been definitely settled.

Methane.—Methane has been investigated by Eucken and Karwat⁹⁶ down to 28°K . and by Clusius⁹⁷ down to 10°K . The heat and tem-

⁸⁷ Eucken, A., Über das thermische Verhalten einiger komprimierter und kondensierter Gase bei tiefen Temperaturen: Verh. Deut. phys. Gesell., vol. 18, 1916, p. 4.

⁸⁸ Eucken, A., and Hauck, F., Die spezifischen Wärmen C_p und C_v einiger Stoffe im festen, flüssigen, und hyperkritischen Gebiet zwischen 80° und 320°abs : Ztschr. physikal. Chem., vol. 134, 1928, p. 161.

⁸⁹ Henning, F., and Stock, A., Über die Sättigungsdrucke einiger Dämpfe zwischen $+10$ und -181° : Ztschr. Physik, vol. 4, 1921, p. 226.

⁹⁰ Andrews, J. W., The Heat of Sublimation of Carbon Dioxide: Jour. Am. Chem. Soc., vol. 47, 1925, p. 1597.

⁹¹ Landolt-Börnstein, —, Physikalisch-chemische Tabellen: Vol. 2, Julius Springer, Berlin, 1923, p. 1341.

⁹² Heuse, W., Die spezifische Wärme von Argon und einigen mehratomigen Gasen: Ann. Physik., series 4, vol. 59, 1919, p. 86.

⁹³ See footnote 85.

⁹⁴ See footnote 84.

⁹⁵ Bäckström, H. L. J., The Heat of Dissociation of Calcium Carbonate and the Entropy of Carbon Dioxide: Jour. Am. Chem. Soc., vol. 47, 1925, p. 2443.

⁹⁶ Eucken, A., and Karwat, E., Die Bestimmung des Warmeinhaltes einiger kondensierter Gase: Ztschr. physikal. Chem., vol. 112, 1924, p. 467.

⁹⁷ Clusius, K., Über die spezifischen Wärme einiger kondensierter Gase zwischen 10°abs . und ihrem Tripelpunkt: Ztschr. physikal. Chem., A. B., vol. 3, 1929, p. 41.

perature of fusion have been measured in both investigations. The latter work, having been carried to lower temperatures, makes possible a calculation of the entropy change in the transition range near 20° K. It also appears to be considerably more accurate than the work of Eucken and Karwat. The vapor-pressure data of Stock, Henning, and Kuss⁹⁸ fix the boiling point at 111.7° K. and make possible the calculation of 2,040 calories per mole as the heat of vaporization. Specific-heat measurements on CH₄ gas have been made by Millar,⁹⁹ Heuse,^{99a} and Dixon, Campbell, and Parker.¹

The extrapolated portion of the entropy was $S_{10,0} = 0.31$. The entropy in the transition range was calculated by extending Clusius's² specific-heat curves above and below this region to the mean temperature, 20.4° K., and using his value of 18.1 calories heat absorption, which apparently was obtained in a similar manner. This method results in a value of 0.89 unit. The remaining entropy of the crystals up to the melting point was obtained graphically as 12.43. The entropy of fusion, $\frac{224.0}{90.6}$, is 2.47, and that required for heating the liquid to 111.7° K. is 2.70. For the vaporization the entropy change is $\frac{2,040}{111.7} = 18.26$, and the contribution from warming the gas to 298.1° K. is 7.45. The result for $S_{298.1}$ is, then, $0.31 + 0.89 + 12.43 + 2.47 + 2.70 + 18.26 + 7.45$, or 44.5 ± 0.5 unit.

The equilibrium data of Randall and Mohammad,³ with Rossini's⁴ value for the heat of formation of methane, lead to the value $S_{298.1} = 45.3$, while Randall and Gerard's⁵ data result in $S_{298.1} = 42.4$. The value from the third law, 44.5 ± 0.5 , is probably the more reliable and is close to the mean of those given by studies of equilibria.

Other organic compounds.—Specific-heat data at low temperatures are adequate to enable the calculation of the entropies of a large number of organic compounds. Except for methane, these substances are of practically no importance metallurgically and need not be considered here. In a letter to the author Prof. G. S. Parks, of Stanford University, stated that he is writing a monograph on the thermodynamic properties of organic compounds in which all the existing low-temperature thermal data will be reviewed.

CERIUM

Element.—Lewis and Gibson,⁶ utilizing the mean specific-heat measurement of Dewar,⁷ have calculated the entropy of cerium metal at

⁹⁸ Stock, A., Henning, F., and Kuss, E., Dampdrucktaten für Temperaturbestimmungen zwischen +25° und -185°: Ber. Deut. chem. Gesell., vol. 54, 1921, p. 1119.

⁹⁹ Millar, R. W., The Specific Heats of Polyatomic Gases at Low Temperatures: Jour. Am. Chem. Soc., vol. 45, 1923, p. 874.

^{99a} Heuse, W., Die spezifische Wärme von Argon und einigen mehrtomigen Gasen: Ann., Physik, series 4, vol. 59, 1919, p. 86.

¹ Dixon, H. B., Campbell, C., and Parker, A., On the Velocity of Sound in Gases at High Temperatures, and the Ratio of the Specific Heats: Proc. Roy. Soc. (London), vol. A 100, 1921, p. 1.

² Clusius, K., Über die spezifische Wärme einiger kondensierter Gase zwischen 10° abs. und ihrem Tripelpunkt: Ztschr. physikal. Chem., Abt. B., vol. 3, 1928, p. 41.

³ Randall, M., and Mohammad, A., Synthesis and Free Energy of Methane: Ind. and Eng. Chem., vol. 21, 1929, p. 1048.

⁴ Rossini, F. D., The Heats of Combustion of Methane and Carbon Monoxide: Bureau of Standards Jour. of Research, vol. 6, 1931, p. 37.

⁵ Randall, M., and Gerard, F. W., Synthesis of Methane from Carbon Dioxide and Hydrogen: Ind. and Eng. Chem., vol. 20, 1928, p. 1335.

⁶ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

⁷ Dewar, J. D., Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Hydrogen. I. The Mean Atomic Specific Heats at 50° Abs. of the Elements a Periodic Function of the Atomic Weights: Proc. Roy. Soc. (London), vol. A-89, 1913, p. 158.

298.1° K. by the method outlined under "Beryllium." As no new data have appeared, the author will use this value, 13.8, which may be in error as much as 0.8. The measurements of Simon and Ruhemann⁸ were made at 71° K., where the specific heat of cerium is above 6 calories per gram-atom, which prohibits the calculation of θ_D for a Debye function from their data.

CHLORINE

Element.—Eucken and Karwat⁹ have measured the specific heats of solid and liquid chlorine down to 22° K. and have also determined the melting point and heat of fusion. Eucken and Hoffman¹⁰ have given values for the specific heat of the gas at several temperatures. Estreicher and Schnerr¹¹ have determined 4,380 calories per mole as the heat of vaporization, and Trautz and Gerwig¹² have given the boiling point (760 mm. pressure) as 238.4° K.

The entropy extrapolated below 17.8° K. is 0.59, and the entropy of the crystals at the melting point (170.8° K.) is 17.70. The entropy of fusion, $\frac{1,615}{170.8}$, is 9.46, and that for the liquid range is 5.42. For vaporization, the entropy change is $\frac{4,380}{238.4}$ or 18.37, and the portion due to heating the gas to 298.1° K. is 1.85. Then, $S_{298.1} = 17.70 + 9.46 + 5.42 + 18.37 + 1.85 = 52.8 \pm 0.5$ per mole (Cl_2) of gas.

As an independent method of obtaining the entropy one may use the data of Gerke,¹³ who by means of measurements on cells obtained the value $\Delta S_{298} = -13.7$ for the reaction $\text{Ag} + \frac{1}{2} \text{Cl}_2 = \text{AgCl}$. If the entropy values for silver and silver chloride are used (10.2 ± 0.1 and 23.0 ± 0.1 , respectively), which will be given later, the value for one-half mole of chlorine is

$$\frac{1}{2} S_{298.1} = -\Delta S + S_{\text{AgCl}} - S_{\text{Ag}} = 13.7 + 23.0 - 10.2 = 26.5,$$

which makes the value per mole of chlorine gas $S_{298.1} = 53.0 \pm 0.4$. This result is in complete agreement with the third-law value and is based on data that are somewhat more reliable.

CHROMIUM

Element.—Lewis and Gibson¹⁴ have calculated $S_{298.1} = 5.8$ for chromium metal from Dewar's¹⁵ data. The measurements of Simon and

⁸ Simon F., and Ruhemann, M., Ein neuer Apparat zur schnellen Bestimmung von spezifischen Wärmen fester Körper bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 129, 1927, p. 321.

⁹ Eucken, A., and Karwat, E., Die Bestimmung des Wärmehaltes einiger kondensierter Gase: Ztschr. physikal. Chem., vol. 112, 1924, p. 467.

¹⁰ Eucken, A., and Hoffman, G., Die spezifische Wärme der Gase bei mittleren und hohen Temperaturen. II. Die spezifische Wärme des Chlors zwischen -30° und $+180^\circ \text{C}$.: Ztschr. physikal. Chem., Abt. B, vol. 5, 1929, p. 442.

¹¹ Landolt-Börnstein, —, Physikalisch-chemische Tabellen: Vol. 2, Julius Springer, Berlin, 1923, p. 1475.

¹² Trautz, M., and Gerwig, W., Der Dampfdruck flüssigen Chlors: Ztschr. anorg. Chem., vol. 134, 1924, p. 417.

¹³ Gerke, R. H., Temperature Coefficient of Electromotive Force of Galvanic Cells and the Entropies of Reactions: Jour. Am. Chem. Soc., vol. 44, 1922, p. 1684.

¹⁴ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

¹⁵ Dewar, J. D., Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Hydrogen. I. The Mean Atomic Specific Heats at 50° Abs. of the Elements a Periodic Function of the Atomic Weights: Proc. Roy. Soc. (London), vol. A-89, 1913, p. 158.

Ruhemann¹⁶ between 70° and 80° K. on a sample of chromium of about 92 per cent purity give $\theta_D = 486$, from which $S_{298.1} = 5.5$ (0.1 having been added for $S_p - S_0$). The mean value 5.6 ± 0.2 will be adopted in this work.

COBALT

Element.—The data of Simon and Ruhemann¹⁷ on pure cobalt give $\sigma_D = 383$. The corresponding entropy is $S_{298.1} = 6.8 \pm 0.2$, which is used instead of the value, 7.2, calculated from Dewar's data by Lewis and Gibson.¹⁸

COPPER AND ITS COMPOUNDS

Element.—The true specific heat of copper at low temperatures has been studied by several investigators as follows: Nernst¹⁹ (3° to 88° K.), Keesom and Onnes²⁰ (14° to 90° K.), Eucken and Werth²¹ (recrystallized copper, 95° to 215° K.; beaten copper, 84° to 183° K.), and Griffiths and Griffiths²² (50° to 390° K.). The work of Eucken and Werth was very timely, as it covered a temperature range in which previous data were scarce and showed that the working of copper contributed very little change to the specific heat in the region studied.

The entropy of copper calculated from these data is $S_{298.1} = 7.92 \pm 0.1$ of which only 0.01 is extrapolation below 14.1° K.

Cuprous oxide.—Millar²³ has measured the specific heat of cuprous oxide down to 75° K. The specific-heat curve of this substance is abnormally flat, and work now in progress at the Pacific Experiment Station throws some doubt on the form of the material used by Millar, as it may have been either a mixture of two crystalline forms of cuprous oxide or of solid solutions of cuprous oxide, cupric oxide, and copper. It is also evident that Millar's entropy calculation is in error. The value calculated from his data is $S_{298.1} = 24.1 \pm 1.5$, of which 7.85 is extrapolation below 70.8° K. Further study at lower temperatures is necessary before a more reliable entropy value may be given for this substance.

Cupric oxide.—Millar has also made specific-heat measurements on cupric oxide down to 70° K., while Clusius and Harteck²⁴ have studied this material from 30° to 200° K. Millar found a curious, nonreversible region centered around 220° K. on which more information would be desirable.

The entropy value for cupric oxide from these two sets of measurements is $S_{298.1} = 10.4 \pm 0.2$, of which 0.13 is the extrapolation below 28.2° K.

¹⁶ Simon, F., and Ruhemann, M., Ein neuer Apparat zur schnellen Bestimmung von spezifischen Wärmen fester Körper bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 129, 1927, p. 321.

¹⁷ See footnote 16.

¹⁸ See footnote 14.

¹⁹ Nernst, W., Der Energieinhalt fester Stoffe: Ann. Physik, vol. 36, 1911, p. 395. See also Nernst, W., and Lindemann, F. A., Spezifische Wärme und Quantentheorie: Ztschr. Electrochem., vol. 17, 1911, p. 817.

²⁰ (a) Keesom, W. H., and Onnes, H. K., The Specific Heat at Low Temperatures. I. Measurements on the Specific Heat of Lead between 14° and 80° K. and of Copper between 15° and 22° K.: Com. Phys. Lab. Leiden No. 143, vol. 13, 1914.

(b) Keesom, W. H., and Onnes, H. K., The Specific Heat at Low Temperatures. II. Measurements on the Specific Heat of Copper between 14° and 90° K.: Com. Phys. Lab. Leiden No. 147a, 1915.

²¹ Eucken, A., and Werth, H., Die spezifische Wärme einiger Metalle und Metalllegierungen bei tiefen Temperaturen: Ztschr. anorg. allgem. Chem., vol. 188, 1930, p. 152.

²² Griffiths, E. H., and Griffiths, E., The Capacity for Heat of Metals at Low Temperatures: Proc. Roy. Soc. (London), vol. A-90, 1914, p. 557.

²³ Millar, R. W., The Heat Capacities at Low Temperatures of "Ferrous oxide," Magnetite, and Cuprous and Cupric Oxides: Jour. Am. Chem. Soc., vol. 51, 1929, p. 215.

²⁴ Clusius, K., and Harteck, P., Über die spezifischen Wärmen einiger fester Körper bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 134, 1928, p. 243.

Sulphides.—Anderson²⁵ has studied the specific heats of Cu₂S (synthetic) down to 58° K. and CuS (covellite) down to 60° K. From his data the entropy of Cu₂S is 28.9 ± 0.8 at 298.1° K., while that of CuS is 15.9 ± 0.4. The extrapolation on Cu₂S is 5.43 below 50.1° K., and that on CuS is 2.56 below 56.2° K.

Iodide.—The specific heat of CuI has been studied by Simon²⁶ down to 16° K. The entropy extrapolation below 15.8° K. is 0.50, and the entropy at 298.1° K. is 23.1 ± 0.3

GALLIUM

Element.—The specific heat of gallium metal down to 15° K. has been measured by Clusius and Harteck.²⁷ Unfortunately, the shrinking and flaking of this material, due to cooling and heating at low temperatures, caused poor thermal contact in their calorimeter, which resulted in very large heat-interchange corrections. The entropy calculated from their data is $S_{298.1} = 10.2 \pm 0.5$, of which 0.13 is extrapolation below 14.1° K.

GOLD

Element.—Clusius and Harteck's²⁸ heat-capacity measurements on pure gold extend down to 15° K. The entropy extrapolation on their measurements amounts to only 0.11 below 14.1° K., and the entropy of gold is $S_{298.1} = 11.4 \pm 0.1$

HELIUM

Element.—For helium, the Sackur equation (using $M=4.002$) results in $S_{298.1} = 30.13$. The error in this value is negligible.

HYDROGEN AND ITS COMPOUNDS

Element.—The specific heat of ordinary hydrogen gas at low temperatures has been studied by Eucken²⁹ and by Cornish and Eastman.³⁰ Keesom and Onnes³¹ have made measurements on solid and liquid hydrogen between 11° and 20° K. Simon and Lange³² have also studied condensed hydrogen down to 10° K. and, besides the specific heats, have obtained the heat of fusion at the "triple point" and the heat of sublimation at various temperatures. More recently, Eucken and Hiller³³ and Clusius and Hiller³⁴ have given data on the variation of the specific heat of hydrogen gas on standing at low temperatures and on the specific heat of parahydrogen.

²⁵ Anderson, C. T., Unpublished measurements from Pacific Experiment Station.

²⁶ Simon, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 68, 1922, p. 241.

²⁷ See footnote 24.

²⁸ See footnote 24.

²⁹ Eucken, A., Die Molekularwärme des Wasserstoffs bei tiefen Temperaturen: Sitzb. könig. preuss. Akad. Wiss., 1912, p. 144. Über das thermische Verhalten einiger komprimierter und kondensierter Gase bei tiefen Temperaturen: Verh., Deut. phys. Gesell., vol. 18, 1916, p. 4.

³⁰ Cornish, R. E., and Eastman, E. D., The Specific Heat of Hydrogen Gas at Low Temperatures from the Velocity of Sound; and a Precision Method of Measuring the Frequency of an Oscillating Circuit: Jour. Am. Chem. Soc., vol. 50, 1928, p. 627.

