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CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY

IX. The Entropies of Inorganic Substances. Revision (1940) of Data and Methods of Calculation

By

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IX. The Entropies of Inorganic Substances. Revision (1940) of Data and Methods of Calculation [1]

By K. K. KELLEY [2]

INTRODUCTION

The first bulletin (*245*)[3] in this series, which appeared in 1932, summarized the entropy values then available for the elements and inorganic compounds, results being listed for some 150 substances. In the interim advances in the realms of spectroscopy applicable to the determination of thermodynamic properties and in the development of methods of calculation therefrom have added many highly accurate values. Moreover, through the efforts of Prof. W. M. Latimer (*286*) and his coworkers, satisfactory entropy values are now available for all but a few of the common inorganic ions in aqueous solution. At the same time rapid progress has continued in the study of low-temperature heat capacities in several laboratories, In addition, compilation and correlation of data pertaining to vapor pressures (*247*), thermodynamic properties of carbonates (*258*), thermodynamic properties of sulfur and its inorganic compounds (*250*), and the thermodynamic properties of metal carbides and nitrides (*251*), which were published as members of this series, have yielded many values. As a result, over 500 usable entropy values for inorganic substances may now be tabulated.

This bulletin originally was planned as a second revision of the first member of this series, the first revision (*249*) having appeared in 1936; however, because of requests for the explanatory section of the first bulletin from those teaching thermodynamics, it was decided to combine the information in the first bulletin and its revision with the data that have appeared since 1935 and to repeat the explanatory material in somewhat more detail. The purpose of this bulletin is therefore to give the available values of the entropies at 298.1° K. of the elements and inorganic compounds, together with enough explanation of the methods employed in calculating entropies to make the results comprehensible.

VALUE OF ENTROPY DATA

In the study of chemical and metallurgical reactions the two factors of predominant importance are the free energy of reaction and the

[1] Work on manuscript completed March 1940.
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[3] Italicized numbers in parentheses refer to citations in the bibliography at the end of this bulletin; page numbers refer to the citation and not to this bulletin.

rate of reaction. Although entropy data sometimes are of value in the study of reaction rates, a subject best-treated by the methods of statistical mechanics, this matter will not be discussed here. By far the greatest value of entropy data is their usage in the derivation of reaction free-energies. Knowledge of the reaction free-energy is adequate for determining whether or not the reaction will occur and, if it will, to what extent it will proceed under the conditions that may be imposed by practical considerations. The metallurgist has been slower than the chemist in adopting thermodynamic methods of study, possibly because the labor involved in obtaining adequate free-energy data often is irksome and sometimes may appear to be an indirect approach to the problem at hand. However, failure to consider available thermodynamic data sometimes has been expensive and is to be deplored.

Four general methods are available for obtaining free-energy changes accompanying reactions:

(1) The equilibrium may be studied, in which instance the reaction free-energy is given by (*296*)

$$\Delta F^\circ_T = -R\ T\ ln\ K, \tag{1}$$

in which ΔF°_T is the standard free-energy change at the temperature T°K., R is the gas constant per mole, and $ln\ K$ is the natural logarithm of the equilibrium constant.

(2) The reaction may be allowed to take place reversibly in a galvanic cell and the electromotive force measured. Then (*296*),

$$\Delta F^\circ_T = -n f \epsilon^\circ, \tag{2}$$

in which n is the number of chemical equivalents involved, ϵ° is the standard electromotive force of the cell, and f is Faraday's constant.

(3) The free energy may be obtained in the form $\Delta F^\circ_T - \Delta E^\circ_0$ directly from spectroscopic data by methods analogous to those discussed later for calculating entropies. This method alone is applicable at present only to reactions for which all the reactants and products are gases. In conjunction with other methods, however, it often is useful for reactions in which at least one reactant or product is a gas. In either case data other than spectroscopic ordinarily are required for evaluating ΔE°_0.

(4) Use may be made of the expression for the second law of thermodynamics (*296*),

$$\Delta F^\circ_T = \Delta H_T - T\Delta S_T, \tag{3}$$

in which ΔH_T is the heat of reaction and ΔS_T is the entropy of reaction, both at temperature T°K.

Only a few reactions have been made to take place in reversible cells free from objectionable features and, generally, experimental difficulties at high temperatures almost preclude adequate equilibrium measurements for the majority of reactions of greatest metallurgical interest. These and the limitations already indicated for method (3) mean that in the vast majority of instances method (4) is the only one available. Consequently, it is not surprising that several times as many free-energy values have been obtained from method (4) as from the other three methods combined. The evaluation of entropies for this usage is therefore a problem of considerable importance.

METHODS OF CALCULATING ENTROPIES FROM EXPERIMENTAL DATA

CALCULATIONS BASED UPON LOW-TEMPERATURE HEAT-CAPACITY DATA

Of the various methods of obtaining entropies, that based upon low-temperature heat-capacity data now yields the greatest number of values. This method depends upon the so-called third law of thermodynamics. As the substances to be considered here are, with one exception, crystalline, the discussion is restricted to this field. It is recognized, of course, that crystals usually are solutions of isotopes; but this need not be considered, as the entropy effect balances out in chemical reactions, excluding phenomena that may occur with substances containing comparable amounts of light and heavy hydrogen. Moreover, it is not considered necessary to trace the early history of the third law. It will suffice to say that for several years the statement of this principle generally accepted by chemists was that given by Lewis and Gibson (*293*) in 1920:

> 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.

So far as crystalline substances are concerned, this statement may still be used, provided the definition of "pure crystal" is made stringent enough. It does not suffice that a substance be chemically pure and be in a well-defined macrocrystalline form as the absolute zero is approached, but certain ideas of "internal purity" also must be included. There must be no randomness of position of the constituent atoms, ions, or groups in the crystal such as Pauling (*336*) has discussed for the magnetic form of ferric oxide and other substances or such as are thought to exist in ordinary crystals of carbon monoxide (*74*, *75*) and nitrous oxide (*45*), to be mentioned later. There must be no randomness of position or orientation of bonds, such as Pauling (*336*) has discussed for ice crystals and for which the effects on the application of the third law have been demonstrated experimentally (*171*, *299*). There must be no "freezing-in" of a high-temperature equilibrium, such as is known to exist in the case of ordinary hydrogen crystals (*157*). The inclusion of these and other qualifying conditions would maintain the correctness of Lewis and Gibson's statement. That such qualifications may include more than was originally intended by their statement is no argument against the validity of the principle involved. In fact, modification and extension of definitions are the common methods by which so-called laws of nature are maintained in a currently valid form.

An analogous procedure may be traced in the history of the first law of thermodynamics, the validity of which has been maintained by broadening the concept of energy to include forms and manifestations of energy entirely unknown to the original propounders, the most recent of which is the postulation of the energy particle called the neutrino. All the necessary qualifications are included in and taken care of by Giauque's (*157*) clarification that, for the third law to be obeyed, there must be a condition of true equilibrium in the distribution of energy among such energy states as are actually occupied by the system as absolute zero is approached. Eastman (*127*) has pointed out that Giauque's statement sometimes is too restrictive and

prefers to say that "the entropy at the absolute zero of any phase of sharply defined energy is zero." Tolman (*397*) also has discussed this subject and has stated that the entropy of a system may be taken as zero at the absolute zero only when the system is known to be in a single pure quantum mechanical state.

For the present purpose, the statements of Giauque, Eastman, and Tolman may be considered as equivalent. When they are true, the usual methods of calculation lead to the correct entropy, otherwise some correction must be made. The point of view to be emphasized is that the difficulty lies not in the third law itself, as now stated, but in the lack of knowledge sometimes existing as to the true internal condition of the crystals on which low-temperature heat-capacity measurements are made. Fortunately, the number of substances with which there has been difficulty so far is only a small fraction of the total number that have been studied.

The increase in entropy in warming a substance from 0° to T° K. is, by definition,

$$\Delta S = S_{T_1} - S_o = \int_o^T \frac{dQ}{T}. \tag{4}$$

Here, S_{T_1} is the entropy at T_1, S_o is the entropy at 0°, and dQ is the increment of heat absorbed at the temperature T. If the substance has been cooled and the measurements made under conditions of complete equilibrium, then $S_o = 0$, and

$$S_{T_1} = \int_o^{T_1} \frac{dQ}{T}. \tag{5}$$

Consider first a crystalline substance in complete equilibrium whose change in heat content, $\int_o^{T_1} dQ$, and its first derivative are continuous in the range 0° to T_1°. In such a case, $dQ = C_p dT$ or $dQ = C_v dT$, depending on whether the substance is heated at constant pressure or or 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 (5) gives the entropy either at constant pressure or constant volume, depending on which specific heat is employed. We shall be concerned here only with the calculation of entropies for a constant pressure of 1 atmosphere. Returning to equation (5), then

$$S_{T_1} = \int_o^{T_1} \frac{C_p dT}{T}. \tag{6}$$

In such a simple case, specific-heat measurements down to very low temperatures are all that is required for computing S_{T_1}. Discussion concerning evaluation of this integral will be given later.

Suppose now a more complicated state of affairs and assume a substance in equilibrium crystalline condition as 0° is approached, but which undergoes a transition at some temperature, T', melts at temperature T'', and boils under 1 atmosphere pressure at temperature T''', T', T'', and T''', all lying in the range 0° to T_1°. The

integral in equation (5) may now be separated into several constituent parts as

$$S_{T_1}=\int_0^{T'}\frac{C_p(crystals\ II)}{T}dT+\frac{\Delta H'}{T'}+\int_{T'}^{T''}\frac{C_p(crystals\ I)}{T}dT+\frac{\Delta H''}{T''}$$
$$+\int_{T''}^{T'''}\frac{C_p(liquid)}{T}dT+\frac{\Delta H'''}{T'''}+\int_{T'''}^{T_1}\frac{C_p(gas)}{T}dT, \tag{7}$$

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

The integrals of equation (7), except the first, are evaluated readily by plotting C_p against $ln\ T$ or $\frac{C_p}{T}$ against T and mechanically computing the area bounded by the resulting curve, the $ln\ T$ or T axis, and the two ordinates corresponding to the limits of integration. The first integral of equation (7) and that of equation (6) need further consideration, as an extrapolation of the specific-heat curve, between the lowest temperature reached in the specific-heat measurements and the absolute zero, is required for their evaluation.

As a crystal is cooled to low temperatures the difference between the specific heats at constant pressure and constant volume gradually diminishes and usually is nearly negligible for inorganic crystals around 50° K. Debye (*115*), assuming a monatomic solid to be an isotropic, elastic medium, deduces for the energy the relationship

$$E=9\ N\ k\ T\left(\frac{kT}{h\nu_m}\right)^3\int_0^{\frac{h\nu_m}{kT}}\frac{\left(\frac{h\nu}{kT}\right)^3 d\left(\frac{h\nu}{kT}\right)}{e^{h\nu/kT}-1}. \tag{8}$$

Differentiating with respect to the temperature at constant volume, there is obtained

$$C_v=9\ N\ k\left[4\left(\frac{kT}{h\nu_m}\right)^3\int_0^{h\nu_m/kT}\frac{\left(\frac{h\nu}{kT}\right)^3 d\left(\frac{h\nu}{kT}\right)}{e^{h\nu/kT}-1}-\frac{\frac{h\nu_m}{kT}}{e^{h\nu_m/kT}-1}\right]. \tag{9}$$

In these equations,

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

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

$$C_v=9\ N\ k\left[4\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{\left(\frac{h\nu}{kT}\right)^3 d\left(\frac{h\nu}{kT}\right)}{e^{h\nu/kT}-1}-\frac{\frac{\theta_D}{T}}{e^{\theta_D/T}-1}\right]. \tag{10}$$

Θ_D is a characteristic constant for each substance and has the dimensions of temperature. Equation (10) expresses the specific heat at constant volume as a function of this characteristic constant divided

by the temperature. When T is large so that $h\nu/kT$ is small, $e^{h\nu/kT}$ may be approximated as $1+\frac{h\nu}{kT}$, and equation (8) approaches

$$E=3\,N\,k\,T, \tag{11}$$

and C_v approaches $3\,N\,k=3R$, where R is the gas constant per mole. The latter is the rule of Dulong and Petit (*123*, *291*), which holds approximately for many elements near room temperature. When T is small, the upper limit of integration in equation (8) may be taken as infinite and the integral evaluated as $\pi^4/15$. At low temperatures, then,

$$E=\frac{3\pi^4Nk^4T^4}{5h^3\nu_m{}^3}, \tag{12}$$

and

$$C_v=\frac{12\pi^4Nk^4}{5h^3\nu_m{}^3}T^3=aT^3, \tag{13}$$

where a is substituted for the more-complicated constant multiplier.

Many substances have been studied to low enough temperatures to demonstrate that the T^3 law and general Debye equation usually are adequate means of extrapolating specific-heat data for the evaluation of entropies. Consequently, for substances whose specific heat has been determined to low enough temperatures, these relationships are employed in evaluating the first integral of equation (7) and the integral of equation (6). The procedure is to consider these integrals in two parts, the first of which accounts for the temperature range covered by the measured specific heats and is evaluated mechanically, as are the other integrals of equation (7). The second part is entirely extrapolation. Tables of the specific heat at constant volume and the entropy for values of θ_D/T for the Debye function may be found in several places (*191*; *270*, *pp. 702–707*; *326*; *327*), so that the labor involved in the extrapolation is slight. When the T^3 law is obeyed below a temperature T, the entropy at T is simply $C_v/3$, for

$$S_T=\int_0^T\frac{C_p\,dT}{T}=\int_0^T aT^2dT=\frac{aT^3}{3}=\frac{C_v}{3}. \tag{14}$$

The fact that the specific heats of some substances, such as lead and mercury, have been shown to deviate in various ways from Debye behavior need not be considered here. The fluctuations that have been observed up to the present do not produce errors in the extrapolation that are of much importance, relatively speaking, in the entropies at 298.1° K. However, they are of great theoretical interest. The above remarks do not apply to the departure from Debye behavior caused by the splitting of a multiple lowest-energy state, such as was observed for $Gd_2(SO_4)_3{\cdot}8H_2O$ (to be discussed later).

Unfortunately, the Debye function alone is of little aid in the extrapolation of the entropies of many substances as they are not monatomic solids and their specific-heat curves have been extended experimentally down only to some point in the range 50° to 100°, which, except for metals, is rarely low enough to give coincidence with a Debye function. For such substances, it is necessary to employ a more-complicated and less-sure method of extrapolation based upon a simplified version of the theory of Born and von Karman (*48*, *49*, *50*). It is here assumed

that at low enough temperatures any substance will obey the Debye law well enough to permit a satisfactory entropy extrapolation. At higher temperatures the Debye equation no longer will suffice, and the specific heat will rise above the Debye function because of $C_p - C_v$ becoming appreciable, and, in the case of polyatomic crystals, because of degrees of freedom coming into play that are not accounted for by the Debye function.

The assumption that the atoms in a crystal behave as harmonic oscillators led Einstein (*132*) to the expression

$$C_v = \frac{Nke^{\frac{h\nu}{kT}}\left(\frac{h\nu}{kT}\right)^2}{\left(e^{\frac{h\nu}{kT}}-1\right)^2} \tag{15}$$

for the contribution of a vibrational degree of freedom. The symbols in this equation have the same meaning as in that of Debye. Tables of Einstein functions for different values of $\frac{\theta_E}{T}=\frac{h\nu}{kT}$ also are available (*191; 270, pp. 702–707; 326; 327*). Born and von Karman (*48, 49, 50*) have considered the vibrations in a crystal lattice, and Born (*47*) 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 energy-functions of characteristic temperatures θ_{D_1}, θ_{D_2}, and θ_{D_3}, which are related closely to the elastic properties, and the second part consists of the sum of 3 $(p-1)$ Einstein energy-functions of θ_E's, which may be found from a study of the infrared dispersion of the crystal. In terms of specific heat this may be written as

$$C_v = \frac{1}{3}\left[\sum_{i=1}^{3} D\left(\frac{\theta_{Di}}{T}\right) + \sum_{i=3}^{3(p-1)} E\left(\frac{\theta_{Ei}}{T}\right)\right], \tag{16}$$

where $D\left(\frac{\theta_{Di}}{T}\right)$ and $E\left(\frac{\theta_{Ei}}{T}\right)$ represent, respectively, Debye and Einstein specific-heat functions. This equation gives the specific heat per chemical formula mass of the n unit parallelepipeds. The factors "1/3" and "3" occur because crystals generally have different frequencies of vibration in different directions.

Equation (16) must be modified before it is readily and generally adaptable to the extrapolation of specific-heat curves. As the extrapolated part of the entropy usually is only a relatively small portion of the total at 298.1° K., the assumptions to be 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 1/3 from equation (16). The result is

$$C_v = D\left(\frac{\theta_D}{T}\right) + \sum_{i=1}^{p-1} E\left(\frac{\theta_{Ei}}{T}\right). \tag{17}$$

Each Debye and Einstein function now may be considered as being equivalent to one-third the sum of the three it is replacing. In other words, the θ's are, in effect, "mean" values for three mutually perpendicular directions. For an isotropic crystal, equation (16) automatically becomes equation (17), except for modification of the definition of p. This simplified version has been shown to represent specific heats of oxides, sulfides, halides, etc., over rather wide temperature ranges, to a close enough degree in general to permit reasonably accurate extrapolations.

The method of extrapolation by means of equation (17) is one of trial. The measured specific heats extending down to some point, say in the range 50° to 100°, are plotted against log T, and the curve is extended smoothly into a Debye function. (It is convenient for this purpose to have Debye and Einstein functions cut out of some rigid, transparent material). The Debye function is drawn in, being extended to 298.1° K. Then differences between the measured curve and the Debye are read off. These differences are plotted against log T, and the attempt is made to fit them with a series of Einstein functions, using any obvious symmetry relationships for the substance to reduce the number of distinct functions required. Usually the first trial will result in failure to represent satisfactorily the measured specific heats, but an examination will show the direction and indicate the amount the Debye function should be displaced before the second trial is made. The second trial either will be successful or point the way to placement of the Debye function for the third trial, etc. With a little practice, it is seldom that the specific heats of even the more complicated substances are not represented satisfactorily by the third trial and with care success often is obtained with the second trial. The following random examples of oxides will give an idea of the function sums used and of the temperature interval for which the function sum fits the measured specific heats. The lowest temperature given in each instance is at or near the lower limit of the measurements.

$$C_{SrO}=D\left(\frac{261}{T}\right)+E\left(\frac{444}{T}\right),\ (57-298°),$$

$$C_{TiO_2}=D\left(\frac{386}{T}\right)+2E\left(\frac{670}{T}\right),\ (68-175°),$$

$$C_{Bi_2O_3}=D\left(\frac{97}{T}\right)+2E\left(\frac{225}{T}\right)+2E\left(\frac{568}{T}\right),\ (60°-175°),$$

$$C_{Ta_2O_5}=D\left(\frac{170}{T}\right)+2E\left(\frac{265}{T}\right)+2E\left(\frac{528}{T}\right)+2E\left(\frac{880}{T}\right),(53°-298°).$$

After a satisfactory representation of the measured specific heats is obtained over an adequate temperature interval, the θ-values are computed and the entropy extrapolation between 0° and the temperature of the lowest measurements is evaluated from the before-mentioned tables of Debye and Einstein functions.

Numerous specific-heat curves of compounds for which specific-heat data have been obtained down only to some point in the range 50° to 100° K. have been extrapolated by this method for incorpora-

tion in this bulletin. In very few instances has there been reason to doubt the extrapolation and then usually because the data themselves were erratic or because of questionable purity of the materials studied. Still it should be emphasized that such curve fitting is largely empirical. However, except in a few instances, it would seem that allowance for an error of about 10 percent in the extrapolated part of the entropy should be enough to equal or exceed the uncertainties.

A class of substances, exemplified by $Gd_2(SO_4)_3 \cdot 8H_2O$, $FeCl_2$,$Co\ Cl_2$, $NiCl_2$, $MnCl_2$, and $CrCl_3$, considered separately later, presents additional difficulties, as the lowest energy levels of the metal ions involved are multiple (that is, have quantum weights greater than 1) and, except for $Gd_2(SO_4)_3 \cdot 8H_2O$, the specific-heat measurements presumably have not been extended to temperatures low enough to cause splitting of this level. It is not known definitely just what procedure to follow in all such instances. For $Gd_2(SO_4)_3 \cdot 8H_2O$ and $Sm_2(SO_4)_3 \cdot 8H_2O$ it appears established that $R\ ln\ p$, in which p is the multiplicity of the lowest energy state, should be added to the extrapolation ordinarily made. Incidentally, it also appears reasonably certain that the specific heats of the constituent metals themselves may be extrapolated by the usual methods. The anhydrous chlorides mentioned above occupy a sort of middle ground with regard to the degree of dilution of their magnetic systems by nonmagnetic mediums. Pending experimental proof of the correct treatment for these substances, generally no allowance can be made in the calculation of entrophies for the effects of multiple lowest energy levels.

CALCULATIONS BASED UPON SPECTROSCOPIC DATA

The calculation of entropies from spectroscopic data is restricted to the gaseous state at present. The methods employed have been discussed adequately by Giauque (*156*) and others.

It is customary to separate the translational energy, entropy, and specific heat of gas molecules from the rotational, vibrational, and electronic contributions. The evaluation of the translational entropy has been the subject of several theoretical investigations (*357, 395, 384, 385, 396, 131, 295*), with the result, first obtained by Sackur (*357*) that

$$S_t = 3/2\ R\ ln\ M + 3/2\ R\ ln\ T + R\ ln\ V + 5/2\ R + S_o. \qquad (18)$$

Here, S_t is the translational entropy, M the molecular mass of the gas, T the absolute temperature, V the molal volume, R the gas constant per mole, and S_o a constant for all substances, which was shown by Tetrode (*395*) to have the value $R\ ln\ \frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} = -16.024$ calories per mole per degree, k, h, and N being, respectively, the gas constant per molecule, Plank's constant, and Avogadro's number. Substituting for the molal volume at 1 atmosphere and 298.1° K. and inserting the temperature leads to

$$S_{t,298\cdot1} = 3/2\ R\ ln\ M + 26.001. \qquad (19)$$

(The units employed for the purpose of making this section accord with the majority of applications of these methods in the literature are those given in the International Critical Tables (*200*)).

Equations (18) and (19) give the total entropy (excluding that attributed to nuclear spin) of a monatomic gas provided all the atoms are in one energy state of unit quantum weight. This condition is satisfied by the rare gases at 298.1°, and values obtained from equation (19) are shown in column 2 of table 1 where they may be compared with the values in column 3 based upon low-temperature heat-capacity data. The agreement is seen to be highly satisfactory.