³¹ Keesom, W. H., and Onnes, H. K., The Specific Heat at Low Temperatures. IV. Measurements of the Specific Heat of Liquid Hydrogen and on the Heat of Fusion of Hydrogen: Proc. Acad. Sci. Amsterdam, vol. 20, 1918, p. 1000.

³² Simon, F., and Lange, F., Die thermischen Daten des kondensierten Wasserstoffs: Ztschr. Physik, vol. 15, 1923, p. 312.

³³ Eucken, A., and Hiller, K., Der Nachweis einer Umwandlung des Orthowasserstoffs im Parawasserstoff durch Messung der spezifischen Wärme: Ztschr. physikal. Chem., Abt. B, vol. 4, 1929, p. 142.

³⁴ Clusius, K., and Hiller, K., Die spezifischen Wärmen des Parawasserstoffs im festen, flüssigem und gasförmigen Zustande: Ztschr. physikal. Chem., Abt. B, vol. 4, 1929, p. 158.

The pertinent data have recently been reviewed by Giauque,³⁵ who has calculated the entropy of hydrogen from spectroscopic data as $S_{298.1} = 33.98$, which agrees with the value 34.0 similarly obtained by Rodebush.³⁶ Ordinary hydrogen has been shown to be a mixture of symmetrical and antisymmetrical molecules, between which the rate of transition at low temperatures is so slow that specific-heat measurements as ordinarily made can not give the correct value for the entropy when the third law is applied in the usual manner.³⁷ Giauque has calculated the entropy of mixing from the equation,

$$\Delta S = - \sum_{i=1}^n N_i R \ln N_i,$$

as $\Delta S = -\frac{1}{4} R \ln \frac{1}{4} - \frac{9}{12} R \ln \frac{1}{12} = 4.39$ units. Subtracting this value from 33.98 gives 29.59, which is the figure that should result from the ordinary heat-capacity measurements. Actually, in reviewing the low-temperature data on hydrogen, Giauque obtains 29.74 or 29.64, depending on whether a Berthelot or Van der Waal's gas is assumed in correcting to the ideal state. The value 33.98 may not be used in thermodynamic calculations unless all compounds containing hydrogen have their entropies increased for the effect of nuclear spin. As mentioned on page 12, it seems simpler to decrease the value for hydrogen for this effect (which cancels out in reactions at room temperature or above). In this case, the nuclear-spin entropy, as calculated by Giauque, is $R \ln 4 = 2.75$. This value he subtracts from 33.98 to obtain $S_{298.1} = 31.23$, which is the figure to be used in conjunction with data obtained from the application of the third law of thermodynamics to measurements on other substances. No appreciable error can be assigned to the above value.

Water.—To calculate the entropy of water from the third law the specific-heat data given by Simon³⁸ are used. Nernst³⁹ and Pollitzer⁴⁰ have also measured the low temperature heat capacity of water.

From Simon's data, the entropy of water at 10° K. (extrapolation) is 0.02, and 9.02 units are involved in heating ice from 10° to 273.1° K. Roth,⁴¹ Dickinson, Harper, and Osborne,⁴² and Dickinson and Osborne⁴³ have measured the heat of fusion as 1,436, 1,435, and 1,437 calories per mole, respectively. The entropy of fusion is $1,436 \div 273.1$, or 5.26. The portion due to warming the liquid from 273.1° to 298.1° K. is 1.58. Therefore, $S_{298.1} = 0.02 + 9.02 + 5.26 + 1.58 = 15.9 \pm 0.1$ per formula weight for liquid water.

³⁵ (a) Giauque, W. F., and Johnston, H. L., Symmetrical and Antisymmetrical Hydrogen and the Third Law of Thermodynamics. Thermal Equilibrium and the Triple-Point Pressure: Jour. Am. Chem. Soc., vol. 50, 1928, p. 3221.

(b) Giauque, W. F., The Entropy of Hydrogen and the Third Law of Thermodynamics. The Free Energy and Dissociation of Hydrogen: Jour. Am. Chem. Soc., vol. 52, 1930, p. 4816.

³⁶ Rodebush, W. H., The Entropy of Hydrogen: Proc. Nat. Acad. Sci., vol. 15, 1929, p. 678.

³⁷ Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 440.

³⁸ Simon, F., Thermische Eigenschaften der Stoffe: Handbuch der Physik, vol. 10, ch. 7, Julius Springer, Berlin, 1926.

³⁹ Nernst, W., Der Energieinhalt fester Stoffe: Ann. Physik, vol. 36, 1911, p. 395.

⁴⁰ Pollitzer, F., Bestimmung spezifischer Wärmen bei tiefen Temperaturen und ihre Verwertung zur Berechnung electromotorischer Kräfte: Ztschr. Electrochem., vol. 17, 1911, p. 5; vol. 19, 1913, p. 513.

⁴¹ Roth, W. A., Die Dichte und Schmelzwärme des Eises und die molekulare Gefrierpunktserniedrigung in wässrigen Lösungen: Ztschr. physikal. Chem., vol. 63, 1908, p. 441.

⁴² Dickinson, H. C., Harper, D. R., and Osborne, N. C., Latent Heat of Fusion of Ice: Bull. U. S. Bureau of Standards, vol. 10, 1914, p. 235.

⁴³ Dickinson, H. C., and Osborne, N. S., Specific Heat and Heat of Fusion of Ice: Bull. U. S. Bureau of Standards, vol. 12, 1915, p. 49.

The free-energy equation of Eastman⁴⁴ for the formation of water from its elements results in $S_{298.1} = 16.2 \pm 0.3$ while that of Lewis and Randall,⁴⁵ based on earlier data, gives 16.45 ± 0.5 . The agreement between the values from these free-energy equations, which are based upon equilibrium measurements, and the third-law value is good; however, the third-law value is considerably more reliable.

Halides.—Eucken and Karwat⁴⁶ have obtained low-temperature thermal data on HCl, HBr, and HI. Giauque and Wiebe⁴⁷ have also studied these three compounds with somewhat greater accuracy than the former investigators and have calculated entropies from their thermal data and from the energy levels of the molecules as determined spectroscopically. Clusius⁴⁸ has recently measured the specific heat of HCl down to 10° K., and Clusius, Hiller, and Vaughen⁴⁹ have studied the specific heat of condensed HF between 10° and 77° K. The data on the latter substance are incomplete, and until satisfactory values for the specific heat of the gas and for the heats of fusion and vaporization are obtained calculation of the entropy at 298.1° K. from the third law is not justified.

The results of the calculations of Giauque and Wiebe for the entropies of HCl, HBr, and HI are given in the following table. Their third-law values are in excellent agreement with the spectroscopic data; consequently great reliance may be placed on the results for these three substances. The figures from spectroscopic data are, of course, better, but for most purposes the differences between the values given by the two methods are negligible.

HCl entropy calculations

0 to 16° K., extrapolation.....	0. 30
16° to 98.36° K., graphical.....	7. 06
Transition, 284.3 ÷ 98.36.....	2. 89
98.36° to 158.91° K., graphical.....	5. 05
Fusion, 476.0 ÷ 158.91.....	3. 00
158.91° to 188.07° K., graphical.....	2. 36
Vaporization, 3,860 ÷ 188.07.....	20. 52
Entropy of HCl gas at boiling point.....	third law... 41. 2 ± 0. 1
Entropy of HCl gas at 298.1° K.....	do..... 44. 5
Do.....	spectroscopic... 44. 64 ± . 01

⁴⁴ Eastman, E. D., The Free Energy of Water, Carbon Monoxide, and Carbon Dioxide: Inf. Circ. 6125, Bureau of Mines, 1929, 15 pp.

⁴⁵ Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co., New York, 1923, p. 435.

⁴⁶ Eucken, A., and Karwat, E., Die Bestimmung des Warmehaltes einiger kondensierter Gase: Ztschr. physikal. Chem., vol. 112, 1924, p. 467.

⁴⁷ (a) Giauque, W. F., and Wiebe, R., The Entropy of Hydrogen Chloride. Heat Capacity from 16° K. to Boiling Point. Heat of Vaporization. Vapor Pressures of Solid and Liquid: Jour. Am. Chem. Soc., vol. 50, 1928, p. 101.

(b) The Heat Capacity of Hydrogen Bromide from 15° K. to its Boiling Point and its Heat of Vaporization. The Entropy from Spectroscopic Data: Jour. Am. Chem. Soc., vol. 50, 1928, p. 2193.

(c) The Heat Capacity of Hydrogen Iodide from 15° K. to its Boiling Point and its Heat of Vaporization. The Entropy from Spectroscopic Data: Jour. Am. Chem. Soc., vol. 51, 1929, p. 1441.

⁴⁸ Clusius, K., Über die spezifische Wärme einiger kondensierter Gase zwischen 10° abs. und ihrem Tripelpunkt: Ztschr. physikal. Chem., Abt. B, vol. 3, 1929, p. 41.

⁴⁹ Clusius, K., Hiller, K., and Vaughen, J. V., Über die spezifische Wärme des Stickoxyduls, Ammoniaks und Fluorwasserstoffs von 10° abs. aufwärts: Ztschr. physikal. Chem., Abt. B, vol. 8, 1930, p. 427.

HBr entropy calculations

0 to 14.5° K., extrapolation.....	0.546
Transition, 63.4÷89.2.....	.711
Transition, 78.8÷113.2.....	.695
Transition, 85.7÷116.8.....	.734
14.5° to 186.24° K., graphical.....	17.27
Fusion, 575.1÷186.24.....	3.097
186.24° to 206.38° K., graphical.....	1.464
Vaporization, 4,210÷206.38.....	20.40
<hr/>	
Entropy of HBr gas at boiling point..... third law..	44.9 ± 0.1
Entropy of HBr gas at 298.1° K..... do.....	47.6
Do..... spectroscopic.....	47.48 ± .01

HI entropy calculations

0 to 15.3° K., extrapolation.....	1.085
Transition, 18.6÷70.1.....	.265
Transition, 192.4÷125.6.....	1.531
15.3° to 222.31° K., graphical.....	20.99
Fusion, 686.3÷222.31.....	3.087
222.31° to 237.75° K., graphical.....	.958
Vaporization, 4,724÷237.75.....	19.87
<hr/>	
Entropy of HI gas at boiling point..... third law..	47.8 ± 0.1
Entropy of HI gas at 298.1° K..... do.....	49.5
Do..... spectroscopic.....	49.40 ± .01

For hydrogen fluoride in the ideal state the equation of Tetrode,⁵⁰

$$S_R = R \ln IT + S_0,$$

for the rotational entropy of a gas composed of rigid, dumb-bell molecules is used. Here S_0 is a constant which has the value 177.68 calories per degree per mole when I (the moment of inertia) is expressed in c. g. s. units. The other symbols are T , the absolute temperature, and R , the gas constant per mole. This rotational entropy S_R must be added to the translational entropy as given by the Sackur equation. Birge⁵¹ has given values for the moments of inertia of the hydrogen halides, and in the following table the resulting entropy calculations are given. It will be noticed that the values for HCl, HBr, and HI are practically identical with those obtained directly from energy levels. This is somewhat fortuitous and is due to the vibrational entropy (which has not been considered) being practically zero at 298.1° K. for these substances.

Substance	$I \times 10^{40}$	S_T	S_R	$S_{298.1}$	$S_{298.1}$ (spectroscopic)
HF.....	1.346	34.93	6.59	41.52	-----
HCl.....	2.659	36.72	7.94	44.66	44.64
HBr.....	3.318	39.10	8.38	47.48	47.48
HI.....	4.315	40.46	8.90	49.36	49.40

⁵⁰ Tetrode, H., Die chemische Konstante der Gase und das elementare Wirkungsquantum: Ann. Physik, vol. 38, 1912, p. 434.

⁵¹ Birge, R. T., Molecular Constants Derived from Band Spectra of Diatomic Molecules: International Critical Tables, McGraw-Hill Book Co. (Inc.), New York, 1929, vol. 5, p. 409.

It must be remembered that the value given for hydrogen fluoride can not be applied to the actual gas at 298.1 as it is far removed from the ideal state at that temperature.

Hydrogen sulphide.—Lewis and Randall's ⁵² free-energy equation for the formation of H₂S from the elements agrees with $S_{298.1} = 48.2$ for H₂S gas. The error in this value can not be placed definitely but may be as small as ± 1.0 unit.

IODINE

Element.—The specific heat of iodine at low temperatures has been studied by Nernst ⁵³ (28° to 80° K.), Günther ⁵⁴ (21° to 73° K.) and Lange ⁵⁵ (10° to 52° K.). The data of Nernst and Günther are very erratic, due presumably to a slow transition. Consequently, Lange's data only will be considered, from which $S_{298.1} = 27.9$ per mole (I₂) for solid iodine. Only 0.34 unit of this is extrapolation below 10° K. Giaque ⁵⁶ has recently performed this same calculation and arrived at an identical figure. He has also calculated the entropy of I₂ gas from spectroscopic data as 62.29 per mole at 298.1° K. and has shown that the above value for the solid agrees with the spectroscopic data within ± 0.1 unit. The value, 62.29, for the gas does not include the effect of nuclear spin and is to be used for gaseous iodine with other data listed.

IRIDIUM

Element.—The value for the entropy of iridium metal calculated by Lewis and Gibson ⁵⁷ from Dewar's ⁵⁸ data can not be revised as no new data have appeared; therefore, estimating the error as ± 0.5 , $S_{298.1} = 8.7 \pm 0.5$ for iridium metal.

IRON AND ITS COMPOUNDS

Element.—The specific heat of iron at low temperatures has been studied by Günther ⁵⁹ (32° to 95° K.), Griffiths and Griffiths ⁶⁰ (a few values), and Rodebush and Michalek ⁶¹ (72° to 200° K.); and, more recently, Eucken and Werth ⁶² have measured specific heats on a sample of electrolytic iron from 16° to 206° K. The latter data will be relied on entirely in the present work, from which $S_{298.1} = 6.47 \pm 0.1$. The extrapolation below 17.8° K. is only 0.01.

⁵² Lewis, G. N., and Randall, M., *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Co. (Inc.), New York, 1923, p. 541.

⁵³ Nernst, W., *Der Energieinhalt fester Stoffe*: Ann. Physik, vol. 36, 1911, p. 395.

⁵⁴ Günther, P., *Untersuchungen über die spezifische Wärme bei tiefen Temperaturen*: Ann. Physik, series 4, vol. 51, 1916, p. 828.

⁵⁵ Lange, F., *Untersuchungen über die spezifische Wärme bei tiefen Temperaturen*: Ztschr. physikal. Chem., vol. 110, 1924, p. 343.

⁵⁶ Giaque, W. F., *Nuclear Spin and the Third Law of Thermodynamics*. The Entropy of Iodine: Jour. Am. Chem. Soc., vol. 53, 1931, p. 507.

⁵⁷ Lewis, G. N., and Gibson, G. E., *The Entropy of the Elements and the Third Law of Thermodynamics*, Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

⁵⁸ Dewar, J. D., *Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Hydrogen*. I. The Mean Atomic Specific Heats at 50° Abs. of the Elements a Periodic Function of the Atomic Weights: Proc. Roy. Soc. (London), vol. A-89, 1913, p. 158.

⁵⁹ Günther, P., *Untersuchungen über die spezifische Wärme bei tiefen Temperaturen*: Ann. Physik, series 4, vol. 51, 1916, p. 828.

⁶⁰ Griffiths, E. H., and Griffiths, E., *The Capacity for Heat of Metals at Low Temperatures*: Proc. Roy. Soc. (London), vol. A-90, 1914, p. 557.

⁶¹ Rodebush, W. H., and Michalek, J. C., *The Atomic Heat Capacities of Iron and Nickel at Low Temperatures*: Jour. Am. Chem. Soc., vol. 47, 1925, p. 2117.

⁶² Eucken, A., and Werth, H., *Die spezifische Wärme einiger Metalle und Metallegierungen bei tiefen Temperaturen*: Ztschr. anorg. allgem. Chem., vol. 188, 1930, p. 152.

Ferrous oxide.—Millar⁶³ has made specific-heat measurements on a sample of "ferrous" oxide of 83 per cent purity from 70° to 300° K. His calculation of the entropy, however, could not be checked and evidently contains some arithmetical error. The author finds $S_{298.1} = 14.2 \pm 2.0$ for FeO, of which 1.34 is extrapolation below 70.8° K.

Ferric oxide.—The specific heat of specular hematite of 99.2 per cent purity was studied by Parks and Kelley⁶⁴ down to 89° K. These authors also studied a sample of Fe₂O₃ prepared by igniting the oxalate. The latter material was very finely divided and had a specific heat 2 to 4 per cent higher (depending on the temperature) than the natural hematite; however, X-ray pictures showed that it was largely non-crystalline. From the data on hematite $S_{298.1} = 21.5 \pm 0.5$. The amount of the extrapolation below 89.2° K. is 3.30.

The estimated errors given here for the compounds of iron, and those given later for manganese compounds and other highly paramagnetic materials, include only the inaccuracies in the extrapolations and in the specific-heat measurements. If it is shown that the specific heats as measured on these substances are for systems that are not in complete thermal equilibrium, then a correction similar to that made for the entropy of mixing the different kinds of hydrogen molecules will be necessary. Until such information becomes available there is no choice other than to use the values obtained by applying the third law in the usual manner to the existing data. Such considerations probably do not affect the values for the metals themselves, as they presumably go completely to the lowest energy states.

Magnetite.—Parks and Kelley⁶⁵ and Millar⁶⁶ have measured specific heats down to liquid-air temperatures on similar samples of magnetite of 99 per cent purity. From these data, $S_{298.1} = 35.0 \pm 0.7$, after correcting for the SiO₂ content. The extrapolation below 56.2° K. is 2.17.

Ferrous sulphide.—Anderson⁶⁷ has measured the specific heat of pure, synthetic ferrous sulphide down to 58° K. The entropy values are $S_{58.2} = 1.43$ (extrapolation) and $S_{298.1} = 16.1 \pm 0.3$.

Pyrite.—Eucken and Schwers⁶⁸ have studied FeS₂ between 21° and 84° K. Their results lead to $S_{22.4} = 0.06$ (extrapolation) and $S_{298.1} = 15.6 \pm 0.4$.

KRYPTON

Element.—The equation of Sackur gives $S_{298.1} = 39.17$ for krypton with only a negligible error.

LANTHANUM

Element.—In accordance with Lewis and Gibson,⁶⁹ the entropy of lanthanum metal, to which is assigned the error ± 0.8 , is taken here as $S_{298.1} = 13.7 \pm 0.8$.

⁶³ Millar, R. W., The Heat Capacities at Low Temperatures of "Ferrous Oxide," Magnetite, and Cuprous and Cupric Oxides: Jour. Am. Chem. Soc., vol. 51, 1929, p. 215.

⁶⁴ Parks, G. S., and Kelley, K. K., The Heat Capacities of Some Metallic Oxides: Jour. Phys. Chem., vol. 30, 1926, p. 47.

⁶⁵ See footnote 64.

⁶⁶ Millar, R. W., The Heat Capacities at Low Temperatures of "Ferrous Oxide," Magnetite, and Cuprous and Cupric Oxides: Jour. Am. Chem. Soc., vol. 51, 1929, p. 215.

⁶⁷ Anderson, C. T., The Heat Capacities at Low Temperatures of Manganese Sulphite, Ferrous Sulphide, and Calcium Sulphide: Jour. Am. Chem. Soc. vol. 53, 1931, p. 476.

⁶⁸ Eucken, A., and Schwers, F., Eine experimentelle Prüfung des T³ Gesetzes für den Verlauf der spezifischen Wärme fester Körper bei tiefen Temperaturen: Ber. Deut. phys. Gesell., vol. 15.

⁶⁹ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

LEAD AND ITS COMPOUNDS

Element.—The following investigators have measured the specific heat of lead at low temperatures: Nernst⁷⁰ (23° to 273° K.), Eucken and Schwers⁷¹ (15° to 92° K.), Griffiths and Griffiths⁷² (50° to 380° K.), Keesom and Onnes⁷³ (14° to 80° K.), Keesom and Andrews⁷⁴ (2° to 20° K.), and Keesom and Van den Ende⁷⁵ (2° to 16° K.). The data result in the value $S_{298.1} = 15.63 \pm 0.1$, of which only 0.01 unit is extrapolation below 3.16° K.

Oxides.—The specific-heat data of Nernst and Schwers⁷⁶ on a sample of PbO (presumably the yellow modification) down to 21° K. lead to the value $S_{298.1} = 16.6 \pm 0.5$, with an extrapolation below 20.0° K. of 0.55. This entropy may be calculated independently from the cell measurements of Fried⁷⁷ on the reaction $\text{PbO} + \text{H}_2 = \text{Pb} + \text{H}_2\text{O}$. From his e.m.f. measurements and their variation with the temperature, the value $\Delta S_{298.1} = -16.8$ may be obtained for this reaction, from which the entropy of PbO is found to be 17.1 ± 0.3 . The mean of these two independently calculated values, 16.9 ± 0.4 , will be used here.

Millar⁷⁸ has measured the specific heat of PbO_2 down to 70° K. From his data, $S_{298.1} = 18.3 \pm 0.5$ is calculated. The extrapolation below 70.8° K. amounts to 3.50.

Millar has also studied Pb_3O_4 down to 70° K. Again the author can not agree with his entropy calculation and, in this case, has been able to trace the difference definitely to an arithmetical error. The extrapolation below 70.8° K. is 12.67, and $S_{298.1} = 50.5 \pm 1.6$. (In this case the "n" formula was used for extrapolation.)

Sulphide.—Eastman and Rodebush⁷⁹ and Anderson⁸⁰ have studied galena down to liquid-air temperatures. If the data of the latter investigator are relied on, $S_{298.1} = 21.8 \pm 0.6$, of which 4.50 is extrapolation below 50.1° K.

Chloride.—Nernst⁸¹ has made specific-heat measurements on PbCl_2 down to 15° K. His data result in $S_{298.1} = 34.0 \pm 1.0$. The extrapolation required below 15.8° K. is 0.91.

Gerke's⁸² cell measurements permit two independent calculations of the entropy of PbCl_2 . For the reaction $\text{Pb} + 2\text{AgCl} = \text{PbCl}_2 + 2\text{Ag}$

⁷⁰ Nernst, W., *Der Energieinhalt fester Stoffe*: Ann. Physik, vol. 36, 1911, p. 395. See also Nernst, W., and Lindemann, F. A., *Spezifische Wärme und Quantentheorie*: Ztschr. Electrochem., vol. 17, 1911, p. 817.

⁷¹ See footnote 68.

⁷² Griffiths, E. H., and Griffiths, E., *The Capacity for Heat of Metals at Low Temperatures*: Proc. Roy. Soc. (London), vol. A-90, 1914, p. 557.

⁷³ Keesom, W. H., and Onnes, H. K., *The Specific Heat at Low Temperatures: I. Measurements on the Specific Heat of Lead between 14° and 80° K. and of Copper between 15° and 22° K.*: Com. Phys. Lab. Leiden No. 143, vol. 13, 1914.

⁷⁴ Keesom, W. H., and Andrews, D. H., *The Specific Heats of Solid Substances at the Temperatures Attainable with the Help of Liquid Helium. I. Measurement of the Atomic Heat of Lead*: Com. Phys. Lab. Leiden, No. 185a, 1927.

⁷⁵ Keesom, W. H., and van den Ende, J. N., *The Specific Heat of Solid Substances at the Temperatures Obtainable with the Aid of Liquid Helium. II. Measurement of the Atomic Heats of Lead and Bismuth*: Proc. Acad. Sci. Amsterdam, vol. 33, 1930, p. 243.

⁷⁶ Nernst, W., and Schwers, F., *Untersuchungen über die spezifische Wärme bei tiefen Temperaturen*: Sitzb. könig. preuss. Akad. Wiss., 1914, p. 355.

⁷⁷ Fried, F., *Messungen der E. M. K. galvanischer Elemente vom Typus $\text{Me}/\text{MeO}/\text{NaOH}/\text{H}_2(\text{Pt})$ und ihre Verwertung zur Prüfung des nernstschen Wärmesatzes*: Ztschr. physikal. Chem., vol. 123, 1926, p. 406.

⁷⁸ Millar, R. W., *Heat Capacities at Low Temperatures of the Oxides of Tin and Lead*: Jour. Am. Chem. Soc., vol. 51, 1929, p. 207.

⁷⁹ Eastman, E. D., and Rodebush, W. H., *The Specific Heats at Low Temperatures of Sodium, Potassium, Magnesium, and Calcium Metals, and of Lead Sulphide*: Jour. Am. Chem. Soc., vol. 40, 1918, p. 489.

⁸⁰ Anderson, C. T., *Unpublished measurements from Pacific Experiment Station.*

⁸¹ Nernst, W., *Der Energieinhalt fester Stoffe*: Ann. Physik, vol. 36, 1911, p. 395. See also Nernst, W., and Lindemann, F. A., *Spezifische Wärme und Quantentheorie*: Ztschr. Electrochem., vol. 17, 1911, p. 817.

⁸² Gerke, R. H., *Temperature Coefficient of Electromotive Force of Galvanic Cells and the Entropies of Reactions*: Jour. Am. Chem. Soc., vol. 44, 1922, p. 1684.

he gives $\Delta S_{298.1} = -8.6$. Using the values 23.0 ± 0.1 for AgCl and 10.2 ± 0.1 for Ag, which are listed later, and the value for Pb given above, one finds $S_{298.1} = 32.6 \pm 0.6$. For the reaction $\text{Pb} + 2\text{HgCl} = \text{PbCl}_2 + 2\text{Hg}$ he obtains $\Delta S_{298.1} = 6.7$. Combining this result with the entropies of Hg (18.5 ± 0.2) and HgCl (23.2 ± 0.5), $S_{298.1} = 31.7 \pm 1.5$, is obtained. The value 32.6 ± 0.6 , based on the first cell reaction mentioned, seems to be the most reliable of the three results given.

Bromide.—Latimer and Hoenshel⁸³ have made specific-heat measurements on PbBr_2 down to 18°K. , from which may be obtained $S_{298.1} = 38.6 \pm 0.8$. The extrapolation involved is 1.64 below 17.8°K.

Iodide.—From the data of Nernst and Schwers⁸⁴ (22° to 96°K.) on PbI_2 , Lewis and Gibson⁸⁵ have calculated 41.3 for $S_{298.1}$ by the use of the n -formula. Since the data are meager and the extrapolation large (C_p being 7.05 at 22.3°K.), it is not possible to improve much on this calculation. The error in this value might easily be ± 1.5 units.

A much more reliable value may be obtained from the e. m. f. measurements of Gerke,⁸⁶ which give $\Delta S_{298.1} = -1.2$ for the reaction $\text{Pb} + \text{I}_{2(s)} = \text{PbI}_2$. Using the entropies 15.6 ± 0.1 for Pb and 27.9 ± 0.1 for I_2 , $S_{298.1} = 42.3 \pm 0.2$ for PbI_2 .

LITHIUM AND ITS COMPOUNDS

Element.—No low-temperature specific-heat measurements have appeared for lithium metal since the mean value of Dewar⁸⁷ was published; therefore, the value calculated by Lewis and Gibson,⁸⁸ namely $S_{298.1} = 7.6 \pm 0.5$, is used.

For lithium gas, the Sackur equation, to which must be added *Rln 2*, to account for the multiplicity in the lowest energy state, gives $S_{298.1} = 33.15$.

Hydride.—The data of Günther⁸⁹ between 74° and 293°K. on a somewhat impure sample of LiH give the value $S_{298.1} = 5.9 \pm 0.5$, the extrapolation below 70.8°K. being 0.21 .

MAGNESIUM AND ITS COMPOUNDS

Element.—The specific heat of magnesium metal has been studied by Nernst and Schwers⁹⁰ (27° to 94°K.), Eastman and Rodebush⁹¹ (74° to 289°K.), and Clusius and Vaughen⁹² (11° to 228°K.). The author will rely entirely on the measurements of the latter investigators and calculate $S_{298.1} = 7.77 \pm 0.1$ for the metal.

⁸³ Latimer, W. M., and Hoenshel, H. D., The Heat Capacity and Entropy of Lead Bromide and Bromine: Jour. Am. Chem. Soc., vol. 48, 1926, p. 19.

⁸⁴ Nernst, W., and Schwers, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Sitzb. könig. preuss. Akad. Wiss., 1914, p. 355.

⁸⁵ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

⁸⁶ See footnote 82.

⁸⁷ Dewar, J. D., Atomic Specific Heats Between the Boiling Points of Liquid Nitrogen and Hydrogen. I. The Mean Atomic Specific Heats at 50° Absolute of the Elements, a Periodic Function of the Atomic Weights: Proc. Roy. Soc. (London), vol. A 89, 1913, p. 153.

⁸⁸ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

⁸⁹ Günther, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, vol. 63, 1920, p. 476.

⁹⁰ Nernst, W., and Schwers, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Sitzb. könig. preuss. Akad. Wiss., 1914, p. 355.

⁹¹ Eastman, E. D., and Rodebush, W. H., The Specific Heats at Low Temperatures of Sodium, Potassium, Magnesium, and Calcium Metals, and of Lead Sulphide: Jour. Am. Chem. Soc., vol. 40, 1918, p. 489.

⁹² Clusius, K., and Vaughen, J. V., I. The Specific Heats of Thallium, Calcium, and Magnesium Measured to 10° Absolute. II. The Entropy and Chemical Constants of Magnesium from Spectroscopic Data: Jour. Am. Chem. Soc., vol. 52, 1930, p. 4686.

Clusius and Vaughen have obtained 35.3 for the entropy of magnesium gas at 298.1° K. from experimental data, while the Sackur equation gives for the entropy of the gas in the ideal state $S_{298.1} = 35.51$. This difference is easily accounted for by experimental error and association in the actual gas.

Oxide.—Günther⁹³ has studied the specific heat of MgO between 39° and 84° K., and Parks and Kelley⁹⁴ have investigated a sample of very pure, crystalline MgO between 94° and 291° K. These two sets of data give $S_{298.1} = 6.4 \pm 0.1$ for MgO, with an extrapolation of only 0.02 below 39.8° K.

MANGANESE AND ITS COMPOUNDS

Element.—The value given by Lewis and Gibson⁹⁵ from Dewar's data, $S_{298.1} = 7.3 \pm 0.5$, will be used, as no new measurements have been made.

Oxides.—Millar⁹⁶ has made specific-heat measurements on MnO, MnO₂, and Mn₃O₄ down to liquid-air temperatures. The results of the entropy calculations follow.

Substance	Extrapolation below 70.8° K.	$S_{298.1}$
MnO.....	2.22	14.4±0.6
MnO ₂	1.76	13.9±.4
Mn ₃ O ₄	4.67	35.5±.7

Sulphide.—Anderson's⁹⁷ low-temperature specific-heat data on MnS give $S_{298.1} = 18.7 \pm 0.3$. The extrapolation below 56.2° K. is 2.14.

MERCURY AND ITS COMPOUNDS

Element.—The specific heat of mercury at low temperatures has been studied by Pollitzer⁹⁸ (31° to 243° K.), Simon⁹⁹ (3° to 232° K.), and Carpenter and Stoodley¹ (197° to 234° K.). Pollitzer has measured the heat of fusion as 554.5 calories per gram-atom, while Bridgeman² has obtained 560 calories per gram-atom. A mean value of 557.2 will be used. For the melting point Henning³ gives 234.2° K.

The entropy calculations are $S_{3.16} = 0.03$ (extrapolation), $S_{234.2} = 14.47$ (crystals), $\frac{557.2}{234.2} = 2.38$ (fusion), and 234.2° to 298.1°, 1.65

⁹³ Günther, P., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 51, 1916, p. 828.

⁹⁴ Parks, G. S., and Kelley, K. K., The Heat Capacities of Some Metallic Oxides: Jour. Phys. Chem., vol. 30, 1926, p. 47.

⁹⁵ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

⁹⁶ Millar, R. W., The Specific Heats at Low Temperatures of Manganous Oxide, Manganous-Manganic Oxide and Manganese Dioxide: Jour. Am. Chem. Soc., vol. 50, 1928, p. 1875.

⁹⁷ Anderson, C. T., The Heat Capacities at Low Temperatures of Manganese Sulphide, Ferrous Sulphide, and Calcium Sulphide: Jour. Am. Chem. Soc., vol. 53, 1931, p. 476.

⁹⁸ Pollitzer, F., Bestimmung spezifischer Wärmen bei tiefen Temperaturen und ihre Verwertung zur Berechnung electromotorischer Kräfte: Ztschr. Electrochem., vol. 17, 1911, p. 5; vol. 19, 1913, p. 513.

⁹⁹ Simon, F., Die chemische Konstante des Quecksilbers: Ztschr. physikal. Chem., vol. 107, 1923, p. 279. Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 68, 1922, p. 241.

¹ Carpenter, L. G., and Stoodley, L. G., The Specific Heat of Mercury in the Neighborhood of the Melting Point: Phil. Mag., series 7, vol. 10, 1930, p. 249.

² Bridgeman, P. W., Mercury, Liquid and Solid, under Pressure: Proc. Am. Acad. Sci., vol. 47, 1911, p. 347.

³ Henning, F., Die Fixierung der Temperaturskala zwischen 0 und -193°: Ann. Physik., series 4, vol. 43, 1914, p. 282.

(liquid); therefore, $S_{298.1} = 14.47 + 2.38 + 1.65 = 18.5 \pm 0.2$ for liquid mercury.