TABLE 1.—*Entropies of rare gases at 298.1°*

Substance	$S_{298.1}$ (theor.)	$S_{298.1}$ (exp.)	Substance	$S_{298.1}$ (theor.)	$S_{298.1}$ (exp.)
Argon	36.99	37.0±0.2	Neon	34.96	35.0±0.1
Helium	30.13		Radon	42.10	
Krypton	39.20	39.0±0.3	Xenon	40.54	40.7±0.3

Other examples could be given from the list of monatomic metal gases. The comparison, however, would require the use of vapor-pressure data in computing the values based upon heat capacities. There is no objection to such procedure, but the validity of equations (18) and (19) is now so well-established that Kelley (*247*) has employed the calculation in the reverse sense, rectifying the vapor-pressure data for metal gases by means of the theoretical entropies. Incidentally, the experimental justification of Tetrode's value of S_o does not depend on data for monatomic gases alone, and a variety of checks may be given for gases which are not monatomic, as the translational portions of their entropies also conform to equations (18) and (19). For some examples see table 4.

The other contributions to the entropy will now be considered. Let ϵ_i be the sum of the rotational, vibrational, and electronic energies of a molecule and let A_o and A_1 be the numbers of molecules in two energy states ϵ_o and ϵ_1. Then, according to the Maxwell-Boltzmann distribution law,

$$\frac{A_1}{A_o}=e^{-\frac{(\epsilon_1-\epsilon_o)}{kT}}, \tag{20}$$

e being the natural logarithmic base, k the gas constant per molecule, and T the temperature in degrees Kelvin. Suppose A_o refers to the lowest energy state of the molecule and A_1, A_2, A_3, etc., to the successively higher energy states, and for convenience suppose all the energies, ϵ_i, now are referred to that of the lowest state as a zero base, which obviously leaves the magnitude of the exponent in equation (20) unchanged. Then, considering 1 mole of gas (Avogadro's number of molecules, N), it follows that

$$N=A_o+A_oe^{-\epsilon_1/kT}+A_oe^{-\epsilon_2/kT}+\ldots \tag{21}$$

For a group of states, p_i in number, whose energies are so nearly alike that they may be considered together, the corresponding terms in equation (21) may be replaced by $p_iA_oe^{-\epsilon_i/kT}$ or, in general,

$$N=p_oA_o+p_1A_oe^{-\epsilon_1/kT}+p_2A_oe^{-\epsilon_2/kT}+\ldots=A_o\sum p_ie^{-\epsilon_i/kT}. \tag{22}$$

The quantity p_i is termed the qauntum weight or the a priori probability of the state of energy ϵ_i. Let the sum of the rotational, vibrational, and electronic energies of 1 mole of gas at any temperature be denoted by E_{r+v+e} and let E_o be the corresponding energy at 0° K., the gas being in the ideal state. As the energy of the molecules in a given state is their number times the energy per molecule, it follows that

$$E_{r+v+e}-E_o=0p_oA_o+p_i\epsilon_1A_oe^{-\epsilon_1/kT}+p_2e_2A_oe^{-\epsilon_2/kT}+\ldots=A_o\sum_i p_i\epsilon_ie^{-\epsilon_i/kT}. \tag{23}$$

Eliminating A_o between equations (22) and (23),

$$E_{r+v+e}-E_o=N\frac{\sum_i p_i\epsilon_ie^{-\epsilon_i/kT}}{\sum_i p_ie^{-\epsilon_i/kT}}. \tag{24}$$

Differentiating equation (24) with respect to T,

$$\frac{dE_{r+v+e}}{dT}=\frac{N}{kT^2}\left[\frac{\sum_i p_i\epsilon_i^2e^{-\epsilon_i/kT}}{\sum_i p_ie^{-\epsilon_i/kT}}-\left(\frac{\sum_i p_i\epsilon_ie^{-\epsilon_i/kT}}{\sum_i p_ie^{-\epsilon_i/kT}}\right)^2\right]. \tag{25}$$

Equation (25) gives the sum of the rotational, vibrational, and electronic specific heats of the gas. The total specific heat at constant pressure is obtained by adding this sum to $5/2\ R=4.967$, the specific heat at constant pressure of an ideal monatomic gas.

The entropy of the gas, excluding translational entropy, is defined by

$$d\,S_{r+v+e}=\frac{dE_{r+v+e}}{dT}d\ ln\ T, \tag{26}$$

or

$$S_{r+v+e}-S_o=\int_o^T\frac{dE_{r+v+e}}{dT}d\ ln\ T. \tag{27}$$

Writing Q for $\sum_i p_ie^{-\epsilon_i/kT}$, equation (24) becomes

$$E_{r+v+e}-E_o=Nk\ T^2\frac{d\ ln\ Q}{dT}=R\ T^2\frac{d\ ln\ Q}{dT}, \tag{28}$$

$R=Nk$ being the gas constant per mole. Therefore,

$$S_{r+v+e}-S_o=\int_o^T\frac{d}{dT}\left(R\ T^2\frac{d\ ln\ Q}{dT}\right)d\ ln\ T, \tag{29}$$

$$=-R\int_o^T\frac{d}{dT}\left(\frac{d\ ln\ Q}{d\ 1/T}\right)d\ ln\ T, \tag{30}$$

$$=R\left[ln\ Q+T\frac{d\ ln\ Q}{dT}\right]_o^T, \tag{31}$$

$$=R\left[ln\ Q-ln\ Q_o+T\frac{d\ ln\ Q}{dT}\right], \tag{32}$$

and

$$=R\left[ln\sum_i p_i e^{-\epsilon_i/kT}-ln\ p_o+\frac{1}{kT}\frac{\sum_i p_i\epsilon_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}}\right]. \quad (33)$$

But, as $S_o=R\ ln\ p_o$,

$$S_{r+v+e}=R\left[ln\sum_i p_i e^{-\epsilon_i/kT}+\frac{1}{kT}\frac{\sum_i p_i\epsilon_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}}\right]. \quad (34)$$

The quantity given by equation (34) is the sum of the rotational, vibrational, and electronic entropies. This sum must be added to the result given by the Sackur equation (18) to obtain the total entropy (excluding that due to nuclear spin). Evaluation of this sum is possible for gases on which extensive enough spectroscopic measurements have been made to enable an assignment of ϵ_i and p_i values to all the states occupied by the system at the temperature under consideration. It is customary to omit nuclear spin from consideration in the values of p_i, as Gibson and Heitler (*176*) have shown that the resulting entropy contribution balances out in reactions involving diatomic gases, and it is presumed that it always does so. It will be noted that if all the molecules are in their lowest energy state of quantum weight p_o, then equation (34) reduces to $R\ ln\ p_o$.

To illustrate this method of calculation, two simple cases will be considered, nickel gas at 298.1° K., in which only translational and electronic entropies are concerned, and carbon monoxide at 298.1°, in which only translational and rotational entropies are concerned. The question may arise as to why the calculation is made for nickel which does not exist in the gaseous state at any appreciable pressure at 298.1° K. The answer is that it seems desirable to have a fairly simple, but not too simple, example for illustration. The common substances that exist as monatomic gases under measurable pressures at 298.1° K. have electronic states so separated that calculation reduces to the mere addition of $R\ ln\ p_o$ as mentioned above. Moreover, the entropy of Ni (g) at 298.1° K. may be employed formally in the thermodynamic calculations in the same manner as the entropy of $H_2O(g)$ at 298.1° in the hypothetical state of 1 atmosphere fugacity. Only a question of degree is involved.

The data to be considered for Ni (g) at 298.1° are shown in table 2. Column 1 gives the designation of the state, column 2 the energies in wave numbers (these usually are called term values), column 3 the quantum weights, and column 4 the energies in ergs per molecule ($\epsilon=hc\nu=1.9653\times10^{-16}\nu$). The calculated items for computing the sums in equation (34) are shown in columns 5 and 6.

TABLE 2.—*Data for Ni(g) at 298.1° K*

State	ν_i	p_i	ϵ_i	$p_i e^{-\epsilon_i/298.1°K.}$	$p_i\epsilon_i e^{-\epsilon_i/298.1°K.}$
$^3F_4$	0.0	9	0.0	9.000	0.0
$^3D_3$	204.82	7	4.0253×10^{-14}	2.617	10.533×10^{-1}
$^3D_2$	879.82	5	1.7291×10^{-13}	.073	1.261×10^{-14}
$^3F_3$	1,332.15	7	2.6181×10^{-13}	.012	$.304\times10^{-14}$
$^3D_1$	1,713.11	3	3.3668×10^{-13}	.001	$.027\times10^{-14}$
$^3F_2$	2,216.55	5	4.3562×10^{-13}	.000	$.005\times10^{-14}$
Sum				11.70	12.13×10^{-14}

Substitution of the summation values in equation (34) leads to

$$S_{e,298.1}=R\left[ln\ 11.70+\frac{12.13\times10^{-14}}{4.090\times10^{-14}\times11.70}\right]=5.391,$$

in which $4.090\times10^{-14}=kT$ and $R=1.9869$. The translational entropy is $S_{t,298.1}=3/2\ R\ ln\ 58.69+26.001=38.138$. These two contributions add to give $S_{298.1}=43.53$ for Ni (g) at 298.1°.

In the second example, CO(g), considerably more labor is involved in computing the sums in equation (34). Although it is no longer necessary to use the summation method for this and similar cases, as will be mentioned below, the principles involved are best-illustrated by the summation method. Clayton and Giauque (*74*, *75*) have given the rotational energies (in wave numbers) of CO as

$$\epsilon_r=[1.853-0.020(v+1/2)]m^2-\left[5.418\times10^{-6}-6.918\times10^{-8}\left(v+1/2\right)\right]m^4. \tag{35}$$

In this expression m takes the values 1/2, 3/2, 5/2, etc., and v the values 0, 1, 2, 3, etc. The vibrational energy, in wave numbers, is (*74*, *75*)

$$\epsilon_v=\omega_e(v+1/2)+\omega_eX_e(v+1/2)^2, \tag{36}$$

in which $\omega_e=2167.4$, $\omega_eX_e=-12.70$, and v takes the values 0, 1, 2, 3, etc. It is apparent, on preliminary examination, that only the lowest vibration state ($v=0$) need be considered in evaluating the entropy at 298.1°. Consequently, $\epsilon_r=1.843\ m^2-5.383\times10^{-6}m^4$ gives all the pertinent energy values. There must be computed $\epsilon_{r(m)}-\epsilon_{r(1/2)}$ for enough rotational states to give correct sums in equation (34), in this instance about 40 terms. These values in wave numbers are shown in column 2 of table 3. The quantum weights are shown in column 1 and values of $\epsilon_i=hc\nu$, ergs per molecule, are in column 3. The summation items are in columns 4 and 5.

TABLE 3.—*Data for CO(g) at 298.1° K.*

p_i	ν_i	ϵ_i	$p_i e^{-\epsilon_i/298.1° \text{ K}}$	$p_i \epsilon_i e^{-\epsilon_i/298.1° \text{ K}}$
1	0.0	0.0	1.000	0.0 $\times 10^{-13}$
3	3.686	7.244×10^{-16}	2.947	$.021 \times 10^{-13}$
5	11.06	2.174×10^{-15}	4.741	$.103 \times 10^{-13}$
7	22.12	4.347×10^{-15}	6.294	$.274 \times 10^{-13}$
9	36.86	7.244×10^{-15}	7.539	$.546 \times 10^{-13}$
11	55.28	1.086×10^{-14}	8.435	$.916 \times 10^{-13}$
13	77.40	1.521×10^{-14}	8.962	1.363×10^{-13}
15	103.2	2.028×10^{-14}	9.136	1.853×10^{-13}
17	132.7	2.608×10^{-14}	8.983	2.343×10^{-13}
19	165.8	3.258×10^{-14}	8.565	2.790×10^{-13}
21	202.7	3.984×10^{-14}	7.928	3.158×10^{-14}
23	243.2	4.780×10^{-14}	7.146	3.415×10^{-13}
25	287.4	5.648×10^{-14}	6.282	3.548×10^{-13}
27	335.2	6.588×10^{-14}	5.392	3.553×10^{-13}
29	386.8	7.602×10^{-14}	4.518	3.435×10^{-13}
31	442.0	8.687×10^{-14}	3.704	3.218×10^{-13}
33	500.0	9.844×10^{-14}	2.972	2.926×10^{-13}
35	563.5	1.107×10^{-13}	2.336	2.586×10^{-13}
37	629.7	1.238×10^{-13}	1.793	2.171×10^{-13}
39	699.6	1.375×10^{-13}	1.352	1.859×10^{-13}
41	773.1	1.519×10^{-13}	1.000	1.518×10^{-13}
43	850.3	1.671×10^{-13}	.723	1.208×10^{-13}
45	931.1	1.830×10^{-13}	.513	$.939 \times 10^{-13}$
47	1,016	1.997×10^{-13}	.356	$.711 \times 10^{-13}$
49	1,104	2.170×10^{-13}	.243	$.527 \times 10^{-13}$
51	1,196	2.350×10^{-13}	.163	$.383 \times 10^{-13}$
53	1,291	2.537×10^{-13}	.107	$.272 \times 10^{-13}$
55	1,390	2.732×10^{-13}	.069	$.189 \times 10^{-13}$
57	1,493	2.934×10^{-13}	.044	$.128 \times 10^{-13}$
59	1,599	3.143×10^{-13}	.027	$.085 \times 10^{-13}$
61	1,709	3.359×10^{-13}	.017	$.056 \times 10^{-13}$
63	1,823	3.583×10^{-13}	.010	$.035 \times 10^{-13}$
65	1,940	3.813×10^{-13}	.006	$.022 \times 10^{-13}$
67	2,061	4.050×10^{-13}	.003	$.014 \times 10^{-13}$
69	2,185	4.294×10^{-13}	.002	$.008 \times 10^{-13}$
71	2,313	4.546×10^{-13}	.001	$.005 \times 10^{-13}$
73	2,445	4.805×10^{-13}	.001	$.003 \times 10^{-13}$
75	2,580	5.070×10^{-13}	.000	$.002 \times 10^{-13}$
77	2,719	5.344×10^{-13}		$.001 \times 10^{-13}$
79	2,862	5.625×10^{-13}		.000
81	3,008	5.912×10^{-13}		
83	3,158	6.206×10^{-13}		
Sum			113.31	46.19×10^{-13}

From the summation values there is computed

$$S_{r,298.1}=R\left[ln\ 113.31+\frac{46.19\times10^{-13}}{4.090\times10^{-14}\times113.31}\right]=11.382.$$

The translational entropy is $S_{t,298.1}=3/2\ R\ ln\ 28.01+26.001=35.933$. The total is $S_{298.1}=47.315$ for CO (g). The last figure in this result is not significant, but it is retained for comparison with the value given by Clayton and Giauque (*74*, *75*). These investigators carried out a calculation, which is equivalent to that just made, by means of the approximate integration method of Giauque and Overstreet (*167*). This method gives

$$Q=e^{\frac{hc}{kT}\left(\frac{B}{4}+\frac{D}{16}\right)}\cdot\frac{kT}{Bhc}\left[1+\frac{B}{12}\left(\frac{hc}{kT}\right)-\frac{2D}{B^2}\left(\frac{kT}{hc}\right)+\frac{12D^2}{B^4}\left(\frac{kT}{hc}\right)^2+\cdots\right], \quad (37)$$

in which, for CO, $B=1.843$ and $D=-5.383\times10^{-6}$ and the other symbols are used in the previously given sense. This integrated expression for Q and the result obtained by differentiating it with respect to T serve to evaluate equation (32), which is equation (34) in different form. The result obtained, $S_{298.1}=47.316$, is virtually identical with the value from the summation method.

These two rather simple examples should be enough to illustrate the method of obtaining entropies from spectroscopic data as the principles are the same in more complex cases in which rotational, vibrational, and electronic entropies must be considered simultaneously. The labor of calculation, however, generally is much greater in the latter instances. Table 4 shows the agreement between values computed by this method and those based upon low-temperature heat-capacity data. Substances have been chosen for which none of the difficulties mentioned previously in considering the application of the third law are encountered. The errors in the values from spectroscopic data should not exceed ± 0.01, no allowance being made for errors in the constants h, k, R, and c or in the molecular weights. The third-law values are considered accurate to within about ± 0.1.

TABLE 4.—*Entropies at 298.1° K.*

Substance	$S_{298.1}$ (spectroscopic)	$S_{298.1}$ (third law)	Substance	$S_{298.1}$ (spectroscopic)	$S_{298.1}$ (third law)
HCl	44.66	44.5	N_2	45.79	45.9
HBr	47.48	47.6	O_2	49.03	49.1
HI	49.36	49.5	Cl_2	53.31	53.3

CALCULATIONS BASED UPON MOLECULAR-CONSTANT DATA

For ordinary temperatures but little is gained by making the laborious calculations just illustrated to determine the rotational and vibrational entropies. The electronic contribution must, of course, be calculated in that manner if more than one electronic state is occupied. The method to be described now also may be used for the more complicated gases on which detailed spectroscopic data have not yet been obtained. The data required are the moments of inertia and the fundamental vibration frequencies of the molecule in addition to knowledge of the quantum weights and separations of the lowest electronic levels. For the majority of substances, other than monatomic gases, for which the above data are available at present, only the lowest electronic level need be considered at 298.1° K.

The entropy of a gas assumed to be composed of rigid molecules is considered to be divided into translational, rotational, vibrational, and electronic portions (nuclear-spin entropy again being omitted from consideration) as

$$S=S_t+S_r+S_v+S_e. \tag{38}$$

The translational part S_t already was considered, and equations (18) and (19) serve for its calculation.

For a diatomic gas, Tetrode (*395*) has derived

$$S_r=R\ ln\ I\ T+S_o', \tag{39}$$

in which I is the moment of inertia, T is the absolute temperature' and S_o' is a constant having the value $R\ ln\ \frac{8\pi^2 ke}{h^2}=177.676$. Equations (18) and (39) may be substituted in equation (38) to make

$$S=3/2\ R\ ln\ M+5/2\ R\ ln\ T+R\ ln\ V+R\ ln\ I+S_v+S_e+166.619. \tag{40}$$

At 298.1° K. and 1 atmosphere pressure, and with I in c. g. s. units, this last equation reduces to

$$S_{298.1}=3/2\ R\ ln\ M+R\ ln\ I+S_v+S_e+214.997. \tag{41}$$

Equations (40) and (41) are valid for diatomic gases composed of unlike atoms and also for gases composed of unsymmetrical, linear, polyatomic molecules. For diatomic gases composed of like atoms and gases composed of symmetrical, linear, polyatomic molecules equations (40) and (41) must be reduced by $R\ ln\ 2$, as shown by Tetrode (*395*). The more general expressions are

$$S=3/2\ R\ ln\ M+5/2\ R\ ln\ T+R\ ln\ V+R\ ln\ I-R\ ln\ \sigma+S_v+S_e+166.619, \tag{42}$$

and

$$S_{298.1}=3/2\ R\ ln\ M+R\ ln\ I-R\ ln\ \sigma+S_v+S_e+214.997, \tag{43}$$

in which σ, called the symmetry number, has the values 2 or 1, depending on whether the diatomic molecules or linear, polyatomic molecules are symmetric or unsymmetric.

The expression analogous to equation (39), but for gases composed of rigid, nonlinear, polyatomic molecules, is

$$S_r=3/2\ R\ ln\ (I_1I_2I_3)^{1/3}T+S_o'', \tag{44}$$

in which I_1, I_2, and I_3 are principal moments of inertia, T is the absolute temperature, and S_o'' is a constant having the value $R\ ln\ \frac{8^{3/2}\pi^{7/2}k^{3/2}e^{3/2}}{h^3}=267.649$. Substituting equations (18) and (44) in equation (38), and introducing the term $-R\ ln\ \sigma$ as before, leads to

$$S=3/2\ R\ ln\ M+3R\ ln\ T+R\ ln\ V+\frac{1}{2}R\ ln\ I_1I_2I_3-R\ ln\ \sigma+S_v+S_e +256.592. \tag{45}$$

Also

$$S_{298.1}=3/2\ R\ ln\ M+\frac{1}{2}R\ ln\ I_1I_2I_3-R\ ln\ \sigma+S_v+S_e+310.631 \tag{46}$$

for 1 atmosphere pressure. The symmetry number, σ, is to be considered as the number of permutations of the atoms that can be obtained solely by rotations of the molecule in such ways as to leave its appearance unchanged. If all the atoms in a molecule are different $\sigma=1$. For diatomic molecules composed of like atoms, or symmetrical, linear, polyatomic molecules such as O=C=O and N≡C−C≡N $\sigma=2$. Pyramidal molecules such as NH_3 have $\sigma=3$, but if the atoms are all in the same plane, as for BCl_3, then $\sigma=6$. Tetrahedral molecules like CH_4 have $\sigma=12$ but CH_3Cl has $\sigma=3$. Molecules like SF_6 in which the S atom is at the center and the F atoms at the midfaces of a cube have $\sigma=24$.

In computing S_v it is assumed that the vibrations are purely harmonic, in which case equation (15) may be taken as the specific heat corresponding to a single vibrational degree of freedom. The entropy is computed as follows:

$$S_v=R\int_0^T \frac{e^{h\nu/kT}\left(\frac{h\nu}{kT}\right)^2}{T(e^{h\nu/kT}-1)^2}dT. \tag{47}$$

Replacing $h\nu/kT$ by x leads to

$$S_v=-R\int_{\infty}^{h\nu/kT}\frac{xe^x}{(e^x-1)^2}dx. \tag{48}$$

Equation (48) is integrated by parts with the result that

$$S_v=R\left[\frac{x}{e^x-1}-ln(1-e^{-x})\right]_{\infty}^{-h\nu/kT}, \tag{49}$$

and

$$S_v=R\left[\frac{h\nu/kT}{e^{h\nu/kT}-1}-ln(1-e^{-h\nu/kT})\right]. \tag{50}$$

Equation (50) gives the entropy associated with a single vibrational degree of freedom. Linear molecules composed of n atoms have $3n-5$ vibrational degrees of freedom, and nonlinear molecules composed of n atoms have $3n-6$ vibrational degrees of freedom. All of these are not necessarily active at 298.1° K., and the corresponding vibration frequencies are not necessarily distinct; in fact, the converse often is true, and more than one degree of freedom may be assigned to a fundamental vibration frequency. Throughout this bulletin vibration frequencies are given in wave numbers or reciprocal centimeters and are designated by the symbol ω. There may be written, then,

$$S_v=R\sum_{i=1}^{3n-5}\left[\frac{\frac{hc\omega_i}{kT}}{e^{\frac{hc\omega_i}{kT}}-1}-ln\left(1-e^{-\frac{hc\omega_i}{kT}}\right)\right] \tag{51}$$

for linear molecules and

$$S_v=R\sum_{i=1}^{3n-6}\left[\frac{\frac{hc\omega_i}{kT}}{e^{\frac{hc\omega_i}{kT}}-1}-ln\left(1-e^{-\frac{hc\omega_i}{kT}}\right)\right] \tag{52}$$

for nonlinear molecules. Values of the individual summation items may be found from available tables (*191; 270, pp. 702–707; 326; 327*) which gives S_v as a function of $\frac{\theta_E}{T}=\frac{hc\omega_1}{kT}$, so that but little computation is necessary.