For mercury gas in the ideal state the Sackur equation gives $S_{298.1} = 41.80$.

Oxide.—Günther ⁴ has measured the specific heats of HgO (red, 25° to 75° K.) which lead to $S_{298.1} = 16.6 \pm 1.0$, the extrapolation below 25.1° K. being 0.83.

The cell measurements of Fried ⁵ give $\Delta S_{298.1} = -13.9$ for the reaction, HgO (yellow) + H₂ = H₂O + Hg. Combination of this value with the entropies of water, hydrogen, and mercury gives $S_{298.1} = 17.1 \pm 0.4$ for HgO (yellow). The free-energy equation of Lewis and Randall ⁶ enables one to calculate 16.9 ± 0.4 for this yellow modification. The mean, 17.0 ± 0.4 , may be taken.

Chloride.—The specific heat of mercurous chloride has been measured by Pollitzer ⁷ (22° to 198° K.). His data give $S_{298.1} = 23.0 \pm 0.7$ per formula weight of HgCl. (The molecule is probably Hg₂Cl₂, but the author prefers to express the result in this manner.) The extrapolation involved is 1.35 below 22.4° K.

A better value is obtainable from the cell measurements of Gerke,⁸ who gives $\Delta S_{298.1} = -21.8$ for the reaction $\text{Hg} + \frac{1}{2}\text{Cl}_2 = \text{HgCl}$. From this value and the entropies of mercury and chlorine, $S_{298.1} = 23.2 \pm 0.5$ for HgCl. For the reaction $\text{Ag} + \text{HgCl} = \text{AgCl} + \text{Hg}$, Gerke finds $\Delta S_{298.1} = 7.8$, which leads to $S_{298.1} = 23.6 \pm 0.5$. The mean of the two latter computations, $S_{298.1} = 23.4 \pm 0.5$, will be adopted here.

Still another method of obtaining the entropy of HgCl is by utilizing the residual-ray data of Rubens.⁹ As several other entropies will be calculated in a similar manner, it may be well to give a detailed account of the method. Rubens gives $\lambda = 98.8 \times 10^{-4}$ cm as the mean wave length. Dividing the velocity (cm per second) of light by this figure $\left(\frac{3 \times 10^{10}}{98.8 \times 10^{-4}}\right)$ results in 3.04×10^{12} for the frequency, which has been interpreted as the frequency associated with the Einstein function. To calculate θ_E , 6.554×10^{-27} c. g. s. is substituted for h and 1.372×10^{-16} c. g. s. for k in the relationship $\theta_E = \frac{h\nu}{k}$, from which $\theta_E = 145$. From the expression¹⁰ $\theta_E = 1.35 \theta_D$, one obtains $\theta_D = 107$. The calculation from this point is the same as if, for the specific heat of HgCl, $C_v = D\left(\frac{107}{T}\right) + E\left(\frac{145}{T}\right)$. θ_D and θ_E are divided by 298.1; then using tables of Debye and Einstein functions 14.1 and 10.3 are obtained for the entropy contributions of these functions at 298.1° K. The difference, $S_p - S_v$, is close to 0.3 for most salts of this type, as may

⁴ Günther, P. Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 51, 1916, p. 828.

⁵ Fried, F., Messungen der E. M. K. galvanischer Elemente vom Typus Me/MeO/NaOH/H₂ (Pt) und ihre Verwertung zur Prüfung des ernerstehen Wärmesatzes: Ztschr. physikal. Chem., vol. 123, 1926, p. 406.

⁶ Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 484.

⁷ Pollitzer, F., Bestimmung spezifischer Wärmen bei tiefen Temperaturen und ihre Verwertung zur Berechnung electromotorischer Kräfte: Ztschr. Electrochem., vol. 17, 1911, p. 5; vol. 19, 1913, p. 513.

⁸ Gerke, R. H., Temperature Coefficient of Electromotive Force of Galvanic Cells and the Entropies of Reactions: Jour. Am. Chem. Soc., vol. 44, 1922, p. 1684.

⁹ Rubens, H., Über die Absorption des Wasserdampfs und über neue Reststrahlengruppen: Berlin Sitzb., 1913, p. 513.

¹⁰ Taylor, H. S., A Treatise on Physical Chemistry (vol. 2, Ch. 17, by W. H. Rodebush): D. van Nostrand Co., New York, 1925, p. 1157.

readily be seen by examining the data on several substances. Then, $S_{298.1} = 14.1 + 10.3 + 0.3 = 24.7$.

Sulphate.—The data of Pollitzer¹¹ on Hg_2SO_4 , which are quite erratic, lead to the estimate $S_{298.1} = 49.3 \pm 5.0$ for this substance.

MOLYBDENUM

Element.—Simon and Zeidler¹² have measured the specific heat of molybdenum metal between 15° and 275° K. From their results the value $S_{298.1} = 6.83 \pm 0.1$ may be calculated, the extrapolation below 15.8° K. being only 0.01.

NEON

Element.—The Sackur equation leads to the value 34.96 for the entropy of neon gas at 298.1° K.

An independent value is due to the work of Clusius,¹³ who measured specific heats (10° to 53° K.) and vapor pressures of neon. From his vapor-pressure data the heat of sublimation was calculated as 510.6 calories per mole at 24.59° K., the melting point. The specific-heat data give $S_{24.59} = 3.55$, involving an extrapolation of 0.58 below 10° K. The entropy of vaporization at the melting point (to form vapor at a pressure of 323.5 mm.) is $510.6 \div 24.59$, or 20.76. The compression of the gas to 1 atmosphere pressure involves an entropy change

$$\Delta S = -R \ln \frac{760}{323.5} = -1.70. \quad \text{To warm the gas to room temperature,}$$

4.97, the theoretical value for an ideal, monatomic gas was taken as the specific heat per mole, which contributes 12.39 units to the entropy; therefore, $S_{298.1} = 3.55 + 20.76 - 1.70 + 12.39 = 35.0 \pm 0.1$. This value is in excellent agreement with the Sackur equation and again indicates the accuracy of that method of calculation and the exactness of Tetrode's constant. The value from the Sackur equation is preferable, however.

NICKEL

Element.—The specific heat of nickel at low temperatures has been measured by Rodebush and Michalek¹⁴ (67° to 204° K.), Simon and Ruhemann¹⁵ (71° to 83° K.), and Eucken and Werth¹⁶ (15° to 204° K.). The latter investigators have studied both recrystallized and beaten nickel and, as for copper, have found that working produces only small differences in specific heat.

The calculation of entropy was based entirely on the data of Eucken and Werth, with the result $S_{298.1} = 7.12 \pm 0.1$, of which only 0.02 is extrapolation below 17.8° K.

NITON

Element.—The Sackur equation gives $S_{298.1} = 42.10$ for niton gas, which can not be in error except to a negligible extent.

¹¹ See footnote 7, p. 33.

¹² Simon, F., and Zeidler, W., Untersuchungen über die spezifischen Wärmen bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 123, 1926, p. 383.

¹³ Clusius, K., Die Dampfdruckkonstante des Neons: Ztschr. physikal. Chem., Abt. B, vol. 4, 1929, p. 1.

¹⁴ Rodebush, W. H., and Michalek, J. C., The Atomic Heat Capacities of Iron and Nickel at Low Temperatures: Jour. Am. Chem. Soc., vol. 47, 1927, p. 2117.

¹⁵ Simon, F., and Ruhemann, M., Ein neuer Apparat zur schnellen Bestimmung von spezifischen Wärmen fester Körper bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 129, 1927, p. 321.

¹⁶ Eucken, A., and Werth, H., Die spezifische Wärme einiger Metalle und Metallegierungen bei tiefen Temperaturen: Ztschr. anorg. allgem. Chem., vol. 188, 1930, p. 162.

NITROGEN AND ITS COMPOUNDS

Element.—Specific-heat measurements on solid and liquid nitrogen have been made by Eucken¹⁷ (16° to 73° K.), Keesom and Onnes¹⁸ (14° to 77° K.), and Clusius¹⁹ (10° to 74° K.). These investigators have also determined the melting point and transition point, heat of fusion, and heat of transition. Eucken gives the heat of vaporization as 1,363 calories per mole (mean value), while Dana²⁰ and Alt²¹ have both given 1,336 calories per mole. Henning and Heuse²² have determined the boiling point; and the specific heat of the gas has been measured at two temperatures by Scheel and Heuse.²³ For the specific heats of the solid and liquid the author will rely largely on the data of Clusius and for the transformation points, entirely on his data.

The entropy extrapolation below 10° K. is 0.47 and that given by the area under the C_p versus $\log T$ curves up to the melting point is 11.59. To these must be added the entropy of transition, $\frac{51.4}{35.4}$, or 1.45 units, to give $S_{63.08} = 13.51$ for the crystals at the melting point. The entropy of fusion, $\frac{170.95}{63.08}$, is 2.71, and that due to warming the liquid from the melting point to the boiling point is 2.77. For vaporization, the entropy change is $\frac{1,336}{77.3} = 17.28$, and the portion due to heating the gas to 298.1° K. amounts to 9.57. These figures give $S_{298.1} = 13.51 + 2.71 + 2.77 + 17.28 + 9.57 = 45.8 \pm 0.3$.

Nitrous oxide.—Clusius, Hiller, and Vaughan²⁴ have measured specific heats on solid N_2O from 10° to 61° K. and Eucken and Hauck,²⁵ from 90° to 170° K. As these results are all for temperatures below the melting point, the heat of sublimation obtained by Eucken and Donath,²⁶ which is 5,695 calories per mole at 160° K. will be used to form gas at 72.3 mm. pressure. The data of Heuse²⁷ on the specific heat of gaseous N_2O at constant pressure will be used, although they must be extrapolated about 40°.

The entropy results are as follows: $S_{10.0} = 0.08$ (extrapolation), $S_{160.0} - S_{10.0} = 15.10$ (from the specific heat measurements on solid N_2O), ΔS (sublimation) = $\frac{5,695}{160.0} = 35.59$, ΔS (compression) = $-R \ln \frac{760}{72.3}$

¹⁷ Eucken, A., Über das thermische Verhalten einiger komprimierter und kondensierter Gase bei tiefen Temperaturen: Verh. deut. phys. Gesell., vol. 18, 1916, p. 4.

¹⁸ Keesom, W. H., and Onnes, H. K., The Specific Heat at Low Temperatures. III. Measurements of the Specific Heat of Solid Nitrogen between 14° K. and the Triple Point and of Liquid Nitrogen between the Triple Point and the Boiling Point: Proc. Acad. Sci. Amsterdam, vol. 18, 1916, p. 1247.

¹⁹ Clusius, K., Über die spezifische Wärme einiger kondensierter Gase zwischen 10° abs. und ihren Tripelpunkt: Ztschr. physikal. Chem., Abt. B, vol. 3, 1929, p. 41.

²⁰ Dana, L. T., The Latent Heat of Vaporization of Liquid Oxygen-Nitrogen Mixtures: Proc. Am. Acad. Sci., vol. 60, 1925, p. 241.

²¹ Alt, H., Über die Verdampfungswärme des flüssigen Sauerstoffs und flüssigen Stickstoffs und deren Änderung mit der Temperatur: Ann. Physik, series 4, vol. 19, 1906, p. 739.

²² Henning, F., and Heuse, W., Eine neue Bestimmung der normalen Siedepunkte von Sauerstoff, Stickstoff und Wasserstoff: Ztschr. Physik, vol. 23, 1924, p. 105.

²³ Scheel, K., and Heuse, W., Die spezifische Wärme von Helium und einigen zweiatomigen Gasen: Ann. Physik, series 4, vol. 40, 1913, p. 473.

²⁴ Clusius, K., Hiller, K., and Vaughan, J. V., Über die spezifische Wärme des Stickoxyduls, Ammoniaks und Fluorwasserstoffs von 10° abs. aufwärts: Ztschr. physikal. Chem., Abt. B, vol. 8, 1930, p. 427.

²⁵ Eucken, A., and Hauck, F., Die spezifischen Wärmen C_p und C_v einiger Stoffe im festen, flüssigen und hyperkritischen Gebiet zwischen 80° und 320° abs.: Ztschr. physikal. Chem., vol. 134, 1928, p. 161.

²⁶ Eucken, — and Donath, Ed., ———: Ztschr. physikal. Chem., Abt. B, vol. 5, 1929, p. 439.

²⁷ Heuse, W., Die spezifische Wärme von Argon und einigen mehratomigen Gasen: Ann. Physik, series 4, vol. 59, 1919, p. 86.

= -4.67, and ΔS (warming the gas from 160° to 298.1°) = 5.31. These figures result in $S_{298.1} = 0.08 + 15.10 + 35.59 - 4.67 + 5.31 = 51.4 \pm 1.0$.

Nitric oxide.—The specific heat of condensed nitric oxide has been measured by Eucken and Karwat²⁸ (22° to 117° K.) and by Johnston and Giauque²⁹ (15° to 121° K.). In both investigations the temperature and heat of fusion were measured, and in the latter the boiling point and heat of vaporization were also carefully determined. The results of Johnston and Giauque appear to be the more reliable, and their calculated results (taken from their publication) for both the third law and spectroscopic values are repeated here.

Entropy calculations for NO

0 to 14.35° K., extrapolation.....	0. 27
14.35° to 109. 49°, graphical.....	8. 79
Fusion, 549.5÷109.49.....	5. 02
109.49° to 121.36°, graphical.....	1. 73
Vaporization, 3,292.6÷121.36.....	27. 13
<hr/>	
Entropy of actual NO gas at the boiling point..... third law..	42. 94±0. 1
Entropy of ideal NO gas at the boiling point..... do.....	43. 03
Do..... spectroscopic.....	43. 75

The difference of 0.72 unit between the spectroscopic value and that from specific heats is very nearly $\frac{1}{2} R \ln 2$, or 0.69, which can be explained if the solid nitric oxide is a solution of two isomers. This explanation seems reasonable, as a similar state of affairs has also been found for hydrogen. Consequently, the spectroscopic value which depends upon the actual, measured energy levels will be used. The entropy at 298.1° K. from spectroscopic data is 50.43.

Ammonia.—Eucken and Karwat³⁰ (24° to 222° K.) and Clusius, Hiller, and Vaughen³¹ (10° to 135° K.) have measured the specific heat of condensed ammonia. The former also determined the heat of fusion as 1,426 calories per mole (mean value) and the temperature of fusion as 195.5° K. The boiling point has been given by Henning and Stock³² and Bergstrom³³ as 239.7° K. From the vapor-pressure data of several investigators³⁴ the heat of vaporization at the boiling point was calculated as 5,640 calories per mole. For the gas, the measurements of Dixon and Greenwood³⁵ and Voller³⁶ enable the calculation of two values for the specific heat at constant pressure at 290° K. The mean, 8.47, of these results is taken, and constant specific heat from 239.7° to 298.1° K. is assumed.

Then for the entropy values, $S_{195.5} = 10.77$ for the crystals at the melting point (0.02 being extrapolated below 10° K.), ΔS (fusion) = 1,426÷195.5 = 7.29, ΔS (liquid, 195.5° to 239.7°) = 3.74, ΔS (vapor-

²⁸ Eucken, A., and Karwat, E., Die Bestimmung des Wärmehaltes einiger kondensierter Gase: Ztschr. physical Chem., vol. 112, 1924, p. 467.

²⁹ Johnston, H. L., and Giauque, W. F., The Heat Capacity of Nitric Oxide from 14° K. to the Boiling Point and the Heat of Vaporization. Vapor Pressures of Solid and Liquid Phases. The Entropy from Spectroscopic Data: Jour. Am. Chem. Soc., vol. 51, 1929, p. 3194.

³⁰ See footnote 28.

³¹ See footnote 24, p. 35.

³² Henning, F., and Stock, A., Über die Sättigungsdrucke einiger Dämpfe zwischen +10 und -181°: Ztschr. Physik, vol. 4, 1921, p. 226.

³³ Bergstrom, F. W., The Vapor Pressure of Sulphur Dioxide and Ammonia: Jour. Phys. Chem., vol. 26, 1922, p. 358.

³⁴ Landolt-Börnstein, —, Physikalisch-chemische Tabellen: Julius Springer, Berlin, vol. 2, 1923, p. 1345.

³⁵ Dixon, H. B., and Greenwood, G., On the Velocity of Sound in Gases and Vapors and the Ratio of the Specific Heats: Proc. Roy. Soc. London, vol. A 105, 1924, p. 199.

³⁶ Landolt-Börnstein, —, Physikalisch-chemische Tabellen: Julius Springer, Berlin, vol. 2, 1923, p. 1278.

ization) = $5,640 \div 239.7 = 23.53$, and ΔS (gas, 239.7 to 298.1) = 1.85. Finally, $S_{298.1} = 10.77 + 7.29 + 3.74 + 23.53 + 1.85 = 47.2 \pm 1.0$.

Halides.—Simon³⁷ has studied the specific heat of NH_4Cl down to 20° K.; and Simon, von Simson, and Ruhemann³⁸ have investigated the fluoride, chloride, bromide, and iodide down to about 200° K. All of these substances have transitions where the specific heat rises to very high values. These transitions are not sharp; and the specific heat becomes increasingly greater, reaches a maximum, and then falls off abruptly on the high-temperature side. Consequently, unless the total energy necessary to warm the substance through the greater part of the transition range is measured, it is practically impossible to make a reliable entropy calculation.

The author will try, however, to approximate the entropy of NH_4Cl . In this case, the specific heat increases from about 30 calories to 177 calories per mole (at 243° K.) and falls back to about 19 calories per mole, all in a temperature range of 10°. As the total energy necessary to warm the substance through this interval was not measured as a separate experiment, it is necessary to depend on a graphical method for obtaining the entropy increase in this region, which, of course, is very inaccurate due to the steepness of the specific-heat curves. The result for NH_4Cl is $S_{298.1} = 31.8$ (0.11 extrapolation below 20° K.). As nearly a third of the entropy is involved in the transition, the author will not attempt to guess the accuracy of this result.

No attempt will be made to utilize the data on the other halides, as the same difficulties are encountered as with ammonium chloride; moreover, the measurements extend down only to about 200° K., which would necessitate a very large extrapolation.

OSMIUM

Element.—The value of Lewis and Gibson³⁹ from Dewar's⁴⁰ data will be listed with the probable error, namely, $S_{298.1} = 7.8 \pm 0.5$

OXYGEN

Element.—Specific-heat measurements on condensed oxygen have been made by Eucken⁴¹ (17° to 73° K.), Giaque and Johnston⁴² (12° to 90° K.), and Clusius⁴³ (10° to 73° K.). Giaque and Johnston have calculated the entropy from spectroscopic data as well as from the third law and thermal measurements.

The results of their calculations are repeated in the following table.

³⁷ Simon, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 68, 1922, p. 241.

³⁸ Simon, F., von Simson, Cl., and Ruhemann, M., Die spezifische Wärmen der Ammoniumhalogenide zwischen -70° und Zimmertemperatur: Ztschr. physikal. Chem., vol. 129, 1927, p. 339.

³⁹ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

⁴⁰ Dewar, J. D., Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Hydrogen. I. The Mean Atomic Specific Heats at 50° Abs. of the Elements a Periodic Function of the Atomic Weights: Proc. Roy. Soc. (London), vol. A 89, 1913, p. 158.

⁴¹ Eucken, A., Über das thermische Verhalten einiger Komprimierter und Kondensierter Gase bei tiefen Temperaturen: Verh. Deut. phys. Gesell., vol. 18, 1916, p. 4.

⁴² Giaque, W. F., and Johnston, H. L., The Heat Capacity of Oxygen from 12° K. to its Boiling Point and the Heat of Vaporization. The Entropy from Spectroscopic Data: Jour. Am. Chem. Soc., vol. 51, 1929, p. 2300.

⁴³ Clusius, K., Über die spezifische Wärme einiger Kondensierter Gase zwischen 10° abs. und ihren Tripelpunkt: Ztschr. physikal. Chem., Abt. B, vol. 3, 1929, p. 41.

Entropy calculations on O₂

0 to 11.75° K., extrapolation.....	0. 321
11.75° to 23.66°, graphical.....	1. 697
Transition, 22.42÷23.66.....	. 948
23.66° to 43.76°, graphical.....	4. 661
Transition, 177.6÷43.76.....	4. 058
43.76° to 54.39°, graphical.....	2. 397
Fusion, 106.3÷54.39.....	1. 954
54.39° to 90.13°, graphical.....	6. 462
Vaporization, 1,628.8÷90.13.....	18. 07
<hr/>	
Entropy of actual O ₂ gas at boiling point..... third law..	40. 57± 0. 1
Entropy of ideal O ₂ gas at boiling point..... do.....	40. 7
Do..... spectroscopic.....	40. 68± . 01
Entropy of ideal O ₂ gas at 298. 1° K..... third law..	49. 1
Do..... spectroscopic.....	49. 03± . 01

The value 49.03 obtained from spectroscopic data is considered the better value for thermodynamic calculations.

PALLADIUM

Element.—The value of Lewis and Gibson⁴⁴ $S_{298.1} = 8.9 \pm 0.5$, will be repeated, as no pertinent new data have appeared for this substance.

PLATINUM

Element.—Simon and Zeidler's⁴⁵ specific-heat data on platinum, extending down to about 15° K., result in $S_{298.1} = 10.0 \pm 0.1$ for platinum, of which 0.06 is extrapolation below 15.85° K.

POTASSIUM AND ITS COMPOUNDS

Element.—Eastman and Rodebush⁴⁶ (68° to 287° K.) and Simon and Zeidler⁴⁷ (14° to 277° K.) have studied the specific heat of potassium metal at low temperatures. The author, basing his calculations entirely on the measurements of Simon and Zeidler, obtains $S_{298.1} = 15.2 \pm 0.2$, of which 0.45 is extrapolation below 14.1° K.

For ideal potassium gas, from the Sackur equation (adding *Rln* 2), $S_{298.1} = 38.30$.

Chloride.—The data of Nernst⁴⁸ (22° to 290° K.) and Lindemann and Schwers⁴⁹ (22° to 90° K.) on the specific heat of KCl enable the calculation of $S_{298.1} = 19.8 \pm 0.5$ for the entropy of KCl per formula weight. The extrapolation below 22.3° K. amounts to 0.39.

From the residual ray data of Rubens⁵⁰ and Rubens and Hollnagel,⁵¹ $S_{298.1} = 19.5 \pm 0.5$, which agrees well with the third-law value. The author will use 19.8 ± 0.5 , as it is the more reliable figure.

⁴⁴ See footnote 39, p. 37.

⁴⁵ Simon, F., and Zeidler, W., Untersuchungen über die spezifischen Wärmen bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 123, 1926, p. 383.

⁴⁶ Eastman, E. D., and Rodebush, W. H., The Specific Heats at Low Temperatures of Sodium, Potassium, Magnesium, and Calcium Metals, and of Lead Sulphide: Jour. Am. Chem. Soc., vol. 40, 1918, p. 489.

⁴⁷ See footnote 45.

⁴⁸ Nernst, W., Der Energieinhalt festen Stoffe: Ann. Physik, vol. 36, 1911, p. 395. See also Nernst, W., and Lindemann, F. A., Spezifische Wärme und Quantentheorie: Ztschr. Electrochem., vol. 17, 1911, p. 817.

⁴⁹ Lindemann, F. A., and Schwers, F., Eine neue Methode zur Messung von wahren spezifischen Wärmen: Physikal. Ztschr., vol. 14, 1913, p. 766.

⁵⁰ Rubens, H., Über die Absorption des Wasserdampfs und über neue Reststrahlengruppen: Berlin Sitzb., 1913, p. 513.

⁵¹ Rubens, H., and Hollnagel, H., Messungen im langwelligen Spectrum: Berlin Sitzb., 1910, p. 26.

Bromide.—Nernst⁵² has made a few specific-heat measurements on KBr in the range 75° to 90° K. Lewis and Gibson⁵³ have applied the *n*-formula to these results and have obtained $S_{298.1} = 22.4 \pm 1.0$ (the probable error being estimated by the author).

The residual ray data of Rubens⁵⁴ and of Rubens and Von Wartenburg⁵⁵ give $S_{298.1} = 22.6 \pm 0.5$. The latter value is believed to be more reliable than the former, which was obtained from meager specific-heat data.

Iodide.—From residual ray data⁵⁶ $S_{298.1} = 24.1 \pm 0.5$ for KI.

Perchlorate.—The data of Latimer and Ahlberg⁵⁷ on KClO_4 down to 12° K. give $S_{298.1} = 36.1 \pm 0.4$ for this substance. The entropy extrapolation below 12.6° K. is 0.29.

RHODIUM

Element.—A revision of the entropy of rhodium is not possible as no new data have appeared. The result of Lewis and Gibson,⁵⁸ $S_{298.1} = 7.6 \pm 0.5$, is therefore repeated.

RUBIDIUM

Element.—The entropy of solid rubidium is unobtainable, due to lack of data, but the Sackur equation (with *Rln 2* added) gives $S_{298.1} = 40.64$ for the gas.

RUTHENIUM

Element.—Again, $S_{298.1} = 6.9 \pm 0.5$, as given by Lewis and Gibson,⁵⁹ is taken.

SILICON AND ITS COMPOUNDS

Element.—Nernst and Schwers⁶⁰ (20° to 90° K.) and Anderson⁶¹ (60° to 297° K.) have measured the specific heat of silicon at low temperatures. The data of Anderson were joined to the lower temperature values of Nernst and Schwers, and $S_{298.1}$ was calculated as 4.50 ± 0.05 (with an extrapolation of 0.007 below 20.0° K.).

Quartz.—The specific heat of quartz at low temperatures has been studied by Nernst⁶² and by Günther.⁶³ If the data of Nernst are used, the entropy of quartz is $S_{298.1} = 9.9 \pm 0.2$ per formula weight. The extrapolation involved is 0.06 below 17.8° K.

Christobalite.—Specific-heat measurements have been made by Simon⁶⁴ between 28° and 117° K. on this modification of SiO_2 . The

⁵² See footnote 48, p. 38.

⁵³ See footnote 39, p. 37.

⁵⁴ See footnote 50, p. 38.

⁵⁵ Rubens, H., and von Wartenburg, H., Beitrag zur Kenntnis der langwelligen Reststrahlen: Berlin Sitzb., 1914, p. 169.

⁵⁶ See footnote 55.

⁵⁷ Latimer, W. M., and Ahlberg, J. E., The Heat Capacity and Entropy of Potassium Perchlorate from 12° to 298° Absolute. The Heat of Solution of Potassium Perchlorate. The Entropy and Free Energy of Perchlorate Ion: Jour. Am. Chem. Soc., vol. 52, 1930, p. 549.

⁵⁸ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

⁵⁹ See footnote 58.

⁶⁰ Nernst, W., and Schwers, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Sitzb. Königl. preuss. Akad. Wiss., 1914, p. 355.

⁶¹ Anderson, C. T., The Heat Capacity of Silicon at Low Temperatures: Jour. Am. Chem. Soc., vol. 52, 1930, p. 2301.

⁶² Nernst, W., Der Energieinhalt fester Stoffe: Ann. Physik, vol. 36, 1911, p. 395. See also Nernst, W., and Lindemann, F. A., Spezifische Wärme und Amanten theorie: Ztschr. Electrochem., vol. 17, 1911, p. 817.

⁶³ See Wietzel, R., Die Stabilitätsverhältnisse der Glas und Kristallphase des Siliziumdioxides: Ztschr. anorg. Chem., vol. 116, 1921, p. 71.

⁶⁴ Simon, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 68, 1922, p. 241.

calculated entropy is $S_{298.1} = 10.4 \pm 0.2$, of which 0.08 is the extrapolation below 17.8°K .

Silica glass.—Low-temperature specific heats on silica glass (quartz glass) have been measured by Nernst⁶⁵ (26° to 84°K .), Simon⁶⁶ (18° to 288°K .), and Simon and Lange⁶⁷ (10° to 13°K .). From the data of the two latter investigations the value $S_{298.1} - S_0 = 10.35 \pm 0.1$ is calculated, with an extrapolation below 10°K . of only 0.02. Simon and Lange have given the value $S_0 = 0.9 \pm 0.3$ for the entropy of silica glass at 0°K . Adding this to the value for $S_{298.1} - S_0$ gives $S_{298.1} = 11.2 \pm 0.4$ per formula weight (SiO_2 glass).

Carbide.—Measurements on silicon carbide (carborundum) have been made by Nernst and Schwers⁶⁸ (22° to 97°K .) and by Günther⁶⁹ (27° to 74°K .). The entropy calculated from these data is $S_{298.1} = 5.3 \pm 0.3$.

SILVER AND ITS COMPOUNDS

Element.—Nernst⁷⁰ and Griffiths and Griffiths⁷¹ have measured the specific heat of silver at low temperatures. The calculation of the entropy gives $S_{298.1} = 10.15 \pm 0.1$ (0.46 being extrapolated below 31.6°K .).

Oxide.—The free-energy equation of Lewis and Randall⁷² results in $\Delta S_{298.1} = -17.3$ for the reaction $2\text{Ag} + \frac{1}{2}\text{O}_2 = \text{Ag}_2\text{O}$, which makes $S_{298.1} = 27.5 \pm 2.0$ for Ag_2O .

Chloride.—Specific-heat measurements at low temperatures have been made by Nernst⁷³ (23° to 88°K .), Nernst and Schwers⁷⁴ (22° to 92°K .), Clusius and Harteck⁷⁵ (10° to 126°K .), and Milner⁷⁶ (15° to 293°K .). From the data of the last two investigations, $S_{298.1} = 23.0 \pm 0.1$, of which 0.14 is extrapolation below 10°K .

From residual ray data,⁷⁷ the value $S_{298.1} = 22.5 \pm 0.5$ is obtained for AgCl . This value agrees with the more reliable third-law result.

Bromide.—Milner⁷⁸ has also studied silver bromide down to 24°K . His measurements give $S_{298.1} = 25.6 \pm 0.2$ (the extrapolation below 22.6°K . being 1.46).

The residual ray⁷⁹ data on this substance lead to $S_{298.1} = 26.1 \pm 0.5$, but the previous value is the more reliable.

Iodide.—Nernst⁸⁰ (29° to 80°K .) and Nernst and Schwers⁸¹ (17° to 117°K .) have studied AgI at low temperatures. Their data result in $S_{298.1} = 27.1 \pm 1.0$ (1.93 extrapolation below 17.8°K .).

⁶⁵ See footnote 62.

⁶⁶ See footnote 64.

⁶⁷ Simon, F., and Lange, F., Zur Frage der Entropie amorpher Substanzen: Ztschr. Physik, vol. 38, 1926, p. 227.

⁶⁸ See footnote 60.

⁶⁹ Günther, P., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, series 4, vol. 51, 1916, p. 828.

⁷⁰ See footnote 62.

⁷¹ Griffiths, E. H., and Griffiths, E., The Capacity for Heat of Metals at Low Temperatures: Proc. Roy. Soc. (London), vol. A 90, 1914, p. 557.

⁷² Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw-Hill Book Co. (Inc.), New York, 1923, p. 481.

⁷³ See footnote 62.

⁷⁴ See footnote 60.

⁷⁵ Clusius, K., and Harteck, P., Über die spezifischen Wärmen einiger fester Körper bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 134, 1928, p. 243.

⁷⁶ Milner, R. T., The Third Law of Thermodynamics Applied to a Solid Solution of Silver Chloride and Silver Bromide: University of California, Ph. D. thesis, 1928.

⁷⁷ Rubens, H., Über die Absorption des Wasserdampfs und über neue Reststrahlengruppen: Berlin Sitzb., 1913, p. 613.

⁷⁸ See footnote 76.

⁷⁹ See footnote 77.

⁸⁰ See footnote 62.

⁸¹ Nernst, W., and Schwers, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Sitzb. könig. preuss. Akad. Wiss., 1914, p. 355.

A more reliable figure is obtainable from Gerke's⁸² cell measurements which give $\Delta S_{298.1} = -8.0$ for the reaction $\text{Pb} + 2\text{AgI} = \text{PbI}_2 + 2\text{Ag}$, from which $S_{298.1} = 27.6 \pm 0.4$ is calculated for AgI.

SODIUM AND ITS COMPOUNDS

Element.—The specific heat of sodium metal has been measured at low temperatures by Griffiths and Griffiths,⁸³ Eastman and Rodebush,⁸⁴ Günther,⁸⁵ and Simon and Zeidler.⁸⁶ Relying largely on the data of the latter investigation, $S_{298.1} = 12.2 \pm 0.1$ is obtained (0.09 being the extrapolation below 12.6° K.).

For sodium gas in the ideal state at 298.1° K., the Sackur equation (with *Rln* 2 added) gives $S_{298.1} = 36.72$.

Chloride.—The data of Nernst⁸⁷ on NaCl at low temperatures result in the value $S_{298.1} = 17.3 \pm 0.5$, the extrapolation below 25.1° K. being 0.20.

Residual ray data⁸⁸ give 17.2 ± 0.5 , which agrees with the third-law value.

SULPHUR AND ITS COMPOUNDS

Element.—No new data have appeared on the specific heat of elementary sulphur at low temperatures since the table of atomic entropies of Lewis and Randall, so their values are listed here: $S_{298.1} = 7.6 \pm 0.3$ for rhombic sulphur and $S_{298.1} = 7.8 \pm 0.3$ for monoclinic sulphur.⁸⁹

Sulphur dioxide.—The recent free-energy equation of Eastman⁹⁰ for the formation of SO₂ from the elements agrees with the value $S_{298.1} = 54.9$ per mole of SO₂ gas. This value may be in error by several units and can not be recommended except for purely qualitative thermodynamic calculations.