As mentioned before, quantity S_e should be evaluated by the method described for treating spectroscopic data. Fortunately, in most instances only the lowest electronic state is occupied at 298.1°, so that this term reduces to $R\ ln\ p_o$, in which p_o is the quantum weight.

Abbreviating equations (51) and (52) to $S_v=\sum S$ (Einstein), the relationships of this section may be summarized as follows:

Monatomic gases

$$S=3/2\,R\ ln\ M+3/2R\ ln\ T+R\ ln\ V+S_e-11.057. \tag{53}$$

$$S=3/2\,R\ ln\ M+5/2R\ ln\ T-R\ ln\ P+S_e-2.300. \tag{54}$$

$$S_{298.1}=3/2\,R\ ln\ M+S_e+26.001. \tag{55}$$

Diatomic and linear, polyatomic gases

$$S=\frac{3}{2}R\ ln\ M+\frac{5}{2}R\ ln\ T+R\ ln\ V+R\ ln\ I-R\ ln\ \sigma+\Sigma\ S(\text{Einstein})+S_e+166.619. \quad (56)$$

$$S=\frac{3}{2}R\ ln\ M+\frac{7}{2}R\ ln\ T-R\ ln\ P+R\ ln\ I-R\ ln\ \sigma+\Sigma\ S(\text{Einstein})+S_e+175.376. \quad (57)$$

$$S_{298.1}=\frac{3}{2}R\ ln\ M+R\ ln\ I-R\ ln\ \sigma+\Sigma\ S(\text{Einstein})+S_e+214.997. \quad (58)$$

Nonlinear, polyatomic gases

$$S=\frac{3}{2}R\ ln\ M+3R\ ln\ T+R\ ln\ V+\frac{1}{2}R\ ln\ I_1I_2I_3-R\ ln\ \sigma+\Sigma\ S(\text{Einstein})+S_e+256.592. \quad (59)$$

$$S=\frac{3}{2}R\ ln\ M+4R\ ln\ T-R\ ln\ P+\frac{1}{2}R\ ln\ I_1I_2I_3-R\ ln\ \sigma+\Sigma\ S(\text{Einstein})+S_e+265.349. \quad (60)$$

$$S_{298.1}=\frac{3}{2}R\ ln\ M+\frac{1}{2}R\ ln\ I_1I_2I_3-R\ ln\ \sigma+\Sigma\ S(\text{Einstein})+S_e+310.631. \quad (61)$$

These equations are for the perfect gas state. The units are V in cubic centimeters, P in atmospheres, T in degrees Kelvin, M in grams, and I in gram centimeters squared. Equations (55), (58), and (61) are for a pressure of 1 atmosphere. The equations containing P are obtained from those containing V by means of the relationship $PV=RT$.

Table 5 compares values computed from these equations, $S_{298.1}$ (m. c.), with those obtained from spectroscopic data, $S_{298.1}$ (spec.), and from low-temperature heat-capacity data, $S_{298.1}$ (t. l.). The moments of inertia were taken from the Landolt-Börnstein Physikalisch-chemische Tabellen (*273, pp. 2345–2362*), and in some instances they may not correspond precisely to the constants in the rotational energy equations used by the investigators responsible for the values from spectroscopic data. Many additional similar comparisons may be made, but table 5 is restricted to gases of metallurgical importance. The procedure followed in arriving at the values given for H_2 and H_2O based upon low-temperature heat-capacity data may be questioned, but it is considered here that both the nature and the magnitude of the correction applied have been established by experiment.

TABLE 5.—*Entropies of gases at 298.1° K.*

Substance	$S_{298.1}$ (spec.)	$S_{298.1}$ (m. c.)	$S_{298.1}$ (t. l.)	Substance	$S_{298.1}$ (spec.)	$S_{298.1}$ (m. c.)	$S_{298.1}$ (t. l.)
H_2	31.23	31.20	31.3	SO_2	----------	59.4	59.2
O_2	49.03	48.98	49.1	H_2O	45.13	45.10	45.1
N_2	45.79	45.77	45.9	HCl	44.66	44.65	44.5
Cl_2	53.31	53.29	53.3	H_2S	----------	49.15	49.1
CO	47.32	47.31	----------	NH_3	----------	46.03	45.9
CO_2	----------	51.08	51.1	CH_4	----------	44.52	44.5

CALCULATIONS BASED UPON REACTION ENTROPIES

When the heat and free energy of a reaction are known, equation (3), expressed as

$$\Delta S_T = \frac{\Delta H_T - \Delta F_T^\circ}{T}, \tag{62}$$

permits the calculation of the entropy of reaction. Moreover, some reactions in galvanic cells have been studied thoroughly enough to permit the direct calculation of the reaction entropy from the temperature coefficient of the electromotive force. The relationship connecting these quantities is

$$\Delta S_T = n f \frac{d\epsilon^\circ}{dT}, \tag{63}$$

in which n is the number of chemical equivalents involved, f Faraday's constant, and ϵ° the standard electromotive force of the cell. If the entropy of reaction is known and if the entropies of all the reactants and products except one are known, then that one may be calculated. For example, Gerke (*154*), from cell measurements, has obtained values leading to $\Delta S_{298.1} = 7.8$ for the reaction $Ag + HgCl = AgCl + Hg$. As the entropies of Ag, AgCl, and Hg are known, there may be written $7.8 = 23.0 + 18.5 - 10.2 - S_{298.1}(HgCl)$ or $S_{298.1} = 23.5$ for HgCl. This value probably is accurate to within ± 0.5 unit.

This method is the basis of calculation of all the values given here as entropies of ions in aqueous solution. These values are taken from the compilation of Latimer, Pitzer, and Smith (*286*), and they are relative figures based upon the defining of $S_{298.1} = 0$ for $H^+(aq.)$. It is obvious that, as the charges on opposite sides of a chemical equation must balance, relative entropies suffice for thermodynamic calculations, and they may be used directly in conjunction with other values listed in this bulletin. All ionic entropies given are for hypothetical, 1 molal, ideal solutions. For examples of usage of entropies of aqueous ions the reader is referred to the paper of Latimer and Buffington (*281*) and the reference book of Latimer (*277*).

CALCULATIONS BASED UPON RESIDUAL-RAY DATA

There are a few substances whose entropies may be approximated from residual-ray data. To illustrate the method of calculation an example, KCl, will be considered in detail. Rubens (*352*) and Rubens and Hollnagel (*353*) have given $\nu = 63.4 \times 10^{-4}$ cm. as the mean residual-ray wave length. Dividing the velocity of light by this figure $\left(\frac{3 \times 10^{10}}{63.4 \times 10^{-4}}\right)$ gives $\nu = 4.73 \times 10^{12}$ as the mean frequency. This frequency is considered to be that associated with the Einstein function, in accordance with the previously mentioned theory of Born and von Karman. The characteristic temperature is $\theta_E = \frac{h\nu}{k} = 226$. From an approximate expression, $\theta_E = 1.35\ \theta_D$, given by Rodebush (*394*), $\theta_D = 167$ is evaluated. The calculation from this point is the same as if, for the specific heat of KCl, $C_v = D\left(\frac{167}{T}\right) + E\left(\frac{226}{T}\right)$. At 298.1°,

$\frac{\theta_D}{298.1}=0.560$ and $\frac{\theta_E}{298.1}=0.758$. The corresponding entropy values taken from available tables are 11.47 and 7.75, respectively. The sum, 19.22, is the entropy at constant volume. As the difference S_p-S_v is about 0.3 for salts of this type, there may be written $S_{298.1}=19.5$ for KCl.

Table 6 gives in column 2 entropy values obtained by this method that may be compared with results from low-temperature specific-heat data in column 3. Except for TlCl and HgCl, reasonable agreement is observed.

TABLE 6.—*Entropies of salts at 298.1° K.*

Substance	$S_{298.1}$ (residual rays)	$S_{298.1}$ (specific heats)	Substance	$S_{298.1}$ (residual rays)	$S_{298.1}$ (specific heats)
NaCl	17.2	17.3 ±0.5	AgBr	26.1	25.60±0.1
KCl	19.5	19.76±0.1	HgCl	24.7	23.0 ±0.7
KBr	22.6	22.4 ±1.0	TlCl	23.7	25.9 ±0.6
AgCl	22.4	23.0 ±0.1			

ENTROPIES AT 298.1° K. OF INORGANIC SUBSTANCES

In the following pages entropy values are given for the elements, ions, and compounds, based upon the various available data. The elements are considered in alphabetical order, and the compounds usually are classified according to their more electropositive constituents. All selected values are for a constant pressure of 1 atmosphere and a temperature of 298.1° K. and are expressed in defined calories (1 calorie=4.1833 int. joules) per gram-formula mass.

Temperatures are all in degrees Kelvin. The symbols (*s*), (*l*), and (*g*) refer, respectively, to the crystalline, liquid, and gaseous states. The symbol (*aq.*) following ionic formulas denotes a hypothetical, perfect solution of 1 molal concentration.

An attempt is made to estimate the accuracy of each result, but in many instances the estimate is largely a matter of judgment. For values obtained from specific-heat measurements the general procedure 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 experimental portion depends partly on the estimated errors in the specific-heat data as given by the investigator responsible and partly on information obtained by intercomparing results of several workers. The error in the extrapolated portion generally is taken as about 10 percent, which seems a reasonable compromise, as the uncertainty should increase with the magnitude of the extrapolation and in instances in which the specific heat has been measured down to very low temperatures an error of this magnitude in the extrapolated part of the entropy is only a negligible portion of the total entropy at 298.1° K.

It should be emphasized that the estimate of errors in the third-law calculations applies only to the existing specific-heat data and the necessary extrapolations. Of necessity, it usually is assumed that the substance is in such energy condition at the lowest temperatures reached in the specific-heat measurements that a normal type of extrapolation may be made. The procedure for $Gd_2(SO_4)_3 \cdot 8H_2O$, for example, illustrates the difficulties that may arise in computing

entropies of paramagnetic substances. Moreover, the data and calculations for such substances as CO, H_2O, and N_2O show that correct entropies are not obtained in all instances by indiscriminate application of the usual methods of calculation.

In some instances specific-heat values of several experimenters have been averaged, while in others the results of a single investigator have been used. The bibliography at the end of this bulletin contains a virtually complete (to March 1940) list of references pertaining to true specific-heat data at low temperatures of the elements and inorganic compounds. A table of specific-heat values of the substances whose entropies have been calculated from the third law of thermodynamics is given immediately following this entropy section.

ALUMINUM

Element.—The specific heat of Al has been measured by Kok and Keesom (*263*) (1°–20°), Maier and Anderson (*305*) (54°–297°), Meads (*313*) (15°–302°), Nernst (*327*, *328*) (32°–89°), and Nernst and Schwers (*329*) (19°–80°). The entropy computed from a smooth curve representing these results is $S_{298.1}=6.75\pm0.05$. The extrapolation is negligible, ca. 3×10^{-4} unit.

The spectroscopic data on Al (*g*) (*273 p. 2345*) show that only two states, $^2P_{1/2}$ and $^2P_{3/2}$, separated by 112 waves per centimeter and having quantum weights of 2 and 4, respectively, need be considered at 298.1°. This results in the addition of 3.49 to the Sackur equation, making $S_{298.1}=39.31\pm0.01$ for Al (*g*).

Aluminum ion.—Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=-76\pm10$ for Al^{+++} (*aq.*) based upon data for the reaction $CsAl(SO_4)_2\cdot12H_2O=Cs^+ + Al^{+++} + 2SO_4^{--} + 12H_2O(l)$.

Oxide.—Parks and Kelley (*334*) (91°–291°) have determined the specific heat of Al_2O_3 in the form of sapphires. Simon and Swain (*373*) (30°–280°) have studied corundum. In addition, there are some unpublished measurements of Anderson (*25*) (53°–295°). Considering all these data there is obtained $S_{298.1}=12.5\pm0.15$, the extrapolation below 28.18° being 0.03.

Silicates.—Three forms of Al_2SiO_5, disthen (24°–224°), sillimanite (17°–282°), and andalusite (23°–280°), were studied by Simon and Zeidler (*374*). Entropy calculations yield, respectively, $S_{298.1}=20.7\pm0.5$, $S_{298.1}=27.0\pm0.5$, and $S_{298.1}=25.0\pm0.5$. Extrapolation was made below 22.39° in each instance, the results being, respectively, 0.03, 0.13, and 0.04.

ANTIMONY

Element.—The specific heat of Sb was measured by Anderson (*11*) (66°–294°). His data yield 2.34 for the entropy extrapolation below 63.1° and 8.17 for the portion between 63.1° and 298.1°, making $S_{298.1}=10.5\pm0.3$. The data of Günther (*188*) (80°–99°) and Simon and Ruhemann (*372*) (71°–82°) do not agree with those of Anderson or with each other, and they have been given no weight as they cover such small temperature ranges.

The entropy of Sb (*g*) at 298.1° is obtainable from the Sackur equation, with the addition of $R\ ln\ 4=2.755$ units to account for the quantum weight of 4 for the lowest energy state (*273, p. 2346*). The result is $S_{298.1}=43.07\pm0.01$.

Genard (*153*) has obtained $I=489\times10^{-40}$ as the moment of inertia of the Sb_2 (*g*) molecule. This figure and the Sackur-Tetrode equation give $S_{t+r,298.1}=59.31$ for the translational and rotational entropy. Genard also gives $\omega=277$ as the vibrational frequency, while Almy (*7*) reports $\omega=269.9$ and Naude (*324*) $\omega=268$. The computated vibrational entropy is $S_{v,298.1}=1.61$, making the total $S_{298.1}=60.9\pm0.5$ for Sb_2 (*g*).

Oxides.—Anderson (*11*) has measured the specific heat of Sb_2O_3 (59°–295°), Sb_2O_4 (59°–285°), and Sb_2O_5 (60°–293°). The last material contained some water and lower oxides, for which correction is made.

For Sb_2O_3 the extrapolated entropy below 56.23° is 4.09, and the measured portion between 56.23° and 298.1° is 25.35. Therefore, $S_{298.1}=29.4\pm0.6$.

The Sb_2O_4 data yield $S_{56.23}=4.31$ (extrapolation) and $S_{298.1}-S_{56.23}=26.04$ (measured), making $S_{298.1}=30.4\pm0.7$.

The corresponding figures for Sb_2O_5 are $S_{56.23}=2.54$ (extrapolation) and $S_{298.1}-S_{56.23}=27.32$. The sum is $S_{298.1}=29.9\pm1.2$. The estimated error is large to allow safely for uncertainty in correcting for water and lower oxides.

A rough value of the entropy of Sb_4O_6 (*g*) is obtainable from that of the solid, 2×29.4, and the entropy of sublimation of cubic Sb_4O_6, $\Delta S_{298.1}=42.9$ (*247*). The result is $S_{298.1}=102$, in which the error may be several units.

Sulfide.—From heat and free-energy-of-formation figures given by Kelley (*250*) there is estimated $S_{298.1}=39.6$ for Sb_2S_3, in which the error may be a few units.

Trichloride.—Howard and Wilson (*198*) have considered the prismatic $SbCl_3$ (*g*) molecule and have obtained 134 (2), 165 (1), 320 (2), and 360 (1) as the vibrational frequencies, the numbers in parentheses giving the degrees of freedom. The Sb–Cl distance was given as 2.30×10^{-8} cm. and the valence angle as 94°. A slightly different set of frequencies was reported by Hemptinne, Wouters, and Fayt (*193*), 130 (2), 155 (1), 320 (2), and 360 (1). From Howard and Wilson's figures the moments of inertia are $I_1=660\times10^{-40}$, and $I_2=I_3=470\times10^{-40}$. These, with the Sackur-Tetrode equation and the symmetry number 3, yield $S_{t+r,298.1}=68.82$. The vibrational entropy is $S_{v,298.1}=12.07$, making $S_{298.1}=80.9\pm2$ for $SbCl_3$ (*g*).

The free energy and heat of sublimation of $SbCl_3$ have been reported as $\Delta F^\circ_{298.1}=5{,}111$ and $\Delta H_{298.1}=15{,}855$ (*247*), corresponding to an entropy of sublimation of $\Delta S_{298.1}=36.0$. This figure and the entropy of the gas yield $S_{298.1}=44.8\pm3$ for $SbCl_3$(*s*).

ARGON

Element.—Specific-heat measurements on solid and liquid argon were made by Clusius (*80*) (18°–89°) and Eucken (*137*) (17°–94°). Clusius determined the melting point, heat of fusion, and heat of sublimation at 83.85° to form gas at 516.3 mm. pressure. Eucken (*136*) and Eucken and Hauck (*137*) have measured the melting point and heat of fusion. The heat of vaporization at the boiling point, 87.3°, was determined by Frank and Clusius (*148*) and Born (*46*).

As the heat-capacity measurements of Clusius and Eucken differ appreciably, two independent calculations of $S_{298.1}$ will be made and

compared with the more adequate value obtainable from the Sackur equation.

From the data of Clusius, $S_{10}=0.26$ (extrapolation), $S_{83.85}-S_{10}=8.67$ (crystals), $\Delta S_{83.85}=\frac{1,899}{83.85}=22.65$ (sublimation at 516.3 mm. pressure), $\Delta S_{83.85}=-0.77$ (compression from 516.3 mm. to 1 atmosphere pressure), and $S_{298.1}-S_{83.85}=6.31$ (gas, $C_p=4.97$). The sum is $S_{298.1}=37.1\pm0.3$, no correction being made for gas imperfection.

Turning now to Eucken's data, there are found $S_{17.8}=1.13$ (extrapolation), $S_{83.0}-S_{17.8}=8.10$ (crystals), $\Delta S_{83.0}=267.8/83.0=3.23$ (fusion), and $S_{87.3}-S_{83.0}=0.53$ (liquid). Eucken did not measure the heat of vaporization, and the value obtained by Frank and Clusius will be used. This gives $\Delta S_{87.3}=1557.5/87.3=17.84$ (vaporization). The entropy increment for warming the gas from 87.3° to 298.1° is 6.10 ($C_p=4.97$). Therefore, $S_{298.1}=1.13+8.10+3.23+0.53+17.84+6.10=36.9\pm0.2$.

The most reliable value of the entropy of argon is that computed from the Sackur equation, $S_{298.1}=36.99\pm0.01$. However, it is seen that both the above values based on heat capacities are in substantial agreement with this figure.

ARSENIC

Element.—The specific heat of As was studied by Anderson (*9*) (57°–291°). His data give $S_{56.2}=1.20$ (extrapolation) and $S_{298.1}-S_{56.2}=7.16$, making $S_{298.1}=8.4\pm0.2$.

The entropy of As (g) is obtainable from the Sackur equation with $R\ ln\ 4$ added to account for the quantum weight of the lowest energy state (*273, p. 2346*). The result is $S_{298.1}=41.62\pm0.01$.

Almy (*7*) has reported $\omega=429.4$, the vibration frequency of the As_2 (g) molecule, and has estimated the interatomic distance as 1.95×10^{-8} cm. From the latter figure $I=235\times10^{-40}$. There are computed $S_{t+r,298.1}=56.40$ and $S_{v,298.1}=0.87$, making a total of $S_{298.1}=57.3\pm0.5$ for As_2 (g).

From vapor-pressure data the value $\Delta S_{298.1}=35.1$ was estimated as the entropy of sublimation of arsenic in forming As_4 (g) (*247*). This result and the entropy of the solid yield $S_{298.1}=35.1+4\times8.4=69$ for As_4 (g). The error in this value may be several units.

Oxides.—The specific-heat data of Anderson (*9*) for As_2O_3 (60°–297°) and Sb_2O_5 (63°–297°) give the values As_2O_3, $S_{56.2}=3.54$ (extrapolation), $S_{298.1}-S_{56.2}=22.04$, and $S_{298.1}=25.6\pm0.5$; As_2O_5, $S_{63.1}=1.94$ (extrapolation), $S_{298.1}-S_{63.1}=23.30$, and $S_{298.1}=25.2\pm0.4$.

The entropy of sublimation of orthorhombic As_4O_6 has been computed as $\Delta S_{298.1}=49.5$ from vapor-pressure data (*247*). This value and the entropy of the solid give $S_{298.1}=49.5+2\times25.6=101$ for As_4O_6 (g). The error in this value may be several units.

Trichloride.—Brodskii and Sack (*54*) have given 159 (2), 195 (1), 372 (2), and 410 (1) as the vibration frequencies of the $AsCl_3$ (g) molecule. Howard and Wilson (*198*), Paramasivan (*333*), Yost (*409*), and Yost and Anderson (*410*) have adopted slightly different values—159 (2), 193 (1), 370 (2), and 410 (1). The last-named authors also give $I_1=661.8\times10^{-40}$ and $I_2=I_3=402.0\times10^{-40}$. The symmetry number is 3, as the molecule is pyramidal. Yost and Anderson calculate $S_{298.1}=78.2\pm3$ for $AsCl_3$ (g), superseding the earlier calculation of

Yost and Sherborne (*414*), which is in error. From Howard and Wilson's (*198*) values of valence angle, 96°, and As–Cl distance, 2.24 $\times 10^{-8}$ cm., the moments of inertia are $I_1=640\times10^{-40}$, and $I_2=I_3=420\times10^{-40}$. Calculation of the translational and rotational entropy from these figures gives a result differing by only 0.04 unit from that of Yost and Anderson. Therefore, the value $S_{298.1}=78.2\pm2$ is adopted for $AsCl_3$ (*g*).

The heat and free energy of vaporization of $AsCl_3$ (*l*) have been calculated as $\Delta H_{298.1}=8{,}692$ and $\Delta F^\circ_{298.1}=2{,}009$ (*247*). These figures correspond to an entropy of vaporization of $\Delta S_{298.1}=22.4$ which, when combined with the result for the gas, gives $S_{298.1}=55.8\pm3$ for $AsCl_3$ (*l*).

Trifluoride.—Yost and Anderson (*410*) have calculated the entropy of AsF_3 (*g*), using the moments of inertia $I_1=220.0\times10^{-40}$ and $I_2=I_3=144.8\times10^{-40}$, and the vibration frequencies 274 (2), 341 (1), 644 (2), and 707 (1). They find $S_{298.1}=69.2\pm2$. Howard and Wilson's (*198*) molecular dimensions lead to $I_1=230\times10^{-40}$, and $I_2=I_3=160\times10^{-40}$, which result in a rotational entropy 0.2 greater than that of Yost and Anderson. This difference is negligible compared with the estimated error. The earlier calculations of Yost and Sherborne (*414*) are incorrect.

The reaction $As+3/2\ F_2=AsF_3$ (*l*) was considered by Yost and Sherborne (*415*), who obtained $\Delta H_{298.1}=-198{,}300$ and $\Delta F^\circ_{298.1}=-189{,}000$, which correspond to $\Delta S_{298.1}=-31.2$. This figure and the entropies of As and F_2 yield $S_{298.1}=50.1\pm3$ for AsF_3 (*l*).

BARIUM

Element.—The entropy of Ba (*g*) calculated from the Sackur equation is $S_{298.1}=40.67\pm0.01$. In this instance the quantum weight of the lowest energy state is 1.

Barium ion.—Latimer, Pitzer, and Smith (*286*) have obtained the entropy of Ba^{++} (*aq.*) as $S_{298.1}=2.3\pm0.3$ from data for the reaction $BaCl_2\cdot2H_2O=Ba^{++}+2Cl^-+2H_2O$ (*l*).

Oxide.—Anderson (*18*) (56°–299°) investigated the specific heat of BaO. From his data, $S_{298.1}=16.8\pm0.3$, of which the extrapolation below 56.2° is 2.56.

From band spectra Mahanti (*302*) has obtained $I=76.0\times10^{-40}$ and $\omega=671.5$ for BaO (*g*). The lowest energy state is designated $^1\Sigma$ (quantum weight=1). These figures and the Sackur-Tetrode equation yield $S_{t+r,298.1}=55.61$. The vibrational entropy is $S_{v,298.1}=0.34$. The sum is $S_{298.1}=56.0\pm0.5$ for BaO (*g*).

Chloride.—Brown, Smith, and Latimer (*59*) (14°–302°) studied the specific heat of $BaCl_2\cdot2H_2O$. The extrapolated entropy is 0.33 below 14.13°, and the measured portion is $S_{298.1}-S_{14.13}=48.17$. Therefore, $S_{298.1}=48.5\pm0.3$.

Fluoride.—The specific heat of BaF_2 was measured by Pitzer, Smith, and Latimer (*340*) (13°–301°). Their data yield $S_{298.1}=23.0\pm0.1$, of which only 0.06 is extrapolation below 13.34°.

Bromate.—Greensfelder and Latimer (*185*) (16°–296°) measured the specific heat of $Ba(BrO_3)_2\cdot H_2O$. Their entropy calculation is in serious error, however, as was indicated by Latimer, Schutz, and Hicks (*289*). The extrapolated portion between 0° and 15.85° is 0.80 unit, and the experimental portion between 15.85° and 298.1° is 67.96, making $S_{298.1}=68.8\pm1.5$.

Carbonate.—The specific heat of $BaCO_3$, witherite, was measured by Anderson (*16*) (54°–296°). The calculations give $S_{298.1}=26.8\pm0.5$, of which 3.59 is extrapolation below 56.2°.

Nitrate.—The specific heat of $Ba(NO_3)_2$ was measured by Latimer and Ahlberg (*278*) (16°–296°). Their results yield $S_{298.1}=51.1\pm0.4$, involving an extrapolation of 0.56 below 15.8°.

Sulfate.—Latimer, Hicks, and Schutz (*285*) (15°–299°) measured the specific heat of $BaSO_4$. There is computed $S_{14.13}=0.16$ extrapolation and $S_{298.1}=31.6\pm0.3$.

BERYLLIUM

Element.—The specific heat of Be has been measured by Cristescu and Simon (*108*) (10°–300°), Lewis (*290*) (97°–283°), and Simon and Ruhemann (*372*) (71°–80°). The entropy calculation is based upon the work of Cristescu and Simon, which is the most extensive. Their data yield $S_{298.1}=2.28\pm0.02$. The extrapolation below 10° is virtually negligible, about 0.0002 unit.

The entropy of Be (*g*) is given as $S_{298.1}=32.56\pm0.01$ by the Sackur equation.

Oxide.—Günther (*187*) (76°–85°) and Kelley (*254*) (55°–293°) have measured the specific heat of BeO. Employing the data of the latter investigator, there is obtained $S_{298.1}=3.37\pm0.05$. The extrapolation below 53.1° is 0.037 unit.

The moment of inertia and vibration frequency of BeO (*g*) were determined by Herzberg (*196*) as $I=16.72\times10^{-40}$ and $\omega=1{,}487$. From the first figure $S_{t+r,298.1}=47.19$, and from the second $S_{v,298.1}=0.01$, making $S_{298.1}=47.2\pm0.5$ for BeO (*g*).

Silicate.—Kelley (*254*) (54°–295°) also has measured the specific heat of Be_2SiO_4, phenacite. His data yield $S_{298.1}=15.4\pm0.1$, of which 0.30 is extrapolation below 53.1°.

BISMUTH

Element.—The specific heat of Bi was determined by Anderson (*12*) (60°–299°), Bronson and MacHattie (*55*) (193°–293°), and Keesom and van den Ende (*228, 229*) (3°–20°). Combining these data results in $S_{298.1}=13.6\pm0.6$. The extrapolated portion below 3.16° is 0.005. The estimated error is large because the data of Anderson and of Bronson and MacHattie cannot be connected with those of Keesom and van den Ende in a reasonable manner. It appears likely that a transition ("hump") may occur in the range 20° to 60°, especially in view of the fact that the entropy figure appears low compared with that for Pb. The computed result is a compromise, as Anderson gave 12.4 from his data alone.

The entropy of Bi (*g*) computed from the Sackur equation with $R\ ln\ 4=2.755$ added because of the quantum weight 4 (*273, p. 2347*) of the lowest energy state is $S_{298.1}=44.68\pm0.01$.

Almy and Sparks (*8*) have obtained the internuclear distance as 2.85×10^{-8} cm. for the Bi_2 (*g*) molecule and the vibration frequency as $\omega=172$. The nuclear separation results in $I=1{,}400\times10^{-40}$ which, in turn, yields $S_{t+r,298.1}=63.00$. The vibrational entropy is $S_{v,298.1}=2.41$, and the sum is $S_{298.1}=65.4\pm1$.

Oxide.—Anderson's (*12*) (60°–290°) specific-heat data for Bi_2O_3 lead to the values, $S_{56.2}=6.22$ (extrapolation) and $S_{298.1}-S_{56.2}=29.96$, making $S_{298.1}=36.2\pm0.7$.

Trichloride.—The $BiCl_3$ (*g*) molecule was considered by Howard and Wilson (*198*), who gave 96 (2), 130 (1), 242 (2), and 288 (1) as the vibration frequencies, 2.46×10^{-8} cm. as the Bi–Cl distance, and 93° as the bond angle in the pyramidal model. From the last two figures $I_1=740\times10^{-40}$, and $I_2=I_3=580\times10^{-40}$. These moments of inertia and the symmetry number 3 result in $S_{t+r,298.1}=70.30$. The vibrational entropy is $S_{v,298.1}=15.16$. For $BiCl_3$ (*g*) then, $S_{298.1}=85.5\pm3$.

The heat and free energy of vaporization of $BiCl_3$ (*l*) were obtained formally from vapor-pressure data as $\Delta H_{298.1}=23{,}177$ and $\Delta F^\circ_{298.1}=12{,}228$ (*247*). These correspond to $\Delta S_{298.1}=36.53$. The heat of fusion of $BiCl_3$ (*s*) at its melting point, 497°, was computed as $\Delta H_{497}=2{,}600$ from binary-system freezing-point data (*248*). If it is assumed that $\Delta C_p=4$ for the reaction $BiCl_3$ (*s*)$=BiCl_3$ (*l*) then $\Delta S_{298.1}=3.16$ is calculated for the fusion process. .The entropy of sublimation is therefore $\Delta S_{298.1}=39.7$. From this and the entropy of the gas there is obtained $S_{298.1}=45.8\pm4$ for $BiCl_3$ (*s*).

BORON

Element.—From unpublished measurements of the specific heat of B_4C (*257*) and a comparison of the meager entropy data for carbides with those of their constituent metals there is estimated $S_{298.1}=1.7\pm0.2$ for B.

Spectroscopic data for B (*g*) (*273 p. 2345*) show that in obtaining the entropy at 298.1° only two states, having a separation of 15 waves per centimeter, need be considered, the $^2P_{1/2}$ and $^2P_{3/2}$ states with quantum weights 2 and 4, respectively. It is found that 3.559 is to be added to the translational entropy given by the Sackur equation; making $S_{298.1}=36.66\pm0.01$ for B (*g*).

Tribromide.—Yost (*409*) has reported 151 (2), 279 (1), 743 (1), and 826 (2) as the vibration frequencies of the BBr_3 (*g*) molecule and 1.87×10^{-8} cm. as the B–Br distance, the molecule being planar with the Br atoms at the corners and the B atom at the centroid of an equilateral triangle. The symmetry number is 6. There are computed $I_1=1{,}380\times10^{-40}$ and $I_2=I_3=690\times10^{-40}$, which in turn yield $S_{t+r,298.1}=69.21$. The vibrational entropy is $S_{v,298.1}=7.52$, making $S_{298.1}=76.7\pm3$ for BBr_3 (*g*).

Trichloride.—Cassie (*71*) has recorded 250 (2), 430 (1), 958 (2), and 996 (1) as the vibration frequencies of the BCl_3 (*g*) molecule and 3.03×10^{-8} cm. as the Cl–Cl distance. Yost (*409*) has given somewhat different values—253 (2), 471 (1), 902 (1) and 970 (2), as vibration frequencies and 1.73×10^{-8} cm. as the B–Cl distance. It makes but little difference in the entropy which set of values is used. From Yost's figures, $I_1=525\times10^{-40}$ and $I_2=I_3=262\times10^{-40}$. The symmetry number is 6 as the molecule is planar like BBr_3. There are computed $S_{t+r,298.1}=64.06$ and $S_{v,298.1}=4.54$, making $S_{298.1}=68.6\pm3$ for BCl_3 (*g*). This corrects an error in the previous compolation (*249*) in which the symmetry number was taken as 3.

Trifluoride.—Eucken and Schröder (*140*) (12°–173°) have measured the specific heat and heats of transition, fusion, and vaporization of

BF_3. Recalculation of their data gives $S_{12.6}=0.51$ (extrapolation), $S_{142.15}-S_{12.6}=18.48$ (crystals II), $S_{144.46}-S_{142.15}=1.13$ (transition and crystals I), $\Delta S_{144.46}=1014/144.46=7.02$ (fusion), $S_{154.5}-S_{144.46}=1.64$ (liquid), $\Delta S_{154.5}=4{,}440/154.5=28.74$ (vaporization at 0.2185 atmosphere pressure), and $\Delta S_{154.5}=-3.02$ (compression from 0.2185 to 1 atmosphere). The entropy increment involved in warming the gas from 154.5° to 298.1° was obtained from specific-heat values corresponding to the molecular constants given below, $S_{298.1}-S_{154.5}=6.87$ (*g*). The sum of these quantities is $S_{298.1}=61.4\pm0.5$.

Yost (*409*) has recorded 480 (2), 708 (1), 888 (1), and 1,470 (2) as the vibration frequencies and 1.30×10^{-8} cm. as the B–F distance in the planar, equilateral triangular BF_3 (*g*) molecule. There are computed $I_1=159\times10^{-40}$ and $I_2=I_3=79\times10^{-40}$, resulting in $S_{t+r,298.1}=58.86$. The vibrational entropy is $S_{v,298.1}=1.90$, and the total is $S_{298.1}=60.8$.

The mean of the figures from the specific-heat measurements and the molecular constants is adopted, $S_{298.1}=61.1\pm0.5$.

Carbide.—Unpublished specific-heat measurements of Kelley (*257*) (54°–295°) for B_4C result in $S_{298.1}=6.47\pm0.04$, of which only 0.047 is extrapolation below 53.1°.

BROMINE

Element.—The specific heat of solid bromine has been studied by Latimer and Hoenshel (*283*) (14°–253°) and Suhrmann and von Lüde (*392*) (20°–155°). The results of the former investigators will be used, as the data of the latter are very erratic. Weber (*406*) has given the melting point as 265.9° and Regnault (*345*), the heat of fusion as 2,580 calories per mole. A mean specific heat of Br_2 (*l*), $C_p=8.5$, was measured near room temperature by Andrews (*29*).

The data of Latimer and Hoenshel lead to the values $S_{14.1}=0.68$ (extrapolation), and $S_{265.9}-S_{14.1}=24.32$ (crystals), making the value for Br_2 (*s*) at the melting point $S_{265.9}=25.00$. The entropy of fusion is $\Delta S_{265.9}=2{,}580/265.9=9.70$ and the entropy change in heating the liquid from 265.9° to 298.1° is 1.94. Therefore, $S_{298.1}=25.00+9.70+1.94=36.6\pm0.5$.

Woitinek (*408*) has obtained $\Delta S_{298.1}=-3.00$ for the reaction $Ag+1/2\ Br_2$ (*l*)$=AgBr$. Employing the values $S_{298.1}=10.2\pm0.05$ for Ag and $S_{298.1}=25.60\pm0.1$ for AgBr one obtains $S_{298.1}=36.8\pm0.4$ for Br_2 (*l*), in agreement with the results from heat-capacity data.

The mean value, $S_{298.1}=36.7\pm0.4$, is adopted for Br_2 (*l*).

The spectroscopic data for monatomic, Br (*g*), gas show that all but a negligible portion of the atoms are the lowest energy state, which is a $^2P_{3/2}$ state with quantum weight 4. The Sackur equation with $R\ ln\ 4$ added yields $S_{298.1}=41.81\pm0.01$ for Br (*g*).

Brown (*64*) has computed the following values for Br_2 (*g*) from spectroscopic data—$S_{298.1}=58.56$ for $Br_2^{79,79}$, $S_{298.1}=60.01$ for $Br_2^{79,81}$, and $S_{298.1}=58.70$ for $Br_2^{81,81}$. For the ordinary isotopic mixture he gives $S_{298.1}=58.63$. The latter value is checked approximately by Gordon and Barnes (*184*) who obtained $S_{298.1}=58.67$. Using the data adopted by Stuart (*390*), $I=340\times10^{-40}$ and $\omega=327$, one obtains $S_{t+r,298.1}=57.32$ and $S_{v,298.1}=1.28$, making $S_{298.1}=58.60$. The value given by Brown, $S_{298.1}=58.63$, is considered the most reliable, and the error should not exceed 0.03 unit.

Bromide ion.—Latimer, Pitzer, and Smith (*286*) have obtained the entropy of Br^- (*aq.*) from data on three reactions, $AgBr+Cl^-=AgCl+Br^-$, $AgBr+1/2\ H_2=H^++Br^-+Ag$, and $1/2\ Br_2\ (l)+Cl^-=1/2\ Cl_2\ (g)+Br^-$. The results are, respectively, 19.8 ± 0.2, 19.6 ± 0.3, and 19.5 ± 0.4. Their selected result, $S_{298.1}=19.7\pm0.2$, is adopted here.

Chloride.—From thermal measurements in CCl_4 solutions Blair and Yost (*43*) have obtained $S_{298.1}=57.1$ for BrCl (*g*). The later paper of Beeson and Yost (*41*) gives $\Delta S_{298.1}=2.83$ for the reaction $Br_2\ (g)+Cl_2\ (g)=2BrCl\ (g)$. This figure and the entropies of Br_2 (*g*) and Cl_2 (*g*) leads to $S_{298.1}=57.4$ for BrCl (*g*). Also, Beeson and Yost record $\omega=430$ and the Br–Cl distance as 2.13×10^{-8} cm. From the latter figure, $I=184\times10^{-40}$ is calculated, and in turn $S_{t+r,298.1}=56.51$. The vibrational entropy is $S_{v,298.1}=0.86$. The sum is $S_{298.1}=57.4\pm0.1$, which is adopted.

It is interesting to approximate this value in another way. It may be expected that the entropy of BrCl (*g*) is about the mean of the values for Cl_2 (*g*) and Br_2 (*g*) plus $R\ ln\ 2$. Such calculation gives $S_{298.1}=1/2(53.31+58.63)+1.38=57.35$.

Bromate ion.—The entropy of BrO_3^- (*aq.*) has been obtained by Latimer, Pitzer, and Smith (*286*) from data on the reactions, $KBrO_3=K^++BrO_3^-$ and $Ba(BrO_3)_2\cdot H_2O=Ba^{++}+2BrO_3^-+H_2O\ (l)$. The values are, respectively, 38.7 ± 1 and 38.1 ± 2. Their selection, $S_{298.1}=38.5\pm1.0$, is adopted.

CADMIUM

Element.—The specific heat of Cd was measured by Bronson and Wilson (*56*) (193°–293°), Lange and Simon (*275*) (10°–300°), and Rodebush (*347*) (69°–298°). The most weight has been given to the data of Lange and Simon in obtaining $S_{298.1}=12.3\pm0.1$, of which only 0.07 is extrapolation below 10°.

From the Sackur equation, the entropy of Cd (*g*) is $S_{298.1}=40.07\pm0.01$. The lowest energy state only is effective at 298.1°, and its quantum weight is 1.

Cadmium ion.—Latimer, Pitzer, and Smith (*286*), from data for the reaction $Cd+2H^+=Cd^{++}+H_2$, have obtained $S_{298.1}=-16.4\pm1.5$ for Cd^{++} (*aq.*). This value agrees within the limits of error with the figure given by Bates (*39*), $S_{298.1}=-14.8\pm1.0$. The mean, $S_{298.1}=-15.6\pm1.2$, is adopted.

Oxide.—Millar (*316*) (71°–291°) has measured the specific heat of CdO. His data lead to $S_{70.8}=2.16$ (extrapolation) and $S_{298.1}-S_{70.8}=10.94$ (measured); therefore, $S_{298.1}=13.1\pm0.3$.

The entropy of CdO (*g*) was computed from that of the solid and vapor-pressure data as $S_{298.1}=46.9$ (*247*). The error in this value may be several units.

Sulfide.—Kelley (*250*), in considering the thermodynamic properties of CdS, has estimated $S_{298.1}=17\pm1$.

Telluride.—McAteer and Seltz (*307*) have obtained $\Delta S_{298.1}=-2.0$ for the formation of CdTe from the elements. This result leads to $S_{298.1}=22.2\pm1.0$ for CdTe.

Bromide.—Bates (*40*) has reported $S_{298.1}=32.0$ for $CdBr_2$. This value is adopted, and the error is taken as ±1.0. Reasonable agreement is shown by the value obtainable from the heat and free energy of formation of $CdBr_2$, found by Ishikawa and Ueda (*204*, *205*), namely, $S_{298.1}=34.4$, in which ±1.5 is estimated as the error.

Chloride.—The reaction $Cd+Cl_2=CdCl_2$ was considered by Ishikawa, Kimura, and Murooka (*208*). From cell measurements and thermal data they obtained $\Delta H_{298.1}=-92{,}149$ and $\Delta F^\circ_{298.1}=-81{,}878$, making $\Delta S_{298.1}=-34.5$. The last figure corresponds to $S_{298.1}=31.5$ for $CdCl_2$. A value in good agreement with this has been reported by Bates (*40*), $S_{298.1}=31.2$, while Garner, Green, and Yost (*152*) have obtained a higher result, $S_{298.1}=33.5$. The value given by Bates is adopted, $S_{298.1}=31.2\pm1.0$.

Iodide.—The only available value for CdI_2 is that given by Bates (*40*), $S_{298.1}=39.5$, in which the error is estimated as ±1.0.

Hydroxide.—Ishikawa and Shibata (*202*) have obtained $\Delta F^\circ_{298.1}=-42{,}100$ for the reaction $Cd+HgO+H_2O(l)=Cd(OH)_2+Hg$. The heat of this reaction may be approximated from existing data. Thomsen (*269, p. 1522*) has found $\Delta H=-65{,}680$ as the heat of the reaction $Cd+1/2\ O_2+H_2O(l)=Cd(OH)_2$; and the heat of formation of $H_2O(l)$, $\Delta H_{298.1}=-68{,}300$ (*258*), is known with high accuracy. The heat of formation of $Cd(OH)_2$ from the elements is, therefore, $\Delta H_{298.1}=-133{,}980$. Several values are available for the heat of formation of HgO, of which that of Fried (*269, p. 1535; 270, p. 835*), $\Delta H=-21{,}500$, appears to be reliable and is within 100 calories of the mean of all the determinations. From these figures, the heat of the reaction studied by Ishikawa and Shibata is $\Delta H_{298.1}=-44{,}180$, and the entropy change is $\Delta S_{298.1}=-7.0$. As the other entropies are known, $S_{298.1}=21$ is calculated for $Cd(OH)_2$. This result is one of low probable accuracy, and the error may be a few units.

Carbonate.—The entropy of dissociation of $CdCO_3$ to CdO and CO_2 was estimated previously (*258*) as $\Delta S_{298.1}=39.0$. From this there is obtained $S_{298.1}=25.2$ for $CdCO_3$. This result may be in error (probably high) by a few units.

Sulfate.—From consideration of the thermodynamic properties of $CdSO_4$, Kelley (*250*) has computed $S_{298.1}=31.3$, in which the error may be a few units. He also estimated $S_{298.1}=39.7$ for $CdSO_4\cdot H_2O$ and $S_{298.1}=57.5$ for $CdSO_4\cdot 8/3\ H_2O$.

Antimonides.—The reaction $Cd(l)+Sb(s)=CdSb(s)$ was studied by Seltz and De Haven (*360*). They obtained $\Delta H=-4{,}730$ (ΔC_p assumed zero) and $\Delta F^\circ_{687}=-2{,}559$. From these figures, $\Delta F^\circ=-4{,}730+3.16\ T$, which at the melting point of Cd, 594°, yields $\Delta F^\circ_{594}=-2{,}853$. Taking the heat of fusion of Cd as $\Delta H_{594}=1{,}460$ (*248*), there is obtained $\Delta F^\circ=-3{,}270+0.70\ T$ for the reaction $Cd(s)+Sb(s)=CdSb(s)$. The entropy of this reaction is therefore -0.70, which results in $S_{298.1}=21.1\pm0.7$ for $CdSb(s)$. The difference of 0.6 between this value and that reported by Seltz and DeHaven is attributable to using a different heat of fusion of Cd.

Seltz and DeWitt (*361*) have obtained $\Delta S=21.0$ for the reaction $3Cd+2Sb=Cd_3Sb_2$. This figure leads to $S_{298.1}=78.9\pm2$ for $Cd_3Sb_2(s)$.

CALCIUM

Element.—The specific heat of Ca was measured by Clusius and Vaughen (*101*) (10°–201°), Eastman and Rodebush (*130*) (67°–294°), and Günther (*187*) (22°–62°). Relying almost entirely upon the data of Clusius and Vaughen, there are obtained $S_{10.0}=0.013$ (extrapolation), $S_{298.1}-S_{10.0}=9.94$, and $S_{298.1}=9.95\pm0.1$.

The spectroscopic data on Ca (*g*) (*273, p. 2345*) show that only the lowest energy state, of unit quantum weight, need be considered in obtaining $S_{298.1}=37.00\pm0.01$ from the Sackur equation.

Calcium ion.—Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=-11.4\pm0.3$ for Ca^{++} (*aq.*) from thermal data for the reaction $CaCO_3+2H^+=Ca^{++}+H_2O$ (*l*)$+CO_2$ (*g*).

Oxide.—Nernst and Schwers (*329*) (28°–90°) and Parks and Kelley (*334*) (87°–293°) have measured the specific heat of CaO. The results of the latter investigators extrapolate into the lower temperature portion of the data of Nernst and Schwers. The resulting entropy values are $S_{28.2}=0.04$ (extrapolation), $S_{298.1}-S_{28.2}=9.46$, and $S_{298.1}=9.5\pm0.2$.