TANTALUM

Element.—The data of Simon and Ruhemann⁹¹ between 70° and 80° K. result in the value $\theta_D = 243.5$, from which $S_{298.1} = 9.4 \pm 0.3$. For the difference $S_p - S_r$, 0.14 has been added.

THALLIUM AND ITS COMPOUNDS

Element.—Nernst and Schwers⁹² (22° to 96° K.) and Clusius and Vaughan⁹³ (11° to 249° K.) have measured the specific heat of

⁸² Gerke, R. H., Temperature Coefficient of Electromotive Force of Galvanic Cells and the Entropies of Reactions: Jour. Am. Chem. Soc., vol. 44, 1922, p. 1684.

⁸³ See footnote 71.

⁸⁴ Eastman, E. D., and Rodebush, W. H., The Specific Heats at Low Temperatures of Sodium, Potassium, Magnesium and Calcium Metals, and of Lead Sulphide: Jour. Am. Chem. Soc., vol. 40, 1918, p. 489.

⁸⁵ Günther, P., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ann. Physik, vol. 63, 1920, p. 476.

⁸⁶ Simon, F., and Zeidler, W., Untersuchungen über die spezifischen Wärmen bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 123, 1926, p. 383.

⁸⁷ See footnote 62, p. 39.

⁸⁸ Rubens, H., Über die Absorption des Wasserdampfs und über neue Reststrahlengruppen: Berlin Sitzb., 1913, p. 513.

⁸⁹ Rubens, H., and Hollnagel, H., Messungen im langwelligen Spectrum: Berlin Sitzb., 1910, p. 26.

⁹⁰ For previous data see Nernst, W., footnote 62, p. 39.

⁹¹ Eastman, E. D., Revision of the Free Energy of Formation of Sulphur Dioxide: Inf. Circ.-6454, Bureau of Mines, 1931, 6 pp.

⁹² Simon, F., and Ruhemann, M., Ein neuer Apparat zur schnellen Bestimmung von spezifischen Wärmen fester Körper bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 129, 1927, p. 321.

⁹³ Nernst, W., and Schwers, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Sitzb. könig. preuss. Akad. Wiss., 1914, p. 355.

⁹⁴ Clusius, K., and Vaughan, J. V., I. The Specific Heats of Thallium, Calcium and Magnesium Measured to 10° Absolute. II. The Entropy and Chemical Constants of Magnesium from Spectroscopic Data: Jour. Am. Chem. Soc., vol. 52, 1930, p. 4686.

thallium metal at low temperatures. Relying entirely on the data of Clusius and Vaughen, $S_{298.1} = 15.5 \pm 0.1$, with 0.37 extrapolation below 10° K.

Chloride.—Pollitzer⁹⁴ has determined the specific heat of thallos chloride in the range 23° to 94° K. The value $S_{298.1} = 25.9 \pm 0.6$ was calculated (the extrapolation below 22.4° K. being 0.56).

Gerke⁹⁵ gives $\Delta S_{298.1} = -1.1$ for the reaction, $\text{Tl} + \text{AgCl} = \text{TlCl} + \text{Ag}$. From this figure and the entropies of Tl, AgCl, and Ag, the value $S_{298.1} = 27.2 \pm 0.4$ for thallos chloride may be obtained.

These two values, 25.9 ± 0.6 and 27.2 ± 0.4 , do not agree within the limits of the estimated errors. It may easily be that the two sets of data involved were obtained for thallos chloride in different crystalline forms or in different physical forms, so that the entropies calculated should not be comparable.

The residual ray data⁹⁶ for thallos chloride give $S_{298.1} = 23.7$, which disagrees with the other two values. For the present, the average value (third law and residual ray) of 24.8 ± 1.0 will be taken.

Other halides.—Residual ray data⁹⁷ result in $S_{298.1} = 26.8 \pm 1.0$ for TlBr and $S_{298.1} = 29.9 \pm 1.0$ for TlI.

THORIUM

Element.—Lewis and Gibson's⁹⁸ value with an estimate of the probable error will be listed $S_{298.1} = 13.6 \pm 0.8$

TIN AND ITS COMPOUNDS

Element.—Rodebush⁹⁹ has studied white tin in the range 69° to 101° K., while Lange¹ has made measurements on white tin down to 9° K. and on gray tin down to 15° K. The values for the two modifications are $S_{298.1} = 10.7 \pm 0.1$ for the gray tin and $S_{298.1} = 12.3 \pm 0.1$ for the white. The extrapolations involved are 0.25 below 12.6° K. for the gray, and 0.06 below 8.9° K. for the white.

Oxides.—Millar² has studied the specific heats of SnO and SnO₂ down to liquid-air temperatures. His data give $S_{298.1} = 13.5 \pm 0.3$ for SnO (2.07 units extrapolation below 63.1° K.) and $S_{298.1} = 12.5 \pm 0.3$ for SnO₂ (1.38 units extrapolation below 70.8° K.).

TITANIUM

Element.—For titanium, in accordance with Lewis and Gibson, $S_{298.1} = 6.6 \pm 0.4$, is used.

TUNGSTEN

Element.—Lange⁴ has made specific-heat measurements on tungsten metal from 26° to 92° K. From his data $S_{298.1} = 8.0 \pm 0.2$, of which the extrapolation below 25.1° K. is 0.07.

⁹⁴ Pollitzer, F., Bestimmung spezifischer Wärmen bei tiefen Temperaturen und ihre Verwertung zur Berechnung electromotorischer Kräfte: Ztschr. Electrochem., vol. 17, 1911, p. 5; vol. 19, 1913, p. 513.

⁹⁵ See footnote 82, p. 41.

⁹⁶ Rubens, H., and Hollnagel, H., Messungen im langwelligen Spectrum: Berlin Sitzb., 1910, p. 26.

⁹⁷ See footnote 96.

⁹⁸ Lewis, G. N., and Gibson, G. E., The Entropy of the Elements and the Third Law of Thermodynamics: Jour. Am. Chem. Soc., vol. 39, 1917, p. 2554.

⁹⁹ Rodebush, W. H., The Atomic Heats of Cadmium and Tin at Low Temperatures: Jour. Am. Chem. Soc., vol. 45, 1923, p. 1413.

¹ Lange, F., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen: Ztschr. physikal. Chem., vol. 110, 1924, p. 343.

Millar, R. W., The Heat Capacities at Low Temperatures of the Oxides of Tin and Lead: Jour. Am. Chem. Soc., vol. 51, 1929, p. 207.

² See footnote 98.

⁴ See footnote 1.

URANIUM

Element.—Lewis and Gibson,⁵ from Dewar's data, give for uranium $S_{298.1} = 11.1 \pm 0.6$.

XENON

Element.—The Sackur equation gives $S_{298.1} = 40.51$ for xenon gas.

ZINC AND ITS COMPOUNDS

Element.—Several investigators have studied the specific heat of zinc at low temperatures; Nernst⁶ (33° to 274° K.), Pollitzer⁷ (67° to 210° K.), Griffiths and Griffiths⁸ (50° to 390° K.), and Clusius and Harteck⁹ (12° to 202° K.). Considering largely the data of Clusius and Harteck, $S_{298.1} = 9.95 \pm 0.1$ (0.03 being the extrapolation below 12.6° K.).

For ideal zinc gas at 298.1° K., the Sackur equation gives 38.46. Maier¹⁰ has obtained 38.92 for actual zinc vapor at 298.1, based entirely on experimental data. The difference, 0.46, is within the limits of experimental errors in the various measurements involved plus whatever corrections are necessary for association and imperfection of gas.

Oxide.—The combined low-temperature specific-heat data of Maier, Parks, and Anderson,¹¹ Millar,¹² and Clusius and Harteck,¹³ which cover the temperature range 30° to 298.1° K., were used, and the value $S_{298.1} = 10.43 \pm 0.1$ was calculated for ZnO per formula weight.

Maier¹⁴ has determined $\Delta H_{298.1} = -83,156$ calories per gram formula weight for the heat of formation of zinc oxide from its elements and has also obtained $\Delta F_{298.1}^{\circ} = -75,930$ calories (from oxide cell measurements) and $\Delta F_{298.1}^{\circ} = -75,928$ calories (from equilibrium measurements on the reaction $\text{ZnO}(s) + \text{CO} = \text{Zn}(g) + \text{CO}_2$). These figures result in an entropy of formation, $\Delta S_{298.1} = -24.24$, from which $S_{298.1} = 10.3$ may be calculated for zinc oxide. The value of Maier is in such close agreement with the third-law result that these data may be considered as one of the best tests of that principle.

Sulphide.—Zinc sulphide has been studied by Günther¹⁵ (21° to 59° K.) and by Clusius and Harteck¹⁶ (18° to 197° K.). The data of the latter workers result in $S_{298.1} = 13.8 \pm 0.3$, with only 0.09 unit extrapolation below 17.8° K. This value is higher than that given by Maier,¹⁷ due to a numerical error in his calculations.

⁵ See footnote 98.

⁶ Nernst, W., *Der Energieinhalt festen Stoffe*: Ann. Physik, vol. 36, 1911, p. 395. See also Nernst, W. and Lindemann, F. A., *Spezifische Wärme und Quantentheorie*: Ztschr. Electrochem., vol. 17, 1911, p. 817.

⁷ See footnote 94.

⁸ Griffiths, E. H., and Griffiths, E., *The Capacity for Heat of Metals at Low Temperatures*: Proc. Roy. Soc. (London), vol. A 90, 1914, p. 557.

⁹ Clusius, K., and Harteck, P., *Über die spezifischen Wärmen einiger fester Körper bei tiefen Temperaturen*: Ztsch. physikal. Chem., vol. 134, 1928, p. 243.

¹⁰ Maier, C. G., *Zinc Smelting from a Chemical and Thermodynamic Viewpoint*: Bull. 324, Bureau of Mines, 1930, p. 40.

¹¹ Maier, C. G., Parks, G. S., and Anderson, C. T., *The Free Energy of Formation of Zinc Oxide*: Jour. Am. Chem. Soc., vol. 48, 1926, p. 2564.

¹² Millar, R. W., *The Heat Capacity at Low Temperatures of Zinc Oxide and of Cadmium Oxide*: Jour. Am. Chem. Soc., vol. 50, 1928, p. 2653.

¹³ See footnote 9.

¹⁴ Maier, C. G., *Zinc Smelting from a Chemical and Thermodynamic Viewpoint*: Bull. 324, Bureau of Mines, 1930, pp. 21-24.

¹⁵ Günther, P., *Untersuchungen über die spezifische Wärme bei tiefen Temperaturen*: Ann. Physik, series 4, vol. 51, 1916, p. 828.

¹⁶ See footnote 9.

¹⁷ Maier, C. G., *Zinc Smelting from a Chemical and Thermodynamic Viewpoint*: Bull. 324, Bureau of Mines, 1930, p. 26.

ZIRCONIUM

Element.—For zirconium, in accordance with Lewis and Gibson,¹⁸ $S_{298.1} = 9.5 \pm 0.6$.

ELECTRON GAS

The application of the Sackur equation (with $R \ln 2$ added for electron spin) to electron gas gives $S_{298.1} = 4.99$. The molecular weight was taken from the values of Avogadro's number (6.061×10^{23}) and the mass of the electron at rest (8.999×10^{-28} gram).¹⁹

METHODS OF ESTIMATING ENTROPIES

In this section some methods of estimating entropies will be considered where enough experimental data for accurate calculations are lacking. The rules given are semiempirical relationships which, although they are not well grounded theoretically, are of considerable use and give reasonably accurate values.

The Sackur equation expresses the entropy of an ideal, monatomic gas or the translational entropy of any ideal gas as a function of M (the molecular mass), T (the absolute temperature), and V (the molal volume). At constant temperature and pressure, therefore, the entropies of monatomic gases differ only in the " $3/2 R \ln M$ " term, which causes the entropy to increase with the molecular mass. This mass-effect regularity applies qualitatively to solids. Thus, for example, the entropies of Mg, Zn, and Cd increase in the order named, while those of Fe, Co, and Ni are about the same. In a solid, however, there is another equally important factor to consider, namely, the interatomic constraints or binding forces. If data on solids of a somewhat similar type are compared, it will readily be apparent that the entropy decreases as the constraints (of which hardness is a rough measure) increase. Thus, diamond has the lowest known entropy, while soft substances such as thallium or lead have high entropies. Of course, the effect of mass is partly responsible in these cases; however, the importance of the binding forces is seen readily from the fact that lithium and beryllium, which are of lower atomic weight than carbon, have larger entropies than diamond or graphite, while bismuth and uranium, which are higher in atomic mass than lead, have smaller entropies than the latter. The considerations to follow are based upon these qualitative regularities. In all cases care should be taken to apply the rules only when the postulated conditions are fulfilled.

METALS

For the metals Eastman²⁰ has proposed two equations in which the effect of mass is accounted for in a manner analogous to that in the Sackur equation. The first relationship assumes that at the melting point, T_m , the volume through which atomic oscillation takes place is proportional to the atomic volume, V . This assumption results in the equation

$$S_{298.1} = \frac{3}{2} R \ln A + R \ln V T_m^{-3/2} + 13.0. \quad (1)$$

¹⁸ See footnote 98, p. 42.

¹⁹ International Critical Tables, McGraw-Hill Book Co. (Inc.), New York, 1926, vol. 1, p. 18.

²⁰ Eastman, E. D., The Mass Effect in the Entropy of Substances: Jour. Am. Chem. Soc., vol. 45, 1923, p. 80.

The constant term was obtained from known entropy values. The second equation connects the atomic volume and compressibility, β , with the amplitude of vibration to give

$$S_{298.1} = \frac{3}{2} R \ln A + R \ln V^{-1} \beta^{3/2} + 42.1. \quad (2)$$

Again the constant term was determined from experimental data. Either of these equations represents the known entropy data within an average deviation of 0.7 to 0.8 unit per substance. Eastman has expressed preference for the first, however, since the largest deviations from it, which occur for the alkali metals, are in the direction and of the order of magnitude that can be explained by such consideration of the effect of very loosely bound electrons.

The following table is a reproduction of that given by Eastman, except that the author has substituted his recalculated entropies in place of some of the less accurate values that were accepted at the time Eastman's work was published.

Atomic entropies of metals, calories per degree at 298.1° K.

Metal	Experimental	Equation (1)	Equation (2)	Metal	Experimental	Equation (1)	Equation (2)
Li.....	7.6±0.5	5.6	8.1	Rh.....	7.6±0.5	8.0	-----
Na.....	12.2±.1	10.9	12.1	Pd.....	8.9±.5	9.1	8.5
Mg.....	7.8±.1	7.2	8.4	Ag.....	10.2±.1	10.3	10.2
Al.....	6.8±.1	6.9	7.3	Cd.....	12.3±.1	13.0	12.0
Si.....	4.5±.05	5.7	2.6	Sn (white).....	12.3±.1	14.1	11.5
K.....	15.2±.2	14.1	14.5	La.....	13.7±.8	13.0	-----
Ca.....	10.0±.1	9.6	10.7	Ce.....	13.8±.8	13.3	-----
Ti.....	6.6±.4	6.3	-----	W.....	8.0±.2	8.6	8.1
Cr.....	5.6±.2	6.3	8.3	Os.....	7.8±.5	9.0	-----
Mn.....	7.3±.5	6.9	8.2	Ir.....	8.7±.5	9.3	-----
Fe.....	6.5±.1	6.5	7.0	Pt.....	10.0±.1	10.2	9.3
Co.....	6.8±.2	6.5	-----	Au.....	11.4±.1	11.8	10.6
Ni.....	7.1±.1	6.5	6.7	Tl.....	15.5±.1	15.6	13.6
Cu.....	7.9±.1	7.7	8.5	Pb.....	15.6±.1	15.5	13.6
Zn.....	10.0±.1	10.3	10.5	Th.....	13.6±.8	12.4	-----
Mo.....	6.8±.1	7.5	7.4	U.....	11.1±.6	10.5	-----
Ru.....	6.9±.5	7.9	-----				

Of the metals whose entropies have not been measured equation (1) gives $S_{298.1} = 10.9$ for Ba, $S_{298.1} = 9.7$ for Ge, $S_{298.1} = 14.5$ for In, $S_{298.1} = 12.7$ for Pr, $S_{298.1} = 17.2$ for Rb (probably low), $S_{298.1} = 6.5$ for V, and $S_{298.1} = 19.0$ for Cs (probably low).²¹

SALTS

A rule for calculating entropies for the simpler types of salts has been given by Latimer.²² He assumes that when the specific heat has reached the equipartition value of 6 calories per mean gram-atom, the effect of constraint on the entropy is either negligible or the same for each atom in any of the simpler salts. Consequently, the "con-

²¹ The data used in making these calculations were those given in Landolt-Börnstein, —, Physikalisch-chemische Tabellen, Julius Springer, Berlin, 1923, vols. 1 and 2; also Erster Ergänzungsband, 1927.