The values, $I=57.2\times10^{-40}$ and $\omega=714$ (*273, p. 2350*) are available for CaO (*g*), the latter figure being uncertain. There are computed $S_{t+r,298.1}=52.04$ and $S_{v,298.1}=0.29$, making $S_{298.1}=52.3\pm0.5$ for CaO (*g*).

Sulfide.—The specific heat of CaS was measured by Anderson (*13*) (58°–295°). The data yield $S_{298.1}=13.5\pm0.3$, of which $S_{56.2}=1.32$ is extrapolation.

Fluoride.—Eucken and Schwers (*141*) (17°–328°) have measured the specific heat of CaF_2. The extrapolated portion of the entropy is $S_{17.8}=0.02$ and the measured part is $S_{298.1}-S_{17.8}=16.38$, making $S_{298.1}=16.4\pm0.4$.

Hydride.—Günther (*187*) (69°–86°) has made specific-heat measurements of CaH_2. The temperature range covered is too small for a good entropy calculation, but there is estimated $S_{298.1}=9.9\pm1.0$.

Hydroxide.—The specific heat of $Ca(OH)_2$ was measured by Nernst and Schwers (*329*) (21°–86°). These measurements suffice only for a rough entropy calculation, $S_{298.1}=17.4\pm1.0$.

Carbonates.—The specific heat of $CaCO_3$, calcite, was measured by Anderson (*16*) (57°–297°), Nernst and Schwers (*329*) (22°–89°), and Simon and Swain (*373*) (15°–80°). Recalculation, using all the available data, gives $S_{298.1}=22.2\pm0.2$. The extrapolation below 14.12° is 0.05 unit.

Anderson (*16*) (54°–293°) and Günther (*187*) (23°–57°) have measured the specific heat of $CaCO_3$, aragonite. Anderson's results, which differ considerably from the older values of Günther, are used. The result is $S_{298.1}=21.2\pm0.3$, of which 1.51 is extrapolation below 56.2°.

The difference in entropy between these two varieties of $CaCO_3$ is 1.0 ± 0.5 from the specific-heat data. This is in agreement with the independently determined value of Backström (*32*), 0.74 ± 0.2.

Oxalate.—Latimer, Schutz, and Hicks (*287*) (19°–300°) have studied the specific heat of $CaC_2O_4\cdot H_2O$. From their data $S_{298.1}-S_{17.78}=37.23$ is computed and $S_{17.78}=0.20$ is extrapolated, making $S_{298.1}=37.4\pm0.2$.

Phosphates.—Southard and Milner (*380*) (15°–297°) have investigated the specific heat of α and β $Ca_3(PO_4)_2$. The entropy values are respectively, $S_{298.1}=57.6\pm0.2$ and $S_{298.1}=56.4\pm0.4$. The extrapolation for the α form is 0.09 below 14.13°, while for the β modification 0.20 is the extrapolation below 17.78°.

Silicates.—The specific heat of $CaSiO_3$, wollastonite, was measured by Cristescu and Simon (*108*) (10°–210°) and Wagner (*404*) (10°–304°). The combined data yield $S_{298.1}=19.6\pm0.2$, of which only 0.016 is extrapolation below 10°.

Parks and Kelley (*335*) (88°–299°) and Wagner (*404*) (10°–296°) have measured the specific heat of $CaSiO_3$, pseudowollastonite. The results of the two investigations are in fair agreement. Calculation gives $S_{298.1}=20.9\pm0.2$, with only 0.013 extrapolation below 10°.

Wagner (*404*) (20°–40°), in addition, has made a few determinations of the specific heat of $CaMg(SiO_3)_2$, diopside. The temperature range covered is too small to permit a reasonable entropy calculation.

Sulfates.—Anderson (*25*) (53°–298°) and Latimer, Hicks, and Schutz (*285*) (18°–302°) have measured the specific heat of $CaSO_4 \cdot 2H_2O$, selenite. The results are in good agreement and yield $S_{298.1}=46.4\pm0.2$, with 0.20 extrapolation below 17.78°.

Calcium sulfate hemihydrate, $CaSO_4 \cdot 1/2\ H_2O$, exists in two forms having different but definite thermal properties. A rather detailed study of these two materials and of three forms of anhydrous calcium sulfate has been made at the Pacific Experiment Station of the Bureau of Mines, and the results will be discussed at length elsewhere. For the present purpose macrocrystalline hemihydrate, obtained by dehydrating gypsum in the presence of liquid water, is designated as $CaSO_4 \cdot 1/2\ H_2O(\alpha)$. The ordinary variety, prepared by dehydrating under conditions where the water is gaseous, is microcrystalline and is designated as $CaSO_4 \cdot 1/2\ H_2O\ (\beta)$. The specific heat of both varieties was measured by the author (54°–295°), and Anderson (54°–298°) has measured the specific heat of a mixture of the two forms.

The values obtained for $CaSO_4 \cdot 1/2\ H_2O(\alpha)$ are $S_{53.1}=2.62$ (extrapolation) and $S_{298.1}-S_{53.1}=28.61$, making $S_{298.1}=31.2\pm0.6$.

For $CaSO_4 \cdot 1/2\ H_2O(\beta)$, $S_{53.1}=2.82$ (extrapolation), $S_{298.1}-S_{53.1}=29.26$, and $S_{298.1}=32.1\pm0.6$.

Anhydrous or nearly anhydrous $CaSO_4$ exists in three forms having different but definite thermal properties. The variety obtained by heating gypsum or hemihydrate to temperatures around 900° C. is distinguishable by its low solubility in water and is designated here by the symbol $CaSO_4$ (insol.). The other two varieties are obtained by low-temperature dehydration of the two forms of hemihydrate mentioned above. Both are several times as soluble in water as $CaSO_4$ (insol.), and they have different heats of solution and hydration. These forms are symbolized by $CaSO_4$ (sol. α) and $CaSO_4$ (sol. β), the α and β corresponding to the hemihydrates from which they are formed.

Anderson (*25*) (54°–298°) has studied the specific heat of $CaSO_4$ (insol.). His data yield $S_{298.1}=25.5\pm0.4$, of which 1.50 is extrapolation below 50.1°. The entropy of this substance may be approximated from the data of Kamiike (*220*), who obtained $\Delta S_{298.1}=11.1$ for the reaction $CaSO_4 \cdot 2H_2O = CaSO_4$ (insol.) $+ 2H_2O\ (l)$. This figure corresponds to $S_{298.1}=24.0\pm2.0$ for $CaSO_4$ (insol.). No weight is given this result in comparison with the figure from Anderson's work.

The author has made specific-heat measurements of the other two forms. Although some small differences are apparent in the specific heats compensation occurs, and these two forms, $CaSO_4$ (sol. α) and $CaSO_4$ (sol. β), have virtually the same entropies. The results obtained are $S_{298.1}=25.9\pm0.3$ for $CaSO_4$ (sol. α), of which 1.76 is extrapolation below 53.1° and $S_{298.1}=25.9\pm0.3$ for $CaSO_4$ (sol. β), of which 1.57 is extrapolation below 53.1°.

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CARBON

Element.—The specific heat of graphite was measured by Jacobs and Parks (*210*) (93°–294°) and Nernst (*325*) (28°–284°). Relying on the work of Jacobs and Parks, there is obtained $S_{298.1}=1.36\pm0.03$ for C (graphite). The extrapolation below 89.12° is 0.168.

Nernst (*325*) (86°–220°), Pitzer (*337*) (70°–288°), and Robertson, Fox, and Martin (*346*) (92°–327°) have measured the specific heat of diamond. Pitzer's data yield $S_{298.1}=0.585\pm0.005$. The extrapolation below 70.8° is 0.008.

In obtaining the entropy of C (*g*) at 298.1° three states must be considered—$^3P_0$, $^3P_1$, and $^3P_2$ (*273, p. 2345*). These states have the term values 0, 14.8, and 42.3 and quantum weights 1, 3, and 5, respectively. They result in the addition of 4.361 to the Sackur equation to obtain $S_{2981.}=37.77\pm0.01$ for C (*g*).

Allen and Longair (*6*) have given $I=16.8\times10^{-40}$ and $\omega=1{,}642$ for the C_2 (*g*) molecule. These figures are not for the lowest energy state, but in this instance the difference probably is small. The computed entropy is $S_{298.1}=47.89$, the assumption being made that the quantum weight of the lowest energy state is 3. Because of the possibility of this assumption being wrong, no estimate of error is given.

Monoxide.—The specific heat of solid and liquid CO was measured by Clayton and Giauque (*74, 75*) (14°–85°), Clusius (*76*) (11°–82°), Eucken (*136*) (17°–78°), and Kaischew (*219*) (54–76°). Clayton and Giauque also have calculated the entropy from spectroscopic data. Their results are adopted, namely, $S_{11.70}=0.46$ (extrapolation), $S_{61.55}-S_{11.70}=9.63$ (crystals II), $\Delta S_{61.55}=151.3/61.55=2.46$ (transition), $S_{68.09}-S_{61.55}=1.23$ (crystals I), $\Delta S_{68.09}=199.7/68.09=2.93$ (fusion), $S_{81.61}-S_{68.09}=2.61$ (liquid), $\Delta S_{81.61}=1{,}443.6/81.61=17.69$ (vaporization), $\Delta S_{81.61}=0.21$ (correction for gas imperfection), and $S_{298.1}-S_{81.61}=9.00$ (gas). These figures add to give $S_{298.1}=46.22$. The result from spectroscopic data is $S_{298.1}=47.32$. The difference of 1.1 unit, which is of the order of $R\ ln\ 2$, is attributed to random orientation of the molecules in the crystal lattice of solid CO. The spectroscopic value, which can be in error by only a negligible amount, is adopted. This result has been checked by Gordon and Barnes (*182*), who found $S_{298.1}=47.32$, and by the author, using the data given by Stuart (*390*), $I=15.0\times10^{-40}$ and $\omega=2{,}162$, in conjunction with the Sackur-Tetrode equation. The latter calculation gives $S_{298.1}=47.31\pm0.01$, the vibrational portion being negligible.

Dioxide.—The specific heat of CO_2 at low temperatures was measured by Eucken (*136*) (19°–201°), Eucken and Hauck (*137*) (80°–320°), and Giauque and Egan (*164*) (15°–190°). Giauque and Egan determined accurately the heat of sublimation, lack of knowledge of which for several years has hindered accurate calculation of the entropy from heat-capacity data. The present calculation is based entirely upon the work of Giauque and Egan. There is computed $S_{14.96}=0.19$ (extrapolation), $S_{194.67}-S_{14.96}=16.33$ (crystals), $\Delta S_{194.67}=6{,}030/194.67=30.98$ (sublimation), $\Delta S_{194.67}=0.09$ (correction to the perfect gas state), and $S_{298.1}-S_{194.67}=3.52$ (gas). The sum of these quantities is $S_{298.1}=51.11\pm0.1$.

Giauque and Egan have computed $S_{t+r,298.1}=40.34$ and $S_{v,298.1}=0.73$, making $S_{298.1}=51.07$, from molecular constants. Virtually the same result was reported by the author (*258*), $S_{298.1}=51.08$, calculated

from $I=70.4\times10^{-40}$, $\omega_1=1{,}321.7$ (1), $\omega_2=667.9$ (2), and $\omega_3=2{,}362.8$ (1). Also, Badger and Woo (*35*) have reported $S_{298.1}=51.07$; Gordon (*178*), $S_{298.1}=51.1$; Gordon and Barnes (*182*), $S_{300}=51.19$, which corresponds to $S_{298.1}=51.13$; Kassel (*224*), $S_{300}=51.14$, which corresponds to $S_{298.1}=51.08$; and Rodebush (*349*), $S_{298.1}=51.0$. The value $S_{298.1}=51.08\pm0.01$ is adopted.

Monosulfide.—From the moment of inertia, $I=33.88\times10^{-40}$, vibration frequency, $\omega=1{,}276$, and assignment of 1 as the quantum weight of the lowest energy state of the CS (*g*) molecule (*273, p. 2351*), there are computed $S_{t+r,298.1}=50.28$, $S_{v,298.1}=0.03$, and $S_{298.1}=50.3\pm0.2$.

Disulfide.—Brown and Manov (*58*) (15°–298°) measured the specific heat of CS_2. Calculation yields $S_{14.96}=0.64$ (extrapolation), $S_{161.1}-S_{14.96}=17.92$ (crystals), $\Delta S_{161.1}=1{,}049/161.1=6.51$ (fusion), and $S_{298.1}-S_{161.1}=11.09$ (liquid). The sum is $S_{298.1}=36.2\pm0.3$ for CS_2 (*l*). The heat and free energy of vaporization of CS_2 (*l*) are $\Delta H_{298.1}=6{,}682$ and $\Delta F°_{298.1}=441$ (*250*), giving $\Delta S_{298.1}=20.9$. Consequently, $S_{298.1}=57.1\pm0.5$ for CS_2 (*g*).

Stuart (*390*) records $I=260\times10^{-40}$, $\omega_1=665$ (1), $\omega_2=396.8$ (2), and $\omega_3=1{,}523$ (1) for the linear CS_2 (*g*) molecule. From these figures $S_{t+r,298.1}=54.58$ and $S_{v,298.1}=2.34$, making $S_{298.1}=56.9\pm0.3$. Cross and Brockway (*112*) and Cross (*111*) also have considered this substance. They find $S_{298.1}=56.84\pm0.3$ from slightly different molecular constants. The last figure is adopted for CS_2 (*g*), and the result from heat capacities is adopted for CS_2 (*l*).

Carbonyl sulfide.—Kemp and Giauque (*259*) (15°–223°) have investigated the specific heat of solid and liquid COS and have measured the heat of vaporization. Their calculations give $S_{15.0}=0.55$ (extrapolation), $S_{134.31}-S_{15.0}=14.96$ (crystals), $\Delta S_{134.31}=1129.8/134.31=8.41$ (fusion), $S_{222.87}-S_{134.31}=8.66$ (liquid), $\Delta S_{222.87}=4{,}423/222.87=19.85$ (vaporization), $\Delta S_{222.87}=0.13$ (correction to perfect gas state), and $S_{298.1}-S_{222.87}=2.71$ (gas). These figures add to give $S_{298.1}=55.27\pm0.1$. All calculations have been checked by the author.

Kemp and Giauque also have computed $S_{298.1}=55.37$, of which $S_{v,298.1}=1.39$, from the molecular constants $I=137\times10^{-40}$, $\omega_1=859.2$ (1), $\omega_2=521.5$ (2), and $\omega_3=2{,}050.5$ (1). Cross and Brockway (*112*) and Cross (*111*), using constants only slightly different, obtained $S_{298.1}=55.34$ in substantial agreement. The value $S_{298.1}=55.37\pm0.1$ is adopted for COS (*g*).

Tetrabromide.—Stevenson and Beach (*387, 388*) give 123 (2), 265 (1), 183 (3), and 667 (3) as the vibration frequencies of the CBr_4 (*g*) molecule and 1.91×10^{-8} cm. as the C–Br distance. The last figure yields $I_1=I_2=I_3=1{,}320\times10^{-40}$. There is computed $S_{t+r,298.1}=69.90$, $S_{v,298.1}=15.60$, and $S_{298.1}=85.5\pm1.0$.

Tetrachloride.—Yost and Blair (*411*) have computed $S_{298.1}=74.3$ for CCl_4 (*g*). Later figures given by Yost (*409*), 1.755×10^{-8} cm., C–Cl distance and 214 (2), 311 (3), 450 (1), and 775 (3), vibration frequencies result in $I=480\times10^{-40}$. Therefore, $S_{t+r,298.1}=64.60$ and $S_{v,298.1}=9.62$, making $S_{298.1}=74.2\pm0.5$.

Lord and Blanchard (*300*) have reported some new specific-heat data of Blanchard and Blue and of Stull for CCl_4 and have calculated the entropy from the better data available. They find $S_{10}=0.25$ (extrapolation), $S_{85}-S_{10}+S_{225.4}-S_{85}=36.29$ (crystals II, based upon the measurements of Blanchard and Blue and of Stull, respectively),

$\Delta S_{225.4}=1{,}080.8/225.4=4.79$ (transition, based upon the measurement of Johnston and Long (*216*)), $S_{250.2}-S_{225.4}=3.08$ (crystals I, based upon Stull's measurements), $\Delta S_{250.2}=577.2/250.2=2.31$ (fusion, from Johnston and Long's data), and $S_{298.1}-S_{250.2}=5.45$ (liquid, from Stull's data). The sum is $S_{298.1}=52.2\pm0.3$ for CCl_4 (l). The entropy of vaporization at 298.1° and 114.5 mm. pressure is taken as 25.94 and the entropy of compression to 1 atmosphere as −3.76. Thus, from heat-capacity data, $S_{298.1}=74.35$ for CCl_4 (g), in excellent agreement with the value obtained from molecular constants. It should be recorded in addition that Lord and Blanchard also computed $S_{298.1}=74.05$ for CCl_4 (g) and that Latimer (*276*) (39°–290°) has measured the specific heat of the condensed phases.

The values selected here are $S_{298.1}=52.2\pm0.3$ for CCl_4 (l) and $S_{298.1}=74.2\pm0.5$ for CCl_4 (g).

Tetrafluoride.—The specific heat of CF_4 was measured by Eucken and Schröder (*140*) (12°–145°), who also determined the heats of transition, fusion, and vaporization. A recalculation of their results yields $S_{11.9}=0.70$ (extrapolation), $S_{76.23}-S_{11.9}=15.62$ (crystals II), $\Delta S_{76.23}=353.2/76.23=4.63$ (transition), $S_{89.47}-S_{76.23}=2.59$ (crystals I), $\Delta S_{89.47}=167.4/89.47=1.87$ (fusion), $S_{122}-S_{89.47}=5.76$ (liquid), $\Delta S_{122}=3{,}120/122=25.57$ (vaporization at 0.1365 atmosphere), and $\Delta S_{122}=-3.96$ (compression from 0.1365 to 1 atmosphere). From vibration frequencies given below C_p (g) was computed at several temperatures and $S_{298.1}-S_{122}=10.02$ (gas) computed graphically. The total is $S_{298.1}=62.8\pm0.5$ for CF_4 (g).

Yost (*409*) has reported 1.36×10^{-8} cm. as the C–F distance and 437 (2), 635 (3), 904 (1), and 1,350 (3) as the vibration frequencies of the CF_4 (g) molecule. From the first figure $I_1=I_2=I_3=155\times10^{-40}$. There are computed $S_{t+r,298.1}=59.57$ and $S_{v,298.1}=3.11$, making $S_{298.1}=62.7\pm0.5$, in excellent agreement with the value from heat capacities.

Carbonyl chloride.—Stevenson and Beach (*387*, *388*) have reported 1.68×10^{-8} cm. as the C–Cl distance, 1.28×10^{-8} cm. as the C–O distance, and 117° as the Cl–C–Cl angle in the $COCl_2$ (g) molecule. These figures yield $I_1=340\times10^{-40}$, $I_2=240\times10^{-40}$, and $I_3=100\times10^{-40}$. The symmetry number is 2. Consequently, there is obtained $S_{t+r,298.1}=64.30$. Stevenson and Beach's frequency assignment is 302 (1), 442 (1), 573 (1), 832 (1), and 1,807 (1), which results in $S_{v,298.1}=2.93$. The sum is $S_{298.1}=67.2\pm1.0$. It should be noted that one vibration frequency is unknown and is omitted from consideration in the above calculation, which explains the relatively high estimate of error.

Methane.—Specific-heat data for CH_4 have been reported by Clusius (*76*) (10°–106°), Clusius and Perlich (*99*) (10°–80°), Eucken and Veith (*142*) (10°–80°), Eucken and Karwat (*139*) (28°–109°), and Frank and Clusius (*147*, *148*) (15°–26°). Additional information concerning the transition and fusion was given by Clusius, Popp, and Frank (*104*) and Kruis, Popp, and Clusius (*266*).

Previous calculations by the author (*245*) gave $S_{10}=0.31$ (extrapolation), $\Delta S_{20.4}=0.89$ (for the extra heat capacity at the "hump"), $S_{90.6}-S_{10}=12.43$ (crystals less extra heat capacity at the hump), $\Delta S_{90.6}=224.0/90.6=2.47$ (fusion), $S_{111.7}-S_{90.6}=2.70$ (liquid), $\Delta S_{111.7}=1{,}988/111.7=17.80$ (vaporization), from the vapor-pressure data of

Stock, Henning, and Kuss (*389*)), and $S_{298.1}-S_{111.7}=7.91$ (gas). The sum is $S_{298.1}=44.51\pm0.2$.

A later calculation of Frank and Clusius (*147*) yields $S_{90.6}=13.66$ (crystals), $\Delta S_{90.6}=2.47$ (fusion), $S_{99.54}-S_{90.6}=1.21$ (liquid), $\Delta S_{99.54}=20.45$ (vaporization at 246.13 mm. pressure), $\Delta S_{99.54}=-2.24$ (compression from 246.13 mm. to 1 atmosphere pressure), and $\Delta S_{99.54}=0.08$ (correction to perfect gas state). To bring the gas to 298.1° requires an entropy increment of $S_{298.1}-S_{99.54}=8.83$ (gas). The sum is $S_{298.1}=44.46\pm0.2$, virtually identical with the author's calculation.

From the values (*273, p. 2359*) $I_1=I_2=I_3=5.267\times10^{-40}$, $\omega_1=1{,}305$ (3), $\omega_2=1{,}520$ (2), $\omega_3=2{,}915$ (1), $\omega_4=3{,}020$ (3), and symmetry number=12, there are computed $S_{t+r,298.1}=44.42$ and $S_{v,298.1}=0.10$, making $S_{298.1}=44.52\pm0.1$.

Giauque, Blue, and Overstreet (*175*) have given $S_{t+r,298.1}=44.35$ and MacDougall (*301*), $S_{298.1}=44.46$.

The value $S_{298.1}=44.5\pm0.1$ is adopted for CH_4 (*g*).

Neutral CN.—Zeise (*417*) has computed $S_{298.1}=48.42\pm0.01$ for neutral CN (*g*) as a result of spectroscopic data. This value may be checked, using the following values (*273, p. 2351*), $I_1=14.63\times10^{-40}$, $\omega=2{,}056$, and quantum weight=2 for the lowest energy state. The result is $S_{298.1}=48.41$ of which $S_{v,298.1}=0.001$.

Cyanogen.—Ruehrwein and Giauque (*355*) (14°–252°) have measured the heat capacity of C_2N_2. Their calculations, the sum of which has been checked to 0.05 unit, are as follows: $S_{15}=0.31$ (extrapolation), $S_{245.27}-S_{15}=24.30$ (crystals), $\Delta S_{245.27}=1{,}938/245.27=7.90$ (fusion), $S_{251.95}-S_{245.27}=0.68$ (liquid), $\Delta S_{251.95}=5{,}576/251.95=22.13$ (vaporization), $\Delta S_{251.95}=0.11$ (correction to the perfect gas state), and $S_{298.1}-S_{251.95}=2.21$ (gas). The sum is $S_{298.1}=57.64$.

The C_2N_2 (*g*) molecule is linear, and Ruehrwein and Giauque use $I=176\times10^{-40}$, $\omega_1=230$ (2), $\omega_2=512$ (2), $\omega_3=860$ (1), $\omega_4=2{,}150$ (1) and $\omega_5=2{,}336$ (1). These figures yield $S_{298.1}=57.88$, of which $S_{v,298.1}=5.22$. Agreeing values have been calculated by Stevenson (*386*), $S_{298.1}=57.90$, and McMorris and Badger (*310*), $S_{298.1}=57.8$. The value $S_{298.1}=57.9\pm0.1$ is adopted.

Cyanogen bromide.—Stevenson (*386*) has given $I=200\times10^{-40}$, $\omega_1=368$ (2), $\omega_2=580$ (1), and $\omega_3=2{,}187$ (1) for the CNBr (*g*) molecule. These figures give $S_{t+r,298.1}=56.42$ and $S_{v,298.1}=2.68$, making $S_{298.1}=59.1\pm0.5$. Stevenson's calculation for this substance and for CNCl (*g*) and CNI (*g*) apparently are in error.

Cyanogen chloride.—From Stevenson's (*386*) $I=142\times10^{-40}$, $\omega_1=397$ (2), $\omega_2=729$ (1), and $\omega_3=2{,}201$ (1), there are obtained $S_{t+r,298.1}=54.12$ and $S_{v,298.1}=2.23$, making $S_{298.1}=56.4\pm0.5$ for CNCl (*g*).

Cyanogen iodide.—Stevenson (*386*) also has recorded $I=249\times10^{-40}$, $\omega_1=321$ (2), $\omega_2=470$ (1), and $\omega_3=2{,}158$ (1) for the CNI (*g*) molecule. There is computed $S_{298.1}=61.3\pm0.5$, of which $S_{v,298.1}=3.36$.

Carbonate ion.—From data on the reaction $HCO_3^-=H^++CO_3^{--}$, Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=-13.0\pm1.0$ for CO_3^{--} (*aq.*).

Bicarbonate ion.—Latimer, Pitzer, and Smith (*286*) also report $S_{298.1}=22.2\pm0.8$ for HCO_3^- (*aq.*) from data for the reaction $H_2CO_3=H^++HCO_3^-$.

Carbonic acid.—The value, $S_{298.1}=45.1\pm0.7$, for H_2CO_3 (*aq.*) is reported by Latimer, Pitzer, and Smith (*286*) from data for the reaction CO_2 (*g*)$+H_2O$ (*l*)$=H_2CO_3$ (*aq.*).

Cyanide ion.—From data for the reaction HCN (*g*)$=H^+ + CN^-$, Latimer, Pitzer, and Smith (*286*) obtained $S_{298.1}=25\pm5$ for CN^- (*aq.*).

Oxalate ion.—Data for the reaction $CaC_2O_4\cdot H_2O=Ca^{++}+C_2O_4^{--}+H_2O$ yield $S_{298.1}=9.6\pm1.0$, according to Latimer, Pitzer, and Smith (*286*).

CERIUM

Element.—Lewis and Gibson (*292*) have computed the entropy of Ce from Dewar's (*117*) value of the mean specific heat between 20° and 77°. Their method consisted essentially of dividing Dewar's result by 1.085 and then computing θ_D for a Debye function. They obtain $S_{298.1}=13.8$, in which the error may be as much as ±0.8 unit. No other specific-heat data at low temperatures for Ce are available except those of Simon and Ruhemann (*372*) (71°–72°) on an impure sample. The specific heat at this temperature is too high (6.14) for obtaining θ_D.

From Karlson's (*223*) tabulation of energy levels and assignment of the quantum number "*j*" values, it is calculated that entropy of Ce (*g*) at 298.1° is that given by the Sackur equation plus 7.37. The result is $S_{298.1}=48.1\pm0.1$.

CESIUM

Element.—The entropy of Cs (*g*) calculated from the Sackur equation with *R ln* 2 added is $S_{298.1}=41.95\pm0.01$.

The entropy of sublimation of Cs has been computed from vapor-pressure and heat-capacity data at high temperatures (*247*) as $\Delta S_{298.1}=22.13$. This value and that for Cs (*g*) leads to the estimate $S_{298.1}=19.8\pm1.0$ for Cs (*s*).

Cesium ion.—From data for the reaction $CsClO_4=Cs^+ + ClO_4^-$, Latimer, Pitzer, and Smith (*286*) compute $S_{298.1}=31.8\pm0.6$ for Cs^+ (*aq.*).

Halides.—Niwa (*331*) has estimated $S_{298.1}=58.9\pm2.0$ for CsCl (*g*) and $S_{298.1}=63.8\pm1.7$ for CsBr (*g*) from vapor-pressure data for the solids and assumed entropies of the solids.

Perchlorate.—Pitzer, Smith and Latimer (*340*) (15°–298°) have measured the specific heat of $CsClO_4$. There are computed $S_{15.0}=0.82$ (extrapolation) and $S_{298.1}-S_{15.0}=41.07$, making $S_{298.1}=41.9\pm0.2$.

Cesium-aluminum sulfate.—The specific heat of $CsAl(SO_4)_2\cdot12\ H_2O$ was measured by Latimer and Greensfelder (*282*) (18°–298°). The calculation of the entropy results in $S_{298.1}=163\pm5$. The extrapolation below 17.78° is 3.00.

CHLORINE

Element.—The specific heat of Cl_2 was measured by Eucken and Karwat (*139*) (21°–197°) and Giauque and Powell (*168*) (14°–240°). Relying on the work of the latter investigators, whose calculations have been checked and are repeated here, there are obtained $S_{15.0}=0.33$ (extrapolation), $S_{172.12}-S_{15.0}=16.57$ (crystals), $\Delta S_{172.12}=1{,}531/172.12=8.89$ (fusion), $S_{239.05}-S_{172.12}=5.23$ (liquid), $\Delta S_{239.05}=4{,}878/239.05=20.41$ (vaporization), $\Delta S_{239.05}=0.12$ (correction to

perfect gas state), and $S_{298.1}-S_{239.05}=1.76$ (gas). The sum is $S_{298.1}=53.31\pm0.1$.

As an independent method of obtaining the entropy one may use the data of Gerke (*154*), who, by means of measurements on cells, obtained $\Delta S_{298.1}=-13.7$ for the reaction $Ag+1/2Cl_2=AgCl$. This result and the entropies of Ag (10.2 ± 0.05) and AgCl (23.0 ± 0.1) lead to $S_{298.1}=53.0\pm0.4$ for Cl_2 (*g*).

Giauque and Overstreet (*167*) have computed the entropy of Cl_2 (*g*) from spectroscopic data. They find $S_{298.1}=53.24$ for $Cl_2^{35,35}$, $S_{298.1}=53.39$ for $Cl_2^{35,37}$, $S_{298.1}=53.54$ for $Cl_2^{37,37}$, and $S_{298.1}=53.31$ for the ordinary mixture of isotopes. Gordon and Barnes (*183*) have obtained a higher result, but the calculation of Giauque and Overstreet may be checked by means of the values (*273, p. 2353*) $I=113.9\times10^{-40}$, $\omega=561$ (1), and symmetry number=2. There is obtained $S_{298.1}=53.26$, of which $S_{v,298.1}=0.53$. The value $S_{298.1}=53.31\pm0.01$ is adopted for Cl_2 (*g*).

The entropy of monatomic Cl (*g*) may be obtained from the Sackur equation and spectroscopic data. At 298.1° only two energy levels need be considered, the $^2P_{3/2}$ and $^2P_{1/2}$, having a separation of 881 cm.$^{-1}$ (*273, p. 2381*) and quantum weights of 4 and 2, respectively. The entropy associated with these states is 2.831 units, and the translational entropy is $S_{t,298.1}=36.636$. The sum is $S_{298.1}=39.47\pm0.01$ for Cl (*g*).

Chloride ion.—From data for the reactions $HCl\ (g)=H^++Cl^-$ and $AgCl+1/2H_2=H^++Cl^-+Ag$, Latimer, Pitzer, and Smith (*286*) obtain, respectively, 13.52 ± 0.15 and 13.49 ± 0.15 as values of the entropy of Cl^- (*aq.*). The value $S_{298.1}=13.5\pm0.1$ is adopted. This figure has been checked by Rossini (*351*) who obtained $S_{298.1}=13.40\pm0.15$ for HCl (*aq.*) at hypothetical 1 molal concentration. Since by convention $S_{298.1}=0$ for H^+ (*aq.*) it follows that 13.40 ± 0.15 is also the entropy of Cl^- (*aq.*).

Monoxide.—Yost and Felt (*413*) obtained $\Delta F°_{298.1}=21{,}207$ and $\Delta H_{298.1}=18{,}260$ for the formation of Cl_2O (*g*) from the elements. The entropy of formation is, therefore, $\Delta S_{298.1}=-9.89$. This figure and the entropies of Cl_2 and O_2 lead to $S_{298.1}=67.4$ for Cl_2O (*g*).

Sutherland and Penney (*393*) have reported Cl–O distance=1.71×10^{-8} cm., Cl–O–Cl angle=110°, $\omega_1=320$ (1), $\omega_2=680$ (1), and $\omega_3=973$ (1) for Cl_2O (*g*). There are computed $I_1=250\times10^{-40}$, $I_2=230\times10^{-40}$, and $I_3=20.7\times10^{-40}$, which in turn give $S_{t+r,298.1}=61.95$. The computed vibrational entropy is $S_{v,298.1}=1.75$. The sum $S_{298.1}=63.7\pm0.5$ for Cl_2O (*g*) is adopted.

Dioxide.—Brockway (*53*) has reported 1.53×10^{-8} cm. as the Cl–O distance and 137° as the O–Cl–O angle in the ClO_2 (*g*) molecule. These figures lead to $I_1=115\times10^{-40}$, $I_2=106\times10^{-40}$, and $I_3=8.7\times10^{-40}$ and to $S_{t+r,298.1}=58.80$. According to Ku (*267*) the vibration frequencies are 529 (1), 954 (1) and 1,105 (1), giving $S_{v,298.1}=0.77$. The sum is $S_{298.1}=59.6\pm0.5$ for ClO_2 (*g*).

Hypochlorite ion.—Latimer, Pitzer, and Smith (*286*) obtain $S_{298.1}=10.0\pm2.0$ for ClO^- (*aq.*) from data for the reaction $Cl_2\ (g)+2OH^-=H_2O\ (1)+Cl^-+ClO^-$.

Chlorite ion.—Latimer, Pitzer, and Smith (*286*) also report $S_{298.1}=24.1\pm0.5$ for ClO_2^- (*aq.*) obtained from data for the reaction $AgClO_2=Ag^++ClO_2^-$.

Chlorate ion.—The value $S_{298.1}=39.4\pm0.5$ for ClO_3^- (*aq.*) was reported by Latimer, Pitzer, and Smith (*286*). Data for the reaction $KClO_3=K^+ + ClO_3^-$ formed the basis of their calculation.

Perchlorate ion.—In addition, Latimer, Pitzer, and Smith (*286*) have given $S_{298.1}=43.6\pm0.5$ for ClO_4^- (*aq.*), based upon data for the reaction $KClO_4=K^+ + ClO_4^-$.

CHROMIUM

Element.—The specific heat of Cr was measured by Anderson (*23*) (56°–292°) and Simon and Ruhemann (*372*) (71°–79°). The data of the former give $S_{298.1}=5.68\pm0.07$, of which 0.22 is extrapolation below 56.2°.

The spectroscopic data on Cr (*g*) show that all but a negligible fraction of atoms are in the lowest energy state, $^7S_3$, at 298.1° (*273, p. 2347*). The entropy may be computed, therefore, by adding $R\ ln\ 7$ to the Sackur equation. The result is $S_{298.1}=41.64\pm0.01$.

Oxide.—Anderson (*23*) (56°–335°) has measured the specific heat of Cr_2O_3. His data yield $S_{56.2}=0.53$ (extrapolation), $S_{298.1}-S_{56.2}=18.88$ (measured), and $S_{298.1}=19.4\pm0.3$.

Dichloride.—The specific heat of $CrCl_2$ was measured by Anderson (*23*) (43°–297°). Recalculation of his data gives $S_{298.1}=27.7\pm0.7$, of which 5.05 is extrapolation below 44.7°. On the other hand, Doerner (*122*), from equilibrium studies at elevated temperatures of the reaction $CrCl_2+H_2=Cr+2HCl$, obtained $S_{298.1}=29.7$. The latter value depends on an assumed specific-heat equation for $CrCl_2$ (*s*) employed in extrapolating the high temperature results to 298.1°. C. G. Maier, Metallurgical Division, Bureau of Mines, has recalculated Doerner's data in the preparation of a forthcoming bulletin dealing with chromium. He obtained $S_{298.1}=27.3$, using a different, but at least equally reasonable, specific-heat relationship for $CrCl_2$ (*s*). Evidently any apparent discrepancy is within the limits of error in the assumptions involved in computing the result based upon the equilibrium data. The value from specific-heat data, $S_{298.1}=27.7\pm0.7$, is adopted.

Trichloride.—Anderson (*23*) (54°–297°) and Trapeznikova, Shubnikov, and Miljutin (*401*) (12°–130°) have measured the specific heat of $CrCl_3$. Unfortunately, the two sets of data are in bad disagreement over their common temperature range. The reason for this is not apparent unless it can be attributed to lack of purity of the material studied by the latter investigators. Really pure $CrCl_3$ may be obtained and maintained only by exercising extreme care.

The lack of agreement between the two sets of specific-heat data, coupled with the fact that Trapeznikova, Shubnikov, and Miljutin found an anomalous region just below 20°, creates a difficult situation. Anderson's data alone give $S_{298.1}=27.3$, of which 3.19 is extrapolation below 56.2°. If allowance is made for a specific-heat maximum below 20°, by constructing a curve resembling that of Trapeznikova, Shubnikov, and Miljutin, then about 1.3 must be added to both the extrapolated portion and to the entropy at 298.1°, making $S_{298.1}=28.6$. However, the procedure that will be followed here is to accept the value from Anderson's measurements without this allowance and to add $R\ ln\ 4=2.75$, corresponding to the splitting of the lowest-energy state of Cr^{+++} which is designated $^4F_{3/2}$ (quantum weight=4) by

Bowen (*51*). This procedure leads to $S_{298.1}=30.0\pm1.5$, in which the large allowance for error appears necessary because of doubt concerning the maximum near 20°. Doerner (*122*), from rather meager indirect equilibrium data for the reaction $2CrCl_3=2CrCl_2+Cl_2$, computed $S_{298.1}=31.0$ for $CrCl_3$. However, Maier's before-mentioned recalculations show that values in the range 28.2 to 31.0 may be obtained from these data, depending on the judgment of the calculator. For the present, the value $S_{298.1}=30.0\pm1.5$ is adopted.

Chromate ion.—Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=10.5\pm1.0$ for CrO_4^{--} (*aq.*) from data for the reaction $Ag_2CrO_4=2Ag^+ + CrO_4^{--}$.

COBALT

Element.—The specific heat of Co was measured by Duyckaerts (*124*) (2°–18°) and Simon and Ruhemann (*372*) (71°–72°). Duyckaerts' specific-heat values are all below 0.06 calorie per gram atom and are not usable for the present purpose. The data of Simon and Ruhemann give $\theta_D=383$, from which $S_{298.1}=6.8\pm0.2$.

The spectroscopic data (*273, p. 2348*) for Co (*g*) show that the states $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, and $^4F_{3/2}$ must be considered in obtaining $S_{298.1}$. The quantum weights of these are 10, 8, 6, and 4, and the term values are 0, 816, 1,407, and 1,809 cm.$^{-1}$, respectively. Calculation results in the addition of 4.74 to the Sackur equation, making $S_{298.1}=42.89\pm0.01$ for Co (*g*).

Chloride.—Trapeznikova, Shubnikov, and Miljutin (*401*) (13°–131°) have measured the specific heat of $CoCl_2$. Their data yield $S_{298.1}=25.4\pm1.0$, of which 0.23 is extrapolation below 13.3°.

COLUMBIUM

Element.—Data are not available for obtaining the entropy of solid Cb. However, the entropy of Cb (*g*) may be obtained from spectroscopic data (*31*) and the Sackur equation. The states to be considered are $^6D_{1/2}$, $^6D_{3/2}$, $^6D_{5/2}$, and $^6D_{9/2}$, with quantum weights 2, 4, 6, 8, and 10 and term values 0, 154.3, 392, 695, and 1,050 cm.$^{-1}$, respectively. The result is that 4.955 must be added to the value given by the Sackur equation, making $S_{298.1}=44.46\pm0.01$.

COPPER

Element.—Several investigators have measured the specific heat of Cu—Dockerty (*120, 121*) (28°–299°), Eucken and Werth (*144*) (83°–216°), Keesom and Onnes (*241, 242*) (14°–90°), Kok and Keesom (*262*) (1°–20°), Maier and Anderson (*305*) (53°–295°), Meads (*313*) (14°–301°), and Nernst (*325, 328*) (23°–88°). A recalculation of the entropy, using all the available data, gives $S_{298.1}=7.97\pm0.05$. The extrapolation is negligible (<0.0001 below 1°).

The entropy of Cu (*g*) may be obtained from the Sackur equation with $R\ ln\ 2$ added to account for the quantum weight of the lowest energy state. The result is $S_{298.1}=39.75\pm0.01$. The calculation of Randall, Nielsen, and West (*344*) for this substance is in error.

Randall, Nielsen, and West (*344*) have estimated $S_{298.1}=58.9$ for Cu_2 (*g*). The probable error is not readily ascertained but may be quite large.

Cupric ion.—Latimer, Pitzer, and Smith (*286*) have obtained -25.9 ± 3 and -26.6 ± 1, respectively, as values of the entropy of Cu^{++} (*aq.*) from data for the reactions, $Cu+2H^+=Cu^{++}+H_2$ and $Cu+2Ag^+=Cu^{++}+2Ag$. Their selected value, $S_{298.1}=-26.5\pm1.0$, also is adopted here.

Oxides.—Millar (*318*) (75°–291°) has measured the specific heat of Cu_2O. The specific-heat curve for this substance is abnormally flat, making extrapolation quite uncertain. It is also evident that the entropy calculation of Millar is incorrect. There is calculated $S_{298.1}=24.1\pm1.5$, of which 7.85 is extrapolation below 70.8°.

Clusius and Harteck (*97*) (30°–200°) and Millar (*318*) (71°–302°) have measured the specific heat of CuO. The latter found a curious, nonreversible region centered around 220° on which more information would be desirable. From these data $S_{298.1}=10.4\pm0.2$, of which 0.13 is extrapolation below 28.2°.

Sulfides.—The specific heat of synthetic Cu_2S was measured by Anderson (*14*) (58°–293°). His data give $S_{298.1}=28.9\pm0.8$, of which 5.43 is extrapolation below 50.1°.

Anderson (*14*) (59°–295°) also measured the specific heat of CuS, covellite. The entropy is computed to be $S_{298.1}=15.9\pm0.4$, 2.56 being the extrapolation below 56.2°.

Cuprous bromide.—Ishikawa, Yamazaki, and Murooka (*209*) gave $\Delta F^\circ_{298.1}=-23{,}812$ and $\Delta H_{298.1}=-24{,}872$ for the reaction $Cu+1/2\ Br_2\ (l)=CuBr$, making $\Delta S_{298.1}=-3.56$. From the last figure and the entropies of Cu and Br_2 (*l*), $S_{298.1}=22.8\pm1.0$ is computed for CuBr.

The vibration frequency of CuBr (*g*) has been given as 313 cm.$^{-1}$ (*273, p. 2350*). If the interatomic distance is taken as 2.5×10^{-8} cm., then $I=365\times10^{-40}$. From these, $S_{t+r,298.1}=58.52$ and $S_{v,298.1}=1.35$, making $S_{298.1}=59.9\pm1.0$.

Cuprous chloride.—Watanabe (*405*) has considered the reaction $Cu+1/2\ Cl_2=CuCl$ and obtained $\Delta H_{298.1}=-32{,}605$ and $\Delta F^\circ_{298.1}=-28{,}487$. These figures make $\Delta S_{298.1}=-13.8$, which, with the entropies of Cu and Cl_2, leads to $S_{298.1}=20.8\pm1.0$ for CuCl.

The vibration frequency of CuCl (*g*) is 415 cm.$^{-1}$ (*273, p. 2350*). The interatomic distance is estimated as 2.4×10^{-8} cm., making $I=216\times10^{-40}$. These figures give $S_{298.1}=57.3\pm1.0$ of which 0.91 is vibrational entropy.

Cuprous fluoride.—CuF (*g*) is stated to have the vibration frequency 617 cm.$^{-1}$ (*273, p. 2350*). The interatomic distance is estimated as 2.1×10^{-8} cm., giving $I=106\times10^{-40}$. The resulting entropy is $S_{298.1}=54.9\pm1.0$, of which 0.44 is the vibrational contribution.

Cuprous iodide.—Simon (*368*) (16°–286°) has measured the specific heat of CuI. The entropy extrapolation below 15.8° is 0.50 and $S_{298.1}=23.1\pm0.3$.

Ishikawa, Yamazaki, and Murooka (*209*) gave $\Delta F^\circ_{298.1}=-16{,}658$ and $\Delta H_{298.1}=-16{,}065$ or $\Delta S_{298.1}=1.99$ for the reaction $Cu+1/2\ I_2\ (s)=CuI$. This value leads to $S_{298.1}=24.0\pm1.0$, in agreement with the more reliable result from specifi-heat measurements.

From the vibration frequency, 264 cm.$^{-1}$ (*273, p. 2350*), for CuI (*g*) and an estimate of the interatomic distance, 2.6×10^{-8} cm., there is computed $S_{298.1}=61.6\pm1.0$, of which 1.64 is the vibrational part.

Hydrides.—The values $I=3.542\times10^{-40}$ and $\omega=1{,}903$ have been given for CuH (*g*) (*273, p. 2350*). There is computed $S_{298.1}=46.9\pm0.1$, the vibrational portion being negligible.

For CuD (*g*), $I=6.93\times10^{-40}$ and $\omega=1{,}365$ have been reported (*273, p. 2350*). Therefore, $S_{298.1}=48.3\pm0.1$. The vibrational part is 0.02.

Carbonate.—From thermal data, the value $S_{298.1}=17.7$ was estimated for $CuCO_3$ by Kelley and Anderson (*258*). Although this value seems reasonable in magnitude, the error actually may be relatively large.

Sulfates.—From calculations of the author (*250*) already published, the following values were suggested: $S_{298.1}=25.3$ for $CuSO_4$, $S_{298.1}=34.1$ for $CuO\cdot CuSO_4$, $S_{298.1}=33.0$ for $CuSO_4\cdot H_2O$, $S_{298.1}=52.4$ for $CuSO_4\cdot 3H_2O$, and $S_{298.1}=70.2$ for $CuSO_4\cdot 5H_2O$. No attempt is made to estimate the accuracy of these figures.