²² Latimer, W. M., The Mass Effect in the Entropy of Solids and Gases: Jour. Am. Chem. Soc., vol. 43, 1921, p. 818.

straint" term may be considered either as omitted or as being part of the constant term. By analogy with the Sackur equation

$$S_{298.1} = \frac{3}{2} R \ln A + S_0 \quad (3)$$

for the entropy per gram-atom for each chemical element in the salt, or

$$S_{298.1} = \frac{3}{2} R \ln A_1 A_2 \dots A_n + n S_0 \quad (4)$$

per formula weight of salt. Here the "A's" are atomic weights, n the number of atoms in the chemical formula for the salt, and S_0 is a constant which Latimer evaluated as -0.94 from the known entropy of potassium chloride. This rule may be applied to salts at 298.1°K . only when the equipartition value of the specific heat has been reached, which practically limits it to the metallic halides. The following table gives entropy values calculated from Latimer's equation for all salts that practically fulfill the necessary condition and on which sufficient data exist to obtain the entropies by other means.

Entropies of salts at 298.1° K

Substance	$S_{298.1}$ calculated from equation (4)	$S_{298.1}$ adopted from experimental data	Substance	$S_{298.1}$ calculated from equation (4)	$S_{298.1}$ adopted from experimental data
KCl.....	19.7	19.8±0.5	HgCl.....	24.6	23.4±0.5
KBr.....	22.1	22.6±.5	TlCl.....	24.6	24.8±1.0
KI.....	23.5	24.1±.5	TlBr.....	27.0	26.8±1.0
NaCl.....	18.1	17.3±.5	TlI.....	28.4	29.9±1.0
AgCl.....	22.7	23.0±.1	PbCl.....	34.4	32.6±.6
AgBr.....	25.1	25.6±.2	PbBr.....	39.2	38.6±.8
AgI.....	26.5	27.6±.4	PbI ₂	42.0	42.3±.2
CuI.....	25.0	23.1±.3			

This comparison shows that for about half the substances the experimental entropies are represented well within the limits of error by equation 4. For other salts the differences may be accounted for by the fact that the postulated condition as to specific heat is not quite fulfilled at 298.1°K . One need have little hesitancy in applying this equation to other salts similar to those given in the table. It does not work for oxides, sulphides, sulphates, nitrates, etc., but these are usually prohibited by the condition anyhow.

OXIDES

An equation of the form just given for salts would be not expected to represent the known entropy data for oxides, as they show great variation in their specific heats per average atom at room temperature, most of which are still far below the equipartition value. Moreover, due to lack of data, it is not possible to utilize expressions similar to equations (1) and (2). In attempting to find some usable relationship depending upon atomic masses, the author has obtained

$$S_{298.1} = \frac{3}{2} R a \ln A_m + \frac{3}{2} R b r \ln 16 + (a+b) S_0, \quad (5)$$

where A_m is the atomic weight of the metal, a and b are the numbers of metal atoms and oxygen atoms in the chemical formula for the oxide (Me_aO_b), and S_o is a constant. The symbol r is the ratio $\frac{C_{p,298.1} - 6a}{6b}$, where $C_{p,298.1}$ is the true specific heat per formula weight at constant pressure and at 298.1° K.; that is, r is the ratio of the Kopp's law constant for the oxygen atoms in the compound to the equipartition value, assuming that all the oxygen atoms behave alike and that the equipartition specific heat may be assigned to the metal atoms. This expression admittedly is unsound theoretically, but it fits most of the experimental data very well. The largest discrepancies occur in the values calculated for the oxides of iron and manganese and for cuprous oxide; however, for ferrous and cuprous oxides the errors in the experimental values are such that no comparison is warranted. With these few substances omitted, then, the following table contains values calculated from equation (5) and the corresponding results based upon experiment. S_o has been taken as -3.5 for oxides of the types MeO and MeO_2 , and as -3.1 for those of the types Me_2O_3 , Me_2O_4 , Me_2O_5 , and Me_3O_4 .

Entropies of oxides

Substance	$S_{298.1}$ calculated from equation (5)	$S_{298.1}$ (experimental)	Substance	$S_{298.1}$ calculated from equation (5)	$S_{298.1}$ (experimental)
MgO.....	6.4	6.4±0.1	Pb ₃ O ₄	49.4	50.5±1.6
CaO.....	9.8	9.5±.2	As ₂ O ₃	25.2	25.6±.5
ZnO.....	10.3	10.4±.1	As ₂ O ₅	25.9	25.2±.4
CdO.....	13.1	13.1±.3	Sb ₂ O ₃	29.8	29.4±.4
CuO.....	11.0	10.4±.2	Sb ₂ O ₄	30.8	30.4±.7
SnO.....	13.6	13.5±.3	Sb ₂ O ₅	28.7	29.9±1.2
SnO ₂	12.7	12.5±.3	Bi ₂ O ₃	37.1	36.2±.7
PbO (yellow).....	16.5	16.9±.4	Al ₂ O ₃	13.6	12.6±.2
PbO ₂	18.2	18.3±.5	HgO (red).....	16.0	16.6±1.0

In only one case, Al_2O_3 , does the calculated result fall appreciably outside the limit of experimental error in the measured value. It is interesting to note that the form of Al_2O_3 on which the low-temperature specific heats were measured was the sapphire, a substance which is almost as hard as diamond. Consequently, this result may be looked upon as an extreme case, as the value of r is considerably smaller than for any other substance in the list.

Russell²³ has measured mean specific heats on a number of substances near room temperature. Among them are five oxides for which the entropies have not already been listed, and to which equation (5) may be applied to give $S_{298.1} = 17.7$ for CeO_2 , $S_{298.1} = 25.0$ for Sc_2O_3 (this value seems abnormally high), $S_{298.1} = 19.6$ for ThO_2 , $S_{298.1} = 72.7$ for U_3O_8 (assuming $S_o = -3.1$), and $S_{298.1} = 18.3$ for WO_3 (assuming $S_o = -3.5$).

SULPHIDES

The data on sulphides are more meager, true specific heats having been measured at low temperatures on only eight of these substances. Equation (5) does not apply so well to sulphides as to oxides. The

²³ Russell, A. S., Messungen von spezifischen Wärmen bei tiefen Temperaturen: Physikal. Ztschr., vol. 13, 1912, p. 59.

comparisons of experimental values with those calculated by this rule follow, S_0 being taken as -3.1 in all cases.

Entropies of sulphides

Substance	$S_{298.1}$ calculated from equation (5)	$S_{298.1}$ (experimental)	Substance	$S_{298.1}$ calculated from equation (5)	$S_{298.1}$ (experimental)
CaS	13.9	13.5±0.3	FeS	17.8	16.1±0.3
ZnS	14.3	13.8±.3	FeS ₂	17.5	15.6±.4
PbS	19.7	21.8±.7	Cu ₂ S	25.8	28.9±.8
CuS	15.5	15.9±.4	MnS	16.1	18.7±.3

Russell's²⁴ mean specific-heat data on CdS and HgS enable the calculation, by means of equation (5), of $S_{298.1} = 14.0$ for CdS and $S_{298.1} = 19.8$ for HgS.

SILICATES

Parks and Kelley²⁵ have shown that between 200° and 650° K. the specific heat of calcium silicate is equal to the sum of that for calcium oxide and that for silica (glass). At 150° K. the difference between the observed and calculated specific heats is about 5 per cent and at 100° K., about 14 per cent. The data on magnesium silicate do not extend to low temperatures, but between 300° and 650° K. the observed specific heat and the sum for the component oxides are equal for this substance also. Presumably, the same would be true for any simple silicate. Consequently, one might expect that at high temperature the entropies of these substances would be roughly the sum of the entropies of the oxides of which they may be considered as being composed. That this is a fair approximation is shown by the following table.

Entropies of silicates

Substance	$S_{298.1}$ (experimental)	$S_{298.1}$ (sum of entropies of component oxides)
CaSiO ₃ (pseudowollastonite)	22.2±0.7	20.7
Al ₂ SiO ₅ (sillimanite)	25.0±.3	23.8
Al ₂ SiO ₅ (andalusite)	27.0±.3	23.8
Al ₂ SiO ₅ (disthen)	20.7±.3	23.8

GASES

Latimer,²⁶ Eastman,²⁷ and others have given semiempirical equations for calculating entropies of diatomic gases. No discussion of this subject will be included here, as values for the important diatomic gases have already been obtained by more reliable means.

²⁴ See footnote 23, p. 47.

²⁵ Parks, G. S., and Kelley, K. K., The Heat Capacity of Calcium Silicate: Jour. Phys. Chem., vol. 30, 1926, pp. 1175-1178.

²⁶ See footnote 22, p. 45.

²⁷ See footnote 20, p. 44.

I	II	III	IV	V	VI	VII	VIII
<p>(H₂) 31.23 ± nil H₂O 15.9 ± 0.1 HBr 47.48 ± nil HCl 44.64 ± nil HI 49.40 ± nil HF 41.5 ± 0.1 H₂S 48.2 ± 1.0</p>	<p>(He) 2.14 ± 0.05 4</p>	<p>(B) 5</p>	<p>(C) (diamond) 0.6 ± nil C (β-graphite) 1.3 ± nil CO 47.3 ± 0.1 CO₂ 50.0 ± 2.0 CH₄ 44.5 ± 1.0</p>	<p>(N₂) 45.8 ± 0.3 7 N₂O 51.4 ± 1.0 NO 50.43 ± nil NH₃ 47.2 ± 1.0 NH₄Cl 31.8 ± ?</p>	<p>(O₂) 49.03 ± nil 8</p>	<p>(F) 9</p>	<p>(Ne) 34.96 ± nil 10</p>
<p>(Li) 7.6 ± 0.5 3 (33.15 ± nil (g)) LiH 5.9 ± 0.5</p>	<p>(Be) 2.14 ± 0.05 4</p>	<p>(Al) 6.75 ± 0.1 13 Al₂O₃ 12.6 ± 0.2 Al₂SiO₅ (disthen) 20.7 ± 0.3 Al₂SiO₅ (sillimanite) 25.0 ± 0.3 Al₂SiO₅ (andalusite) 27.0 ± 0.3</p>	<p>(Si) 4.50 ± 0.5 14 SiO₂ (quartz) 9.9 ± 0.2 SiO₂ (tristhenite) 10.4 ± 0.2 SiO₂ (glass) 11.2 ± 0.4 SiC 5.3 ± 0.3</p>	<p>(P) 15</p>	<p>(S) (rhombic) 7.65 ± 0.3 16 S (monoclinic) 7.85 ± 0.3 SO₂ 54.9 ± ?</p>	<p>(Cl₂) 53.0 ± 0.4 17</p>	<p>(Ar) 36.99 ± nil 18</p>
<p>(K) 15.2 ± 0.2 19 (38.30 ± nil (g)) KBr 22.6 ± 0.5 KCl 19.8 ± 0.5 KI 24.1 ± 0.5 KClO₄ 36.1 ± 0.4</p>	<p>(Ca) 9.95 ± 0.1 20 CaO 9.5 ± 0.2 CaS 13.5 ± 0.3 CaF₂ 16.4 ± 0.4 CaH₂ 9.9 ± 0.1 CaCO₃ (calc) 20.6 ± 0.7 CaCO₃ (arag) 19.9 ± 0.5 Ca(OH)₂ 17.4 ± 1.0 CaSiO₃ 22.2 ± 0.7</p>	<p>(Sc) 21 Sc₂O₃ (25.0)</p>	<p>(Ti) 6.6 ± 0.4 22</p>	<p>(V) (6.5) 23</p>	<p>(Cr) 5.6 ± 0.2 24</p>	<p>(Mn) 7.3 ± 0.5 25 MnO 14.4 ± 0.6 MnO₂ 13.9 ± 0.4 Mn₂O₃ 35.5 ± 0.7 MnS 16.7 ± 0.3</p>	<p>(Fe) 6.5 ± 0.1 26 FeO 14.2 ± 2.0 Fe₂O₃ 21.5 ± 0.5 Fe₃O₄ 35.0 ± 0.7 FeS 16.1 ± 0.3 FeS₂ 15.6 ± 0.4</p>
<p>(Cu) 7.9 ± 0.1 29 Cu₂O 24.1 ± 1.5 Cu₂S 10.4 ± 0.2 Cu₃S 28.9 ± 0.8 Cu₅S 15.9 ± 0.4 CuI 23.1 ± 0.3</p>	<p>(Zn) 9.95 ± 0.1 30 (38.46 ± nil (g)) ZnO 10.4 ± 0.1 ZnS 13.8 ± 0.3</p>	<p>(Ga) 10.2 ± 0.5 31</p>	<p>(Ge) (9.7) 32</p>	<p>(As) 8.4 ± 0.2 33 As₂O₃ 25.6 ± 0.5 As₂O₅ 25.2 ± 0.4</p>	<p>(Se) 34</p>	<p>(Br₂) 36.6 ± 0.5 35</p>	<p>(Kr) 39.17 ± nil 36</p>
<p>(Rb) (17.2) 37 (40.64 ± nil (g))</p>	<p>(Sr) 38</p>	<p>(Yt) 39</p>	<p>(Zr) 9.5 ± 0.6 40</p>	<p>(Co) 41</p>	<p>(Mo) 6.8 ± 0.1 42</p>	<p>(Nb) 43</p>	<p>(Ru) 6.9 ± 0.5 44</p>
<p>(Ag) 10.2 ± 0.1 47 Ag₂O 27.5 ± 2.0 AgBr 25.6 ± 0.2 AgCl 23.0 ± 0.1 AgI 27.6 ± 0.4</p>	<p>(Cd) 12.3 ± 0.1 48 CdO 13.1 ± 0.3 CdS (14.0)</p>	<p>(In) (14.5) 49</p>	<p>(Sn) (white) 12.3 ± 0.1 50 Sn (gray) 10.7 ± 0.1 SnO 13.5 ± 0.3 SnO₂ 12.5 ± 0.3</p>	<p>(Sb) 10.5 ± 0.3 51 Sb₂O₃ 29.4 ± 0.4 Sb₂O₄ 30.4 ± 0.7 Sb₂O₅ 29.9 ± 1.2</p>	<p>(Te) 52</p>	<p>(I₂) 27.9 ± 0.1 53 (62.29 ± nil (g))</p>	<p>(Xe) 40.51 ± nil 54</p>
<p>(Cs) (19.0) 55 (41.95 ± nil (g))</p>	<p>(Ba) (10.9) 56 Ba(NO₃)₂ 51.1 ± 0.4</p>	<p>Rare earths 57-71</p>	<p>(Hf) 72</p>	<p>(Ta) 9.4 ± 0.3 73</p>	<p>(W) 8.0 ± 0.2 74 WO₃ (18.3)</p>	<p>(Re) 75</p>	<p>(Os) 7.8 ± 0.5 76</p>
<p>(Au) 11.4 ± 0.1 79</p>	<p>(Hg) { 18.5 ± 0.2 (l) 80 (41.80 ± nil (g)) HgO (red) 16.6 ± 1.0 HgO (yellow) 17.0 ± 0.4 HgCl 23.4 ± 0.5 Hg₂SO₄ 49.3 ± 5.0 HgS (19.8)</p>	<p>(Tl) 15.5 ± 0.1 81 TlBr 26.8 ± 1.0 TlCl 24.8 ± 1.0 TlI 29.9 ± 1.0</p>	<p>(Pb) 15.6 ± 0.1 82 PbO (yellow) 16.3 ± 0.4 PbO (red) 16.3 ± 0.4 Pb₂O₃ 30.2 ± 1.3 Pb₃O₄ 31.8 ± 1.6 PbCl₂ 24.6 ± 0.6 PbCl₄ 38.6 ± 0.8 PbBr₂ 38.6 ± 0.8 PbI₂ 42.3 ± 0.2</p>	<p>(Bi) 13.8 ± 0.6 83 Bi₂O₃ 36.2 ± 0.7</p>	<p>(Po) 84</p>	<p>(At) 85</p>	<p>(Rn) 86</p>
<p>87</p>	<p>(Ra) 88</p>	<p>(Ac) 89</p>	<p>(Th) 13.6 ± 0.8 90 ThO₂ (19.6)</p>	<p>(Ux) 91</p>	<p>(U) 11.1 ± 0.6 92 U₃O₈ (72.7)</p>	<p>(Pa) 93</p>	<p>(U) 94</p>
<p>Rare Earths: (Gd) 64</p>	<p>(La) 13.7 ± 0.8 57</p>	<p>(Ce) 13.8 ± 0.8 58 CeO₂ (17.7)</p>	<p>(Pr) (12.7) 59</p>	<p>(Nd) 60</p>	<p>(Pm) 61</p>	<p>(Sm) 62</p>	<p>(Eu) 63</p>
<p>(Tb) 65</p>	<p>(Dy) 66</p>	<p>(Ho) 67</p>	<p>(Er) 68</p>	<p>(Tm) 69</p>	<p>(Yb) 70</p>	<p>(Lu) 71</p>	<p>(Hf) 87 8.7 ± 0.5 77</p>
							<p>(Pt) 10.0 ± 0.1 78</p>
							<p>(Pd) 8.9 ± 0.5 46</p>
							<p>(Ni) 7.1 ± 0.1 28</p>
							<p>(Co) 6.8 ± 0.2 27</p>
							<p>(Rh) 7.6 ± 0.5 45</p>
							<p>(Ir) 8.7 ± 0.5 77</p>
							<p>(Os) 7.8 ± 0.5 76</p>
							<p>(Pt) 10.0 ± 0.1 78</p>
							<p>Electron gas 4.99 ± nil</p>

The letters (l) and (g) denote liquid and gaseous states, respectively.