FLUORINE

Element.—Murphy and Vance (*322*) have computed the entropy of F_2 (*g*) from $I=32.9\times10^{-40}$ and $\omega=856$. The result, which has been checked, is $S_{298.1}=48.58\pm0.1$. The vibrational portion is 0.17. Virtually the same result was obtained by Garner and Yost (*151*), $S_{298.1}=48.6$, from slightly different molecular constants.

In obtaining the entropy of monatomic F (*g*), two energy states are concerned at 298.1°, $^2P_{3/2}$ and $^2P_{1/2}$. These states are separated by 407 cm.$^{-1}$ (*273, p. 2348*) and have quantum weights of 4 and 2, respectively. Calculation gives 3.149 to be added to the Sackur equation. The result is $S_{298.1}=37.93\pm0.01$.

Fluoride ion.—Latimer, Pitzer, and Smith (*286*) have computed the entropy of F^- (*aq.*) from data for three reactions, HF (*g*)$=H^+ + F^-$, $BaF_2=Ba^{++}+2F^-$, and $CaF_2=Ca^{++}+2F^-$. The results, -2.4 ± 2, -0.4 ± 2, and -4.2 ± 2, respectively, are not in good agreement. The mean is $S_{298.1}=-2.3\pm2$.

Monoxide.—Stuart (*391*) has given 1.4×10^{-8} cm. and 2.22×10^{-8} cm., respectively, as the F–O and F–F distances in the F_2O (*g*) molecule and $105°\pm5°$ as the valence angle. From these figures, $I_1=90.6\times10^{-40}$, $I_2=77.2\times10^{-40}$, and $I_3=13.4\times10^{-40}$. $S_{t+r,298.1}=58.02$ is computed. The vibration frequencies reported by Sutherland and Penney (*393*) are 492 (1), 833 (1), and 1,110 (1), which make $S_{v,298.1}=0.93$. Therefore, $S_{298.1}=58.95\pm0.5$ for F_2O (*g*).

GADOLINIUM

Sulfate.—The specific heat of $Gd_2(SO_4)_3\cdot 8H_2O$ was measured by Ahlberg and Clark (*2*) (16°–297°), Clark and Keesom (*73*) (1°–21°), Giauque and Clark (*162*) (15°–289°), and Kürti (*268*) (1.5°–20°). The specific heat of this substance falls off in a normal manner to about 7°, then begins to rise, and near 1.6° reaches some 500 times the value that would correspond to a Debye extrapolation of the data in the region above 7°. This behavior is attributed to the splitting of the ground state, $^8S_{7/2}$, of the gadolinium ion into its eight components. Such splitting involves an entropy change of $R\ ln\ 8$ per gram-ion. Consequently, in computing the entropy, $2\ R\ ln\ 8$ per gram-formula mass of $Gd_2(SO_4)_3\cdot 8H_2O$ has been added to the usual type of extra-

polation below 7.08°. Thus, at 7.08° the entropy is 2 R *ln* 8+0.07 =8.33. Between 7.08° and 298.1° the entropy increment is 147.44. The entropy at 298.1° is therefore $S_{298.1}=155.8\pm0.4$.

GALLIUM

Element.—The specific heat of Ga was measured by Clusius and Harteck (*97*) (15°–200°). Unfortunately, the shrinking and flaking of their sample, owing to cooling and warming at low temperatures, caused poor thermal contact in their calorimeter and resulted in large heat-interchange corrections. The entropy is calculated as $S_{298.1}=10.2\pm0.5$, of which 0.13 is extrapolation below 14.1°.

The entropy of Ga (g) at 298.1° may be obtained from the Sackur equation and available spectroscopic data. Two energy states are to be considered, $^2P_{1/2}$ and $^2P_{3/2}$, separated by 826.3 cm^{-1} and having quantum weights 2 and 4, respectively (*273, p. 2345*). It is found that 1.738 is to be added to the Sackur value, making $S_{298.1}=40.39\pm0.01$ for Ga (g).

GERMANIUM

Element.—Cristescu and Simon (*108*) (10°–200°) have measured the specific heat of Ge. The entropy at 10° obtained by extrapolation is 0.03 and that between 10° and 298.1° is 10.05. Thus, $S_{298.1}=10.1\pm0.2$.

In obtaining the entropy of Ge (g) at 298.1° three states must be considered. These have term values 0, 557, and 1,410 and quantum weights 1, 3, and 5, respectively (*273, p. 2346*). The addition to the Sackur equation is 1.347, making $S_{298.1}=40.12\pm0.01$.

GOLD

Element.—Clusius and Harteck (*97*) (14°–213°) have measured the specific heat of Au. The entropy extrapolation of their measurements amounts to only 0.11 below 14.1°, and the entropy of Au is $S_{298.1}=11.4\pm0.1$.

The entropy of Au (g) calculated from the Sackur equation with R *ln* 2 added for the quantum weight 2 of the lowest energy state (*273, p. 2345*) is $S_{298.1}=43.13\pm0.01$.

Hydride.—For AuH (g), there have been reported $I=3.885\times10^{-40}$ and $\omega=2{,}260$ (*273, p. 2350*). These figures yield $S_{298.1}=50.5\pm0.1$, the vibrational portion being <0.001.

HAFNIUM

Element.—The specific heat of Hf was measured by Cristescu and Simon (*108*) (13°–210°). The results of the entropy calculations are $S_{12.59}=0.013$ (extrapolation), $S_{298.1}-S_{12.59}=13.06$, and $S_{298.1}=13.1\pm0.2$.

The entropy of Hf (g), obtained by adding R *ln* 5 (*31*) to the Sackur equation, is $S_{298.1}=44.65\pm0.01$.

HELIUM

Element.—For *He* (g), the Sackur equation results in $S_{298.1}=30.13\pm0.01$.

HYDROGEN

Element.—The heat capacity of H_2 has been measured by Bartholome and Eucken (*37*) (11°–24°), Eucken and Hiller (*138*) (89°–151°), Clusius and Hiller (*98*) (11°–19° and 83°–162°), Cornish and Eastman (*105*) (81°–373°), Eucken (*135, 136*) (17°–22° and 35°–274°), Keesom and Onnes (*244*) (11°–21°), Mendelssohn, Ruhemann, and Simon (*314*) (4°–11°), and Simon and Lange (*370*) (10°–19°).

Most of the pertinent data were reviewed by Giauque (*157*), who also calculated the entropy of H_2 (g) from spectroscopic data as $S_{298.1}=33.98\pm0.01$, which agrees with the values $S_{298.1}=34.0$, similarly calculated by Rodebush (*348*), and $S_{300}=34.00$, calculated by Gordon and Barnes (*182*). These values include nuclear spin and are not to be used in thermodynamic calculations in combination with other values in this bulletin. Ordinary hydrogen has been shown to be a mixture of symmetrical and antisymmetical molecules between which the rate of transition at low temperatures is so slow that specific-heat measurements, as ordinarily made, do not give the correct entropy when the third law is applied in the usual manner. Giauque has calculated the entropy of mixing from the equation, $\Delta S=-\sum_{i=1}^{n} N_i R \ ln \ N_i$, as $\Delta S=-1/4 \ R \ ln \ 1/4-9/12 \ R \ ln \ 1/12=4.39$ units. Subtracting this value from 33.98 gives 29.59, which is the figure that should result from ordinary heat-capacity measurements. Actually, in reviewing the low-temperature data on H_2, Giauque (*157*) obtained 29.74 or 29.64, depending on whether a Berthelot or van der Waal's gas was assumed in correcting to the ideal state.

The entropy items are $S_{13.95}=0.52$ (crystals), $\Delta S_{13.95}=28.0/13.95=2.01$ (fusion), $\Delta S_{13.95}=217.8/13.95=15.61$ (vaporization at 5.38 cm. pressure), $\Delta S_{13.95}=-5.26$ (compression from 5.38 cm. to 1 atmosphere pressure), $\Delta S_{13.95}=0.13$ (correction to perfect gas state, Berthelot) or $\Delta S_{13.95}=0.03$ (correction to perfect gas state, van der Waal), and $S_{298.1}-S_{13.95}=16.73$ (gas).

The value to be used in thermodynamic calculations in conjunction with other values in this bulletin is obtained by subtracting the nuclear spin contributions, $R \ ln \ 4=2.75$, from 33.98 which gives $S_{298.1}=31.23\pm0.01$ for H_2 (g).

Data pertaining to the entropy of HD (g) have been given by Clusius (*81*), Clusius and Bartholome (*82, 85, 88, 89*), Clusius, Popp, and Frank (*104*), and Johnston and Long (*217, 218*). Symmetrical and antisymmetrical molecules are not possible in HD (g). Clusius, Popp, and Frank (*104*) have computed the entropy from available heat-capacity data. They find $S_{16.60}=0.84$ (crystals), $\Delta S_{16.60}=38/16.60=2.29$ (fusion), $\Delta S_{16.60}=265/16.60=15.96$ (vaporization at 95 mm. pressure), $\Delta S_{16.60}=-4.13$ (compression from 95 mm. to 1 atmosphere pressure), $\Delta S_{16.60}=0.10$ (correction to ideal state), and $S_{298.1}-S_{16.60}=19.39$ (gas). The sum of these quantities is $S_{298.1}=34.45\pm0.15$. Johnston and Long (*217, 218*) report $S_{298.1}=37.95-3.56=34.39$, the first figure including nuclear spin, for which correction is made in the subtraction. From the moment of inertia $I=0.621\times10^{-40}$ (*88*) there may be computed $S_{298.1}=34.36$, as the vibrational entropy is virtually negligible. The value $S_{298.1}=34.39\pm0.1$ is adopted.

Data pertaining to the entropy of D_2 (g) were reported by Bartholome and Eucken (*37*), Clusius (*81*), Clusius and Bartholome (*83,*

84, 85, 86, 87, 88, 89, 90, 91, 92), Johnston and Long (*217, 218*), and Lewis and Hanson (*294*). Symmetrical and antisymmetrical molecules again are encountered in D_2 (*g*). Clusius and Bartholome (*90*) have considered the available heat-capacity data and have computed the entropy. They find $S_{12.0}=0.36$ (extrapolation), $S_{18.65}-S_{12.0}=0.75$ (crystals), $\Delta S_{18.65}=47.0/18.65=2.52$ (fusion), $S_{19.65}-S_{18.65}=0.26$ (liquid), $\Delta S_{19.65}=302.3/19.65=15.38$ (vaporization at 194.5 mm. pressure), $\Delta S_{19.65}=-2.71$ (compression from 194.5 mm. to 1 atmosphere pressure), $\Delta S_{19.65}=0.11$ (correction to ideal state), and $S_{298.1}-S_{19.65}=17.23$ (gas). The sum is $S_{298.1}=33.90$, which, however, is not to be used in thermodynamic calculations for the same reason as was given in the case of H_2 (*g*). The correction involved is $\Delta S=1/3\ R\ ln\ 3=0.72$, making $S_{298.1}=34.63$. Another way of obtaining virtually the same result is by subtracting the nuclear spin term, $R\ ln\ 9=4.365$, from Clusius and Bartholome's (*90*) spectroscopic calculation of total entropy, $S_{298.1}=38.984$. This procedure results in $S_{298.1}=34.62$. Johnston and Long (*217, 218*) have reported $S_{298.1}=38.73-4.37=34.36$ for this quantity. However, using the value $I=0.909\times10^{-40}$, corresponding to their molecular constant data, results in $S_{298.1}=34.59$, which must be too low, if anything. The value $S_{298.1}=34.62\pm0.1$ is adopted for D_2 (*g*).

The entropy of monatomic hydrogen gas H (*g*) is $S_{298.1}=27.40\pm0.01$. $R\ ln\ 2$ has been added to the Sackur equation, as the quantum weight of the lowest energy state is 2 (*273, p. 2345*) and no other states are concerned at 298.1°.

Hydrogen ion.—All the ionic entropies recorded are relative values based upon the definition $S_{298.1}=0$ for H^+ (*aq.*) in hypothetical 1 molal solution.

Water.—Low-temperature heat-capacity measurements of H_2O have been made by Barnes and Maass (*36*) (194°–271°), Giauque and Stout (*171*) (16°–268°), Nernst (*325*) (83°–266°), Pollitzer (*342*) (22°–263°), and Simon (*191*) (10°–373°). The results from the recent work of Giauque and Stout are adopted. They find $S_{10.0}=0.02$ (extrapolation), $S_{273.1}-S_{10.0}=9.08$ (crystals), $\Delta S_{273.1}=1{,}435.7/273.1=5.26$ (fusion), and $S_{298.1}-S_{273.1}=1.58$ (liquid). The sum is $S_{298.1}=15.94$, which differs but little from the value $S_{298.1}=15.88$ computed by the author (*245*) from the older data. This value is not the quantity to be used in thermodynamic calculations, however, but it must be corrected by adding $R\ ln\ 6/4=0.81$, according to Pauling (*336*) (see below). This makes $S_{298.1}=16.75\pm0.03$ for H_2O (*l*).

For H_2O (*g*), Gordon and Barnes (*183*) have obtained $S_{298.1}=45.10$ from spectroscopic calculations. Giauque and Archibald (*159*) have made a small correction to this value, raising it to $S_{298.1}=45.13$. This corrected value is adopted for H_2O (*g*). The error should be of the order of ±0.01. It should be noted that the result from heat-capacity measurements, as corrected, is in agreement with this figure. Following Giauque and Stout (*171*), there is added to $S_{298.1}=16.75$ for H_2O (*l*) the following quantities: $\Delta S_{298.1}=10{,}499/298.1=35.22$ (vaporization at 2.376 cm. pressure), $\Delta S_{298.1}=-6.88$ (compression from 2.376 cm. to 1 atmosphere pressure), and $\Delta S_{298.1}=-0.002$ (correction to perfect gas state). The sum is $S_{298.1}=45.09$. This excellent agreement may be taken as proof of Pauling's (*336*) ideas concerning randomness of hydrogen bonds in ice crystals. Additional checks are furnished by Giauque and Ashley (*160*) who obtained

$S_{298.1}=45.18$ from data for the reaction $H_2+HgO=Hg+H_2O$ and $S_{298.1}=45.1$ from data for the reaction $2HCl+1/2O_2=H_2O+Cl_2$. Also, more recently, the work of Giauque and Archibald (*159*) on the reaction $Mg(OH)_2=MgO+H_2O$ gave the value $S_{298.1}=45.10$.

Specific-heat measurements at low temperatures of D_2O were made by Brown, Barnes, and Maass (*62, 63*) (203°–273°) and Long and Kemp (*299*) (14°–296°). The results of the latter investigators will be employed. There is computed $S_{15.0}=0.09$ (extrapolation), $S_{276.9}-S_{15.0}=10.29$ (crystals), $\Delta S_{276.9}=1{,}501/276.9=5.42$ (fusion), and $S_{298.1}-S_{276.9}=1.47$ (liquid). The sum is $S_{298.1}=17.27$, to which must be added the Pauling correction 0.81, making $S_{298.1}=18.08\pm0.1$ for D_2O (*l*).

For D_2O (*g*), Long and Kemp (*299*) have utilized $\Delta S_{273.1}=12{,}636/273.1=46.27$ (vaporization at 3.65 mm. pressure), and $\Delta S_{273.1}=-10.61$ (compression from 3.65 mm. to 1 atmosphere) in obtaining $S_{273.1}=45.89\pm0.1$, to which must be added 0.81, making $S_{273.1}=46.70$. The last figure is to be compared with their result from molecular-constant data, $S_{273.1}=46.66$. The close agreement again is evidence of the correctness of Pauling's theory. The value at 298.1° is calculated from the values, $I_1=5.752\times10^{-40}$, $I_2=3.812\times10^{-40}$, $I_3=1.790\times10^{-40}$, $\omega_1=2{,}784$ (1), $\omega_2=2{,}666$ (1), and $\omega_3=1{,}179$ (1), given by Long and Kemp. The result is $S_{298.1}=47.38\pm0.1$, of which $S_{v,298.1}=0.05$. Evidently, Long and Kemp have made a small error in their similar calculation.

Sulfide.—Heat-capacity measurements of H_2S at low temperatures were made by Clusius and Frank (*79, 93, 95*) (11°–209°) and Giauque and Blue (*161*) (16°–213°). The calculations of the latter investigators are repeated here. They find $S_{16.0}=0.26$ (extrapolation), $S_{103.52}-S_{16.0}=7.65$ (crystals III), $\Delta S_{103.52}=368.0/103.52=3.55$ (transition), $S_{126.0}-S_{103.52}=2.48$ (crystals II), $S_{127.0}-S_{126.0}=121.3/126.22=0.96$ (transition), $S_{187.61}-S_{127}=5.32$ (crystals I), $\Delta S_{187.61}=568.1/187.61=3.03$ (fusion), $S_{212.77}-S_{187.61}=2.05$ (liquid), $\Delta S_{212.77}=4{,}463/212.77=20.98$ (vaporization), and $\Delta S_{212.77}=0.10$ (correction to ideal gas state). The sum is $S_{212.77}=46.38\pm0.1$. This differs but little from the result calculated by Clusius and Frank (*95*) from their own data, $S_{212.7}=46.31\pm0.1$. An entropy increment of 2.71 is required in warming the gas from 212.77° to 298.1°. This leads to $S_{298.1}=49.10\pm0.1$ from Giauque and Blue's data. The latter investigators have computed the entropy from the molecular constants, $I_1=5.845\times10^{-40}$, $I_2=3.076\times10^{-40}$, $I_3=2.667\times10^{-40}$, $\omega_1=1{,}260$ (1), and $\omega_2=2{,}620$ (2). The result is $S_{298.1}=49.15\pm0.1$. This calculation, which first was reported by Cross (*109, 110*), has been checked by the author.

Bromide.—Eucken and Karwat (*139*) (21°–199°) and Giauque and Wiebe (*173*) (15°–206°) have measured the heat capacity of HBr. Relying on the latter work, there are repeated $S_{14.5}=0.55$ (extrapolation), $S_{186.24}-S_{14.5}=17.27$ (crystalline forms less transition entropies), $\Delta S_{89.2}=63.4/89.2=0.71$ (transition), $\Delta S_{113.2}=78.8/113.2=0.70$ (transition), $\Delta S_{116.8}=85.7/116.8=0.73$ (transition), $\Delta S_{186.24}=575.1/186.24=3.10$ (fusion), $S_{206.38}-S_{186.24}=1.46$ (liquid), $\Delta S_{206.38}=4{,}210/206.38=20.40$ (vaporization), $\Delta S_{206.38}=0.10$ (correction to perfect gas state), and $S_{298.1}-S_{206.38}=2.61$ (gas). These add to give $S_{298.1}=47.6\pm0.15$.

From spectroscopic data, Giauque and Wiebe (*173*) and Gordon and Barnes (*184*) have computed $S_{298.1}=47.48\pm0.01$, which is adopted.

Chloride.—Clusius (*76*) (10°–174°), Eucken and Karwat (*139*) (22°–189°), and Giauque and Wiebe (*172*) (17°–189°) have measured the heat capacity of HCl. The calculations that follow are in accordance with the data of the last-named investigators. They find $S_{16.0}=0.30$ (extrapolation), $S_{98.36}-S_{16.0}=7.06$ (crystals II), $\Delta S_{98.36}=284.3/98.36=2.89$ (transition), $S_{158.91}-S_{98.36}=5.05$ (crystals I), $\Delta S_{158.91}=476.0/158.91=3.00$ (fusion), $S_{188.07}-S_{158.91}=2.36$ (liquid), $\Delta S_{188.07}=3{,}860/188.07=20.52$ (vaporization), $\Delta S_{188.07}=0.10$ (correction to perfect gas state), and $S_{298.1}-S_{188.07}=3.19$ (gas). The sum is $S_{298.1}=44.5\pm0.15$.

Giauque and Wiebe (*172*) and Giauque and Overstreet (*167*) have calculated the entropy from spectroscopic data. The result of the latter, $S_{298.1}=44.66\pm0.01$, is adopted. Gordon and Barnes (*183*) have computed a slightly lower value, $S_{300}=44.65$, corresponding to $S_{298.1}=44.61$.

Fluoride.—Clusius, Hiller, and Vaughen (*102*) (11°–78°) have measured the specific heat of HF and Dahmlos and Yung (*114*) have obtained 1,094 calories as the heat of fusion at 190.09°. These data are insufficient for an entropy calculation, however. Murphy and Vance (*322*) have computed $S_{298.1}=41.53$ from molecular constants corresponding to $I=1.348\times10^{-40}$ and $\omega=4{,}141$. The vibrational contribution is negligible. This value is virtually the same as the figure $S_{298.1}=41.52$, calculated by the author (*245*) several years ago. The value $S_{298.1}=41.53\pm0.01$ is adopted for HF (*g*).

Iodide.—Eucken and Karwat (*139*) (58°–238°) and Giauque and Wiebe (*174*) (17°–238°) have measured the heat capacity of HI. Again, the data of the latter are used in obtaining $S_{15.3}=1.08$ (extrapolation), $S_{222.31}-S_{15.3}=20.99$ (crystalline forms less transition entropies), $\Delta S_{70.1}=18.6/70.1=0.26$ (transition), $\Delta S_{125.6}=192.4/125.6=1.53$ (transition), $\Delta S_{222.31}=686.3/222.31=3.09$ (fusion), $S_{237.75}-S_{222.31}=0.96$ (liquid), $\Delta S_{237.75}=4{,}724/237.75=19.87$ (vaporization), $\Delta S_{237.75}=0.10$ (correction to perfect gas state), and $S_{298.1}-S_{237.75}=1.60$ (gas). The sum is $S_{298.1}=49.5\pm0.15$.

From spectroscopic data, Giauque and Wiebe compute $S_{298.1}=49.4$ in agreement with their third-law value. Murphy (*321*), more recently, has calculated $S_{298.1}=49.36$ from molecular constants corresponding to $I=4.289\times10^{-40}$ and $\omega=2{,}310$, in agreement with the value given by the author (*245*). This result, $S_{298.1}=49.36\pm0.01$, is adopted.

Cyanide.—The heat capacity of HCN was measured by Giauque and Ruehrwein (*169*) (14°–300°). Their calculations, which have been checked, are $S_{15.0}=0.13$ (extrapolation), $S_{259.86}-S_{15.0}=16.77$ (crystals less transition entropy), $\Delta S_{170.37}=3.8/170.37=0.02$ (transition), $\Delta S_{259.86}=2{,}009/259.86=7.73$ (fusion), $S_{298.80}-S_{259.86}=2.36$ (liquid), $\Delta S_{298.80}=6{,}027/298.80=20.17$ (vaporization), $\Delta S_{298.80}=0.03$ (correction to perfect gas state), and $\Delta S_{298.80}=0.73$ (correction for polymerization). The sum is $S_{298.80}=47.94$ for HCN (*g*). The figure for 298.1° is 0.02 less, or $S_{298.1}=47.92$.