FIGURE 1.—Periodic chart of entropy values for elements and compounds
NOTE.—Since the above chart was prepared the following changes have been noted in entropy values: CH₄, 44.5 ± 0.5; Si, 4.50 ± 0.05; CaH₂, 9.9 ± 1.0

SPECIFIC HEAT, ENTROPY, AND HEAT OF TRANSFORMATION
TABLES

EXPLANATION OF TABLES

The following tables constitute a résumé of the experimental data on entropies for the elements and compounds and the methods of estimating them. Table 1 gives specific-heat values read from the smooth curves used in obtaining entropies, except in a few cases where it was not possible to give more than one or two results. The figures in parentheses are extrapolations below or above the range of the actual measurements. For gases where correction was made to the ideal state in calculating the entropy, the specific heats tabulated are theoretical values for perfect gases. The entropies obtained by the various methods are also shown in Table 1, with the value recommended, at present, for use in thermodynamic calculations. Entropy values computed by use of the formulas given under Methods of Estimating Entropies are shown in parentheses. The asterisk is used to distinguish substances having "humps" in their specific-heat curves; that is, transitions that do not occur sharply at one temperature. The dagger marks substances that undergo one or more of the following changes—sharp transition, fusion, vaporization, and sublimation—in the temperature interval 0° to 298.1° K. The letters *s*, *l*, and *g* are used to denote solid, liquid, and gaseous states. The same classification has been followed as in the section on experimental data; and blank spaces have been left under each element, except the rare gases, which may be filled in as new data appear.

Table 2 gives thermal data on changes in state, including sharp transition, for the substances marked with the dagger in Table 1. Specific-heat values for both the high and low temperature forms are tabulated for the temperature designated. For solids and liquids the latter are all slight extrapolations of actual measured specific heats. For gases, some of the specific-heat values are theoretical figures for perfect gases. Small amounts of impurities produce large effects on specific heats measured just below a transition or melting point. Consequently, it is often impossible to state just what the specific heat of the low-temperature form should be at the actual temperature of transition or fusion. The values given here for such cases were read from the curves drawn for obtaining the entropies; and, while they may not be entirely correct, their usefulness for the purpose of checking entropy calculations is not impaired.

Figure 1 is a periodic chart showing entropy values of elements and compounds, arranged with ample space for subsequent additions.

TABLE 1.—*Low-temperature specific heats and entropies at 298.1° K.*

Substance	Specific heats, calories per formula weight							Entropies				Value recom- mended
	10°	25°	50°	100°	150°	200°	298.1° K.	Third law	ΔF and ΔH	Sackur equa- tion, or spectroscopic	Residual rays, or calculated	
Aluminum:												
Al	(.01)	0.13 (.09)	0.94 (.70)	3.09 (3.03)	4.36 (4.36)	5.07 (5.07)	5.81 (5.81)	6.75±0.1				6.75±0.1
Al ₂ O ₃	(.01)	(.01)	(.01)	(.01)	(.01)	(.01)	(.01)	12.6 ± .2				12.6 ± .2
Al ₂ O ₃ (disthen)	(.01)	.19	1.10	6.07	13.15	19.68	(29.03)	20.7 ± .3				20.7 ± .3
Al ₂ SiO ₅ (sillimanite)	(.03)	.47	2.58	8.44	15.22	21.65	30.45	25.0 ± .3				25.0 ± .3
Al ₂ SiO ₅ (andalusite)	(.03)	.55	2.97	9.60	16.91	22.45	32.14	27.0 ± .3				27.0 ± .3
(¹)												
Antimony:												
Sb	(.06)	(.81)	(2.99)	4.92	5.55	5.82	6.03	10.5 ± .3				10.5 ± .3
Sb ₂ O ₃	(.23)	(2.16)	(5.50)	12.02	16.79	20.26	24.23	23.4 ± .4				23.4 ± .4
Sb ₂ O ₄	(.26)	(2.31)	(5.49)	11.16	17.27	21.75	27.39	30.4 ± .7				30.4 ± .7
Sb ₂ O ₅	(.08)	(1.03)	(3.94)	12.67	18.48	22.73	28.11	23.9 ± 1.2				23.9 ± 1.2
Argon: Ar	(.72)	3.75	6.20(6)	4.97(7)	4.97	4.97	4.97	36.8 ± .2		36.90±nil.		36.90±nil.
Arsenic:												
As	(.03)	(.35)	(1.88)	3.99	4.94	5.43	5.89	8.4 ± .2				8.4 ± .2
As ₂ O ₃	(.25)	(2.16)	(4.77)	9.72	14.45	18.26	22.86	25.6 ± .5				25.6 ± .5
As ₂ O ₅	(.03)	(.50)	(2.62)	9.45	15.87	20.93	27.85	25.2 ± .4				25.2 ± .4
Barium:												
Ba	(.45)	4.02	12.27	22.73	27.38	30.60	36.07	51.1 ± .4		(10.9)		(10.9)
Ba(N ₂ O ₇) ₂	(.00)	(.00)	(.05)	.38	1.21	2.26	3.84	2.14 ± .05				2.14 ± .05
Beryllium:												
Be	(.00)	(.00)	(.05)	.38	1.21	2.26	3.84	2.14 ± .05				2.14 ± .05
Bismuth:												
Bi	(.49)	2.60	4.24	5.47	5.83	5.98	6.10	13.8 ± .6				13.8 ± .6
Bi ₂ O ₃	(.49)	(2.95)	(7.33)	15.04	19.48	23.10	27.13	36.2 ± .7				36.2 ± .7

TABLE 1.—Low-temperature specific heats and entropies at 298.1° K.—Continued

Substance	Specific heats, calories per formula weight							Entropies				Residual rays, or calculated	Value recommended	
	10°	25°	50°	100°	150°	200°	298.1° K.	Third law	ΔF and ΔH	Sackur equation, or spectroscopic				
Aluminum: Al														
Indium: In												(14.5)	(14.5)	
Iodine: I ₂	0.98	5.12	8.79	10.96	11.86	12.42	13.14	27.9±0.1		62.29(g)				{ 27.9 ± 0.1(g), 62.29 ± nil(g) }
Iridium: Ir			(7)					8.7 ± .5						8.7 ± .5
Iron: Fe FeO FeO* Fe ₂ O ₃ FeO* Fe ₃ O ₄ FeS	(.01) (.02) (.05) (.06) (.05) (.02)	.09 (.24) (.77) (.85) (.73) (.27)	.71 (1.45) (2.86) (3.72) (2.82) 1.97	2.82 5.85 7.65 13.53 7.13 6.98	4.33 10.00 13.42 22.17 9.85 9.94	5.17 11.73 18.27 27.85 11.33 11.98	6.03 12.43 25.04 34.28 13.06 14.57	6.5 ± .1 14.2 ± 2.0 21.5 ± .5 35.0 ± .7 16.1 ± .3 15.6 ± .4						6.5 ± .1 14.2 ± 2.0 21.5 ± .5 35.0 ± .7 16.1 ± .3 15.6 ± .4
Krypton: Kr														39.17 ± nil.
Lanthanum: La			(9)					13.7 ± .8			39.17 ± nil.			13.7 ± .8

Lead:										
Pb	.74	3.35	5.13	5.91	6.13	6.23	6.34	15.6±.1	17.1±0.3	15.6±.1
PbO (yellow)	(.23)	1.95	3.99	6.75	8.55	9.84	11.00	16.6±.5		16.9±.4
PbO ₂	(.08)	(3.64)	(3.64)	7.56	10.42	12.56	15.45	18.3±.5		18.3±.5
Pb ₂ O ₃	(^g)	(^g)	(^g)	20.84	26.98	31.29	35.14	50.5±1.6		50.5±1.6
PbS	(.37)	(2.88)	(6.18)	9.41	10.65	11.25	11.83	21.8±.6		21.8±.6
PbBr ₂	(1.11)	5.41	12.00	16.30	17.61	18.31	19.15	38.6±.8		38.6±.8
PbCl ₂	(.77)	4.37	10.09	14.32	16.24	17.29	18.35	34.0±1.0		32.6±.6
PbI ₂	(^g)	(^g)	(^g)	(^g)	(^g)	(^g)	(^g)	41.3±1.5		42.3±.2
Lithium:										
Li			(^g)					7.6±.5		7.6±.5
LiH	(.00)	(.03)	(.23)	1.66	4.03	5.79	8.28	5.9±.5	33.15(^g)	33.15±m(^g)
Lutecium:										
Lu										
Magnesium:										
Mg	.01	.19	1.41	3.77	4.90	5.38	5.71	7.8±.1		7.8±.1
MgO	(.00)	(.01)	.11	1.89	4.38	6.30	8.96	6.4±.1	35.51(^g)	35.51±m(^g)
Manganese:										
Mn	(.04)	(.54)	(2.50)	7.88	7.98	9.10	10.27	7.3±.5		7.3±.5
MnO*	(.03)	(.37)	(1.94)	5.96	8.02	10.34	13.67	14.4±.6		14.4±.6
Mn ₂ O ₃ *	(.06)	(.99)	(5.18)	14.41	21.95	27.37	33.29	13.9±.4		13.9±.4
MnS*	(.05)	(.74)	(3.46)	9.41	11.91	11.39	11.94	35.5±.7		35.5±.7
								18.7±.3		18.7±.3
Masurium:										
Ma										

* Denotes substances having humps in their specific-heat curves (transitions which are not sharp) between 0 and 298.1° K.
 † Insufficient data; n-formula used.

7.177 at 48.5° K.
 8.424 at 48.5° K.
 9.124 at 48.5° K.
 10.116 at 48.5° K.

TABLE 1.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula weight								Entropies				Value recom- mended
	10°	25°	50°	100°	150°	200°	298.1° K.	Third law	ΔF and ΔH	Sackur equa- tion, or spectroscopic	Residual rays, or calculated		
Mercury:													
HgI ₂	1.10	3.15	5.02	5.90	6.27	6.57(s)	6.65(l)	18.5±0.2		41.80(g)			$18.5 \pm 0.2(l)$
HgO (red).....	(.19)	1.94	4.31	6.89	8.39	9.46	10.93	16.6±1.0					$41.80 \pm 1.0(g)$
HgO (yellow).....									17.0±0.4				17.0 ± 0.4
HgCl ₂	(.48)	3.52	6.81	9.44	10.67	11.38	12.15	23.0±.7			24.7		$23.4 \pm .5$
HgSO ₄	(1.86)	7.49	12.82	18.57	22.77	25.95	31.27	49.3±5.0			(19.8)		49.3 ± 5.0
HgS.....													(19.8)
Molybdenum:													
Mo.....	(.01)	.13	.94	3.19	4.49	5.10	5.61	6.8±.1					$6.8 \pm .1$
Neodymium:													
Nd.....													
Neon: Nef	1.48(s)									.34.96±nil			$34.96 \pm \text{nil}$
Nickel:													
Ni.....	(.01)	.13	.99	3.24	4.64	5.38	6.16	7.1±.1					$7.1 \pm .1$
Nitron: Ni:													
Nitrogen:													
N ₂ l.....	1.25	6.32	10.00(s)	7.16(g)	7.09	7.04	6.98	45.8±.3		42.10±nil			$45.8 \pm .3$
N ₂ g.....	.23	2.46	6.61	6.09	12.21	8.32(g)	9.28	51.4±1.0					51.4 ± 1.0
N ₂ O.....	(.28)	2.30	3.09	8.61(s)	9.56(s)	18.36(l)	8.5(g)	47.2±1.0		50.43±nil			$50.43 \pm \text{nil}$
NH ₃	(.09)	1.67	3.01	9.00	12.32	16.30	20.71	31.8±					47.9 ± 1.0
NH ₄ C*.....	(.05)	.64	3.67										31.8

TABLE 1.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula weight						Entropies				Residual rays, or calculated	Value recommended	
	10°	25°	50°	100°	150°	200°	298.1° K.	Third law	ΔF and ΔH	Sackur equation, or spectroscopic			
Rhenium:													
Rhodium:													
Rh			(¹)					7.6 ± 0.5					7.6 ± 0.5
Rubidium:													
Rb										40.64 ± ml(θ)		(17.2)	{ (17.2) (θ), 40.64 ± ml(θ).
Ruthenium:													
Ru			(¹)						6.9 ± .5				6.9 ± .5
Samarium:													
Sa													
Scandium:													
Sc ₂ O ₃												(25.0) high	(25.0)
Selenium:													
Se													
Silicon:													
Si	(.00)	0.06	0.48	1.74	2.87	3.74	4.73	4.50 ± .05					4.50 ± .05
SiO ₂ (quartz)	(.03)	.40	1.37	3.73	5.77	7.71	10.67	9.9 ± .2					9.9 ± .2
SiO ₂ (cristobalite)	(.04)	.49	1.53	3.84	6.10	8.03	10.82	10.4 ± .2					10.4 ± .2
SiO ₂ (glass)	(.06)	.56	1.63	3.86	5.89	7.75	10.60	11.2 ± .4					11.2 ± .4
SiC	(.00)	(.00)	.11	2.10	3.70	4.88	6.53	5.3 ± .3					5.3 ± .3

TABLE 2.—*Thermal data for transformation points*

Substance	Temperature °K.	Type of change	Heat absorbed, calories per mole	C _p , low-temperature form	C _p , high-temperature form
Argon: A.....	83.0	Fusion.....	267.8	7.30	10.43
	87.3	Vaporization (1 atmosphere).....	1,544	10.50	4.97
Bromine: Br ₂	285.9	Fusion.....	2,580	14.45	8.5
Carbon monoxide: CO.....	61.5	Transition.....	151.2	14.70	12.04
	68.2	Fusion.....	201.5	12.40	14.26
Carbon dioxide: CO ₂	83.1	Vaporization (1 atmosphere).....	1,414	14.78	7.28
	104.6	Sublimation (1 atmosphere).....	6,220	12.95	8.1
Methane: CH ₄	90.6	Fusion.....	224.0	10.31	12.72
	117.8	Vaporization (1 atmosphere).....	2,040	13.11	6.73
Chlorine: Cl ₂	170.8	Fusion.....	1,615	13.80	16.25
	238.4	Vaporization (1 atmosphere).....	4,380	16.25	8.28
Water: H ₂ O.....	273.1	Fusion.....	1,436	9.81	18.04
Hydrogen bromide: HBr.....	186.2	do.....	575.1	12.48	14.27
	206.4	Vaporization (1 atmosphere).....	4,210	14.27	6.95
Hydrogen chloride: HCl.....	98.4	Transition.....	284.3	8.42	9.38
	158.9	Fusion.....	476.0	11.78	13.85
Hydrogen iodide: HI.....	188.1	Vaporization (1 atmosphere).....	3,860	14.08	6.95
	222.3	Fusion.....	686.3	12.29	14.44
Mercury: Hg.....	237.8	Vaporization (1 atmosphere).....	4,724	14.12	6.95
	234.2	Fusion.....	557.2	6.88	6.83
Neon: Ne.....	24.59	do.....	---	---	---
Nitrogen: N ₂	24.59	Sublimation (323.5 mm).....	510.6	5.94	4.97
	35.4	Transition.....	51.4	11.18	8.57
Nitrous oxide: N ₂ O.....	63.1	Fusion.....	171.0	11.32	13.46
	77.3	Vaporization (1 atmosphere).....	1,336	13.76	7.20
Nitric oxide: NO.....	170.7	Fusion.....	182.4	---	---
	160.0	Sublimation (72.3 mm).....	5,695	12.63	7.78
Ammonia: NH ₃	183.6	Vaporization (1 atmosphere).....	---	---	---
	109.5	Fusion.....	549.5	9.41	15.24
Oxygen: O ₂	121.4	Vaporization (1 atmosphere).....	3,293	19.00	---
	195.5	Fusion.....	1,426	12.02	18.36
Oxygen: O ₃	239.7	Vaporization (1 atmosphere).....	5,640	18.36	8.47
	23.7	Transition.....	22.42	5.16	4.93
	43.8	do.....	177.6	11.38	11.02
	54.4	Fusion.....	106.3	11.10	12.81
	90.1	Vaporization (1 atmosphere).....	1,628.8	12.96	6.95

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