From the values $I=18.72\times10^{-40}$, $\omega_1=2{,}089$ (1), $\omega_2=712.1$ (2), and $\omega_3=3{,}313$ (1), Giauque and Ruehrwein compute $S_{298.1}=48.23$. This value agrees as well as could be expected with the third-law result,

which is subject to unusual uncertainties because of polymerization. Badger and Woo (*35*) have computed an identical result, while Gordon (*181*) gave $S_{298.1}=48.29$. The figure $S_{298.1}=48.23\pm0.1$ is adopted for HCN (*g*).

It may also be seen from the calculated quantities above that $S_{298.80}=27.01$ for HCN (*l*). This corresponds to $S_{298.1}=26.96\pm0.1$ for HCN (*l*), the equilibrium mixture of polymers.

From values given by Bartunek and Barker (*38*), $I=22.92\times10^{-40}$, $\omega_1=2{,}089$ (1), $\omega_2=570$ (2), and $\omega_3=2{,}630$ (1), there is computed $S_{t+r,298.1}=48.16$ and $S_{v,298.1}=1.02$, making $S_{298.1}=49.18\pm0.1$ for DCN (*g*), nonpolymerized, ideal state.

Seleníde.—Kruis and Clusius (*265*) (61°–230°) have measured the heat capacity of H_2Se. The data are insufficient for an entropy calculation, however. Cameron, Sears, and Nielsen (*66*) have reported 1.6×10^{-8} cm. as the H–Se distance and 2.3×10^{-8} as the H–H distance in the H_2Se (*g*) molecule and also $\omega_1=1{,}074$ (1), $\omega_2=2{,}260$ (1), and $\omega_3=2{,}350$ (1) as the vibration frequencies. The interatomic distances correspond to $I_1=8.4\times10^{-40}$, $I_2=4.4\times10^{-40}$, and $I_3=4.0\times10^{-40}$. There is computed $S_{298.1}=52.9\pm1.0$ for H_2Se (*g*), of which 0.07 is vibrational entropy.

Kruis and Clusius (*265*) (64°–233°) also have reported some heat-capacity data for D_2Se, which again are not adequate for the present purpose. Cameron, Sears, and Nielsen (*66*) report $\omega_1=745$ (1), $\omega_2=1{,}630$ (1), and $\omega_3=1{,}696$ (1). If the same interatomic distances as for H_2Se are employed, then $I_1=16.6\times10^{-40}$, $I_2=8.8\times10^{-40}$, and $I_3=7.8\times10^{-40}$ may be estimated. There is calculated $S_{298.1}=55.2\pm1.0$ for D_2Se (*g*), of which 0.26 is vibrational entropy.

The entropy of HDSe (*g*) also may be approximated from values given by Cameron, Sears, and Nielsen (*66*), $\omega_1=905$ (1), $\omega_2=1{,}691$ (1), and $\omega_3=2{,}352$ (1), and the assumption of the same interatomic distances as for H_2Se (*g*). There is estimated $I_1=12.4\times10^{-40}$, $I_2=6.5\times10^{-40}$, and $I_3=5.9\times10^{-40}$. Therefore, $S_{298.1}=55.4\pm1.0$ for HDSe (*g*), of which 0.14 is vibrational entropy.

INDIUM

Element.—The entropy of In (*g*) at 298.1°, calculated from the Sackur equation with $R\ ln\ 2$ added because of the quantum weight 2 of the lowest energy state (*273, p. 2345*), is $S_{298.1}=41.51\pm0.01$.

IODINE

Element.—The specific heat of I_2 was measured by Günther (*187*) (21°–73°), Lange (*274*) (9°–52°), and Nernst (*325*) (28–298°). The data of Günther and Nernst are erratic, consequently only those of Lange are used. There is computed $S_{298.1}=27.9\pm0.1$ for I_2 (*s*) of which 0.34 is extrapolation below 10°. Giauque (*158*) has made the same calculation, obtaining an identical result, and has shown that this value for the solid is in agreement with that of the gas, obtained from spectroscopic data, to within ±0.1 unit.

Giauque (*158*) and Murphy (*321*) have computed the entropy of I_2 (*g*) from spectroscopic data and have found $S_{298.1}=62.29\pm0.01$.

At 298.1° the entropy of monatomic I (*g*) is $S_{298.1}=43.19\pm0.01$. $R\ ln\ 4$ has been added to the Sackur equation (*273, p. 2348*).

Iodide ion.—Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=25.4\pm0.5$ and $S_{298.1}=25.2\pm0.7$, respectively, for I^- (*aq.*) from data for the reactions $AgI+1/2H_2=H^++I^-+Ag$ and $1/2I_2$ (*s*) $+ 1/2\,H_2=H^++I^-$. The mean, $S_{298.1}=25.3\pm0.5$, is chosen.

Bromide.—Blair and Yost (*43*) computed $S_{298.1}=62.0$ for IBr (*g*) from their own thermal data. Previously, McMorris and Yost (*311*) had derived $S_{298.1}=60.6$ from a study of the reaction $CuBr_2+1/2$ I_2 (*s*)$=CuBr+IBr$ (*g*) and had estimated $S_{298.1}=31.8\pm1.4$ for IBr (*s*). The moment of inertia and vibration frequency of IBr (*g*) have been given (*273, p. 2553*) as $I=493\times10^{-40}$ and $\omega=266$. There is computed $S_{t+r,298.1}=60.21$ and $S_{v,298.1}=1.63$, making $S_{298.1}=61.8\pm0.1$, in agreement with the value of Blair and Yost. This last figure is adopted. If the difference in entropy between gas and solid employed by McMorris and Yost is applied, then $S_{298.1}=33.0\pm1.4$ for IBr (*s*).

The entropy of IBr (*g*) also may be obtained in the following manner. The mean of the entropies of Br_2 (*g*) and I_2 (*g*) is 60.46. Both Br_2 (*g*) and I_2 (*g*) have the symmetry number 2, while IBr (*g*) has the symmetry number 1. Consequently, IBr (*g*) may be expected to have an entropy $R\,ln\,2=1.38$ greater than the mean, or $S_{298.1}=61.84$.

Chloride.—Blair and Yost (*43*) obtained $S_{298.1}=59.15$ for ICl (*g*) from their own thermal data. McMorris and Yost (*312*) reported the same figure as a result of calculation from molecular constants and $S_{298.1}=59.6$ from thermal data. Using the values $I=242.3\times10^{-40}$ and $\omega=383$ (*273, p. 2353*), there is obtained $S_{t+r,298.1}=58.08$ and $S_{v,298.1}=1.03$, making $S_{298.1}=59.1\pm0.1$, which is adopted. A calculation similar to that given above for IBr (*g*) results in $S_{298.1}$ $= 1/2(53.31+62.29)+1.38=59.18$.

Trichloride.—Nies and Yost (*330*) obtained $\Delta F^\circ_{298.1}=-21{,}150$ and $\Delta H_{298.1}=-5{,}410$ for the reaction $1/2\ I_2$ (*s*)$+3/2\ Cl_2=\ ICl_3$ (*s*). The entropy of reaction is $\Delta S_{298.1}=-5.28$, consequently $S_{298.1}=41.1\pm0.5$ for ICl_3 (*s*).

Iodate ion.—From data for the reactions, $KIO_3=K^++IO_3^-$ and $AgIO_3=Ag^++IO_3^-$, Latimer, Pitzer, and Smith (*286*) obtained, respectively, $S_{298.1}=27.9\pm1$ and $S_{298.1}=28.3\pm3$ for IO_3^- (*aq.*). They selected the value $S_{298.1}=28.0\pm1.0$, which also is adopted here.

IRIDIUM

Element.—The value of the entropy of Ir, calculated by Lewis and Gibson (*292*) from Dewar's (*117*) mean specific-heat figure, cannot be revised as no new data have appeared; therefore, estimating the error as ±0.5, $S_{298.1}=8.7\pm0.5$ for Ir.

According to the compilation of Bacher and Goudsmit (*31*), only the lowest energy state of Ir (*g*) would be effective at 298.1°. Its quantum weight 6 adds $R\,ln\,6$ to the Sackur equation to make $S_{298.1}$ $=45.25\pm0.1$.

IRON

Element.—The specific heat of Fe was measured by Eucken and Werth (*144*) (16°–206°), Duyckaerts (*125, 126*) (1.5°–21°), Günther (*187*) (32°–95°), Keesom and Kurrelmeyer (*237*) (1°–21°), Rodebush and Michalek (*350*) (72°–199°), and Simon and Swain (*373*) (30°–220°). The entropy obtained from these data is $S_{298.1}=6.47\pm0.1$. The extrapolation is negligible, <0.001 below 1.5°.

Burns and Walters (*65*) have tabulated the energy levels of Fe (*g*). At 298.1°, five levels must be considered in obtaining the entropy, $^5D_4$, $^5D_3$, $^5D_2$, $^5D_1$, and $^5D_0$. The term values are, respectively, 0, 415.93, 704.00, 888.13, and 978.07 and the quantum weights 9, 7, 5, 3, and 1. The translational entropy calculated from the Sackur equation is $S_{298.1}=37.990$. The entropy associated with the above given levels is 5.130. Therefore, $S_{298.1}=43.12\pm0.01$ for Fe (*g*).

Ferrous ion.—Latimer, Pitzer, and Smith (*286*) calculated $S_{298.1}=-25.9\pm1.0$ for Fe^{++} (*aq.*) from data for the reaction $Fe+2H^+=Fe^{++}+H_2$.

Ferric ion.—Similarly, from data for the reaction $Fe^{++}+H^+=Fe^{+++}+1/2\ H_2$, Latimer, Pitzer, and Smith (*286*) found $S_{298.1}=-61\pm5$ for Fe^{+++} (*aq.*).

Ferrous oxide.—Millar (*318*) (70°–302°) has made specific-heat measurements of a sample of "ferrous" oxide of 83 percent purity. His calculation of the entropy, however, could not be checked and evidently contains some arithmetical error. The present calculation gives $S_{298.1}=14.2\pm2.0$, of which 1.34 is extrapolation below 70.8°.

A value that probably is better was calculated by Kelley (*250*) from data available for the reaction $FeO\ (s)+H_2=Fe\ (\alpha)+H_2O\ (g)$. The result is $S_{298.1}=13.4\pm1.0$. This figure should be more certain than the value 12.6 calculated by Kielland (*260*) from data for the reaction $Fe_2O_3\ (l)=2FeO\ (l)+1/2O_2$.

Quite recently, Chipman and Marshall (*72*) have obtained $S_{298.1}=14.1$ for FeO (wüstite) from a combination of their own and Emmett and Schultz's (*134*) equilibrium data for the reaction $FeO+H_2=Fe+H_2O$.

Ferric oxide.—The specific heat of Fe_2O_3, specular hematite of 99.2 percent purity, was measured by Parks and Kelley (*334*) (89°–292°) who also investigated Fe_2O_3 (88°–290°) prepared by igniting the oxalate. The latter material was finely divided and had a specific heat 2 to 4 percent greater, depending on the temperature, than natural hematite; however, X-ray pictures showed the two materials to be not identical. From the data for hematite, $S_{298.1}=21.5\pm0.5$. The amount of extrapolation below 89.2° is 3.30.

Magnetite.—Millar (*318*) (60°–300°) and Parks and Kelley (*334*) (90°–295°) have measured specific heats of similar samples of magnetite of 99 percent purity. From their combined data, $S_{298.1}=35.0\pm0.7$ for Fe_3O_4. The extrapolation below 56.2° is 2.17.

Ferrous sulfide.—Anderson (*13*) (57°–296°) has measured the specific heat of pure, synthetic FeS. Calculation gives $S_{56.2}=1.43$ (extrapolation) and $S_{298.1}=16.1\pm0.3$.

Pyrite.—The specific heat of pyrite, FeS_2, was measured by Anderson (*22*) (55°–297°) and Eucken and Schwers (*141*) (21°–84°). The data of the former yield $S_{298.1}=12.7\pm0.2$ of which 0.35 is extrapolation below 56.2°, while those of the latter workers give $S_{298.1}=12.4\pm0.3$ with an extrapolation of 0.02 below 19.95°. The value $S_{298.1}=12.7\pm0.2$ is adopted.

Ferrous chloride.—Trapeznikova and Shubnikov (*400*) (16°–127°) have measured the specific heat of $FeCl_2$. The "hump" in the specific-heat curve in the neighborhood of 20° makes extrapolation difficult and uncertain and increases the estimate of error over what it would be otherwise. There is obtained $S_{15.85}=0.97$ (extrapolation) and $S_{298.1}-S_{15.85}=28.39$, making $S_{298.1}=29.4\pm0.7$.

Carbide.—Andes (*28*) (102°–324°) has measured the specific heat of carburized iron and extrapolated his results to the composition Fe_3C. He calculates $S_{298.1}=23.55$.

Naeser (*323*) (85°–298°) has made average specific-heat measurements of Fe_3C. His data have been considered by Schwarz and Ulich (*359*), who attempted to extract true specific heats. The latter compute $S_{298.1}=23.9$.

More recently, Seltz, McDonald, and Wells (*363*) (68°–298°) measured the specific heat of iron containing 1.354 weight-percent carbon which showed no signs of graphite. They computed the specific heat of Fe_3C from their results by subtracting that of the contained iron. Their entropy calculation gives $S_{298.1}=25.7\pm1.0$, of which 2.57 is extrapolation below 68°.

In addition, the author (*251*) has obtained $\Delta S_{298.1}=2.99$ as the entropy of formation of Fe_3C from equilibrium data for the reactions $3Fe\ (\alpha)+CH_4=Fe_3C\ (\alpha)+2H_2$ and $3Fe\ (\alpha)+2CO=Fe_3C\ (\alpha)+CO_2$. This figure leads to $S_{298.1}=23.8$ for $Fe_3C\ (\alpha)$, in fortuitous agreement with Schwarz and Ulich's calculation.

It is obvious that these reported values do not deserve the same weight. However, for the present the mean, $S_{298.1}=24.2\pm1.5$, is adopted.

Carbonate.—Anderson (*17*) (54°–297°) measured the specific heat of $FeCO_3$, siderite. Calculation gives $S_{298.1}=22.2\pm0.4$, of which 2.33 is extrapolation below 56.2°.

Nitride.—Kelley (*251*), from data for the reaction $2Fe_4N+3H_2=8Fe\ (\alpha)+2NH_3$, has estimated $S_{298.1}=37.4$ for Fe_4N. This value may be in error, probably high, by several units.

KRYPTON

Element.—Clusius (*80*) (10°–121°) and Clusius, Kruis, and Konnertz (*103*) (63°–124°) have measured the heat capacity of Kr. Calculation from these data gives $S_{10}=0.57$ (extrapolation), $S_{115.95}-S_{10}=12.18$ (crystals), $\Delta S_{115.95}=390.7/115.95=3.37$ (fusion), $S_{119.93}-S_{115.95}=0.35$ (liquid), $\Delta S_{119.93}=2{,}158/119.93=18.00$ (vaporization), and $S_{298.1}-S_{119.93}=4.53$ (gas, $C_p=4.97$). The sum is $S_{298.1}=39.0\pm0.3$. A better value is obtained from the Sackur equation, $S_{298.1}=39.20\pm0.01$, with which the third-law result is in satisfactory agreement.

LANTHANUM

Element.—In accordance with Lewis and Gibson (*292*) the entropy of La, to which is assigned the error ±0.8, is taken as $S_{298.1}=13.7\pm0.8$.

The compilation of Bacher and Goudschmit (*31*) gives $^2D_{3/2}$, $^2D_{5/2}$, and $^4F_{3/2}$ as the lowest energy levels of La (g). The term values are 0, 1,053, and 2,668, respectively, and the quantum weights are 4, 6, and 4. It is calculated that 2.869 must be added to the translational entropy, 40.705, given by the Sackur equation. The result is 43.57 ± 0.1.

LEAD

Element.—The specific heat of Pb was measured by Bronson and Wilson (*56*) (203°–303°), Eucken and Schwers (*141*) (15°–276°), Keesom and Andrews (*225*) (2°–20°), Keesom and van den Ende

(*228*, *229*) (3°–20°), Keesom and Onnes (*241*) (14°–81°), Meads (*313*) (15°–300°), and Nernst (*325*, *328*) (23°–273°). Recalculation of the entropy gives $S_{298.1}=15.49\pm0.05$. The extrapolation is 0.007 below 3°.

Spectroscopic data for Pb (*g*) show that at 298.1° all but a negligible portion of the atoms are in the lowest energy state of quantum weight 1 (*273*, *p. 2346*). The entropy given by the Sackur equation is $S_{298.1}=41.90\pm0.01$.

Lead ion.—From data for the reaction $PbCl_2=Pb^{++}+2Cl^-$, Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=3.9\pm0.9$ for Pb^{++} (*aq.*).

Oxides.—The specific-heat data of Nernst and Schwers (*329*) (21°–93°) on a sample of PbO, presumably the yellow variety, lead to the value $S_{298.1}=16.6\pm0.5$, with an extrapolation below 20° of 0.55. The entropy may be calculated independently from the cell measurements of Fried (*149*) for the reaction $PbO+H_2=Pb+H_2O$ (*l*). From his e. m. f. measurements and their temperature coefficient the value $\Delta S_{298.1}=-16.8$ is calculated, which in turn leads to $S_{298.1}=17.8\pm1.0$ for PbO. The third-law value, $S_{298.1}=16.6\pm0.5$, is adopted.

The moment of inertia of the PbO (*g*) molecule has been given as $I=90.5\times10^{-40}$ by Mecke (*272*, *p. 109*). This makes possible the calculation of $S_{t+r,298.1}=57.07$. The vibrational entropy is $S_{v,298.1}=0.29$, from $\omega=717$ (*192*). Consequently, $S_{298.1}=57.4\pm0.5$ for PbO (*g*). A rough check on this figure is afforded by values of the heat and free energy of sublimation (*247*), which correspond to $\Delta S_{298.1}=39.3$. Combining this figure and the entropy of the solid gives $S_{298.1}=55.9$, which is given no weight in comparison with the result from molecular constants.

Millar (*317*) (69°–298°) has measured the specific heat of PbO_2. From his data, $S_{298.1}=18.3\pm0.5$ is calculated. The extrapolation below 70.8° is 3.50.

Millar (*317*) (71°–293°) also has measured the specific heat of Pb_3O_4. A serious error was made in his entropy calculation, however. The results of the present calculation are $S_{70.8}=12.67$ (extrapolation) and $S_{298.1}=50.5\pm1.6$.

Sulfide.—The specific heat of PbS was measured by Anderson (*14*) (53°–290°) and Eastman and Rodebush (*130*) (63°–283°). The data of Anderson are used in obtaining $S_{298.1}=21.8\pm0.6$ of which 4.50 is extrapolation below 50.1°.

The entropy of sublimation may be obtained from the heat and free energy of sublimation (*247*) as $\Delta S_{298.1}=42.5$. This leads to $S_{298.1}=64.3$ for PbS (*g*), which can be considered only as a rough approximation.

Another value may be obtained from $\omega=427$ (*273*, *p. 2352*) and an estimate of 3.0×10^{-8} as the Pb–S distance. The latter corresponds to $I=412\times10^{-40}$. There is computed $S_{t+r,298.1}=60.29$ and $S_{v,298.1}=0.88$, making $S_{298.1}=61.2\pm1.5$.

Telluride.—McAteer and Seltz (*307*) have given $\Delta S_{298.1}=-1.0$ for the reaction Pb+Te=PbTe. This leads to $S_{298.1}=26.4\pm1.0$ for PbTe.

Bromide.—Latimer and Hoenshel (*283*) (18°–297°) have measured the specific heat of $PbBr_2$. From their data, $S_{298.1}=38.6\pm0.5$. The extrapolated portion is 1.64 below 17.8°. Cann and Sumner (*68*) have obtained $\Delta S_{298.1}=-12.60$ for the reaction $Pb+2AgBr=PbBr_2+2Ag$. Corresponding to this value, $S_{298.1}=33.7$ may be calculated for

$PbBr_2$, which disagrees with the third-law result and also appears erroneous in comparison with the entropies of $PbCl_2$ and PbI_2.

The entropy of sublimation of $PbBr_2$ is $\Delta S_{298.1}=40.2$ (*247*). Combining this figure and the entropy of the solid gives $S_{298.1}=78.6$ for $PbBr_2$ (*g*). The result can be considered only as indicating the order of magnitude of this quantity.

Chloride.—The specific heat of $PbCl_2$ was measured by Nernst (*325*) (15°–206°). His data give $S_{298.1}=34.0\pm1.0$, with an extrapolation of 0.91 below 15.8°.

Gerke's (*154*) cell measurements permit two independent calculations. He gave $\Delta S_{298.1}=-8.6$ for the reaction $Pb+2AgCl=PbCl_2+2Ag$ and $\Delta S_{298.1}=6.7$ for the reaction $Pb+2HgCl=PbCl_2+2Hg$. The corresponding calculated entropies of $PbCl_2$ are $S_{298.1}=32.6\pm0.6$ and $S_{298.1}=31.7\pm1.5$. The value $S_{298.1}=32.6\pm0.6$ is adopted for this substance.

The entropy of $PbCl_2$ (*g*) is obtainable from the entropy of sublimation, $\Delta S_{298.1}=43.3$ (*247*), and that of the solid as $S_{298.1}=75.9$. This can be considered only an order-of-magnitude calculation.

Iodide.—From the specific-heat data of Nernst and Schwers (*329*) (22°–96°), Lewis and Gibson (*292*) have calculated the entropy as $S_{298.1}=41.3$ by the use of their N-formula. As the data are meager and the extrapolation is large, C_p being 7.05 at 22.3°, it is not possible to improve much on this calculation. The error in this value easily may be ±1.5 units.

A much more reliable value may be obtained from the cell measurements of Gerke (*154*), which give $\Delta S_{298.1}=-1.2$ for the reaction $Pb+I_2$ (*s*)$=PbI_2$. This figure leads to $S_{298.1}=42.2\pm0.5$ for PbI_2. The recent measurements of Cann and Taylor (*69*) give $\Delta S_{298.1}=1.1$ for the above reaction, which disagrees with Gerke's value and is given no weight here.

The entropy of sublimation of PbI_2 is $\Delta S_{298.1}=44.7$ (*247*). For PbI_2 (*g*) there is estimated, therefore, $S_{298.1}=86.9$. The error in this value may be several units.

Carbonate.—The specific heat of $PbCO_3$ (cerussite) was measured by Anderson (*17*) (53°–294°). His data give $S_{56.2}=6.45$ (extrapolation) and $S_{298.1}-S_{56.2}=24.82$, making $S_{298.1}=31.3\pm0.8$.

Basic carbonate.—From dissociation pressure and thermal data, the value $S_{298.1}=48.5\pm1.5$ was obtained for $PbO\cdot PbCO_3$ by Kelley and Anderson (*258*).

Phosphate.—Pitzer, Smith, and Latimer (*340*) (15°–292°) have measured the specific heat of $Pb_3(PO_4)_2$. There is computed $S_{298.1}=84.5\pm0.5$, of which 1.10 is extrapolation below 15°.

Sulfate.—Anderson (*19*) (53°–294°) and Haas and Stegeman (*190*) (83°–298°) have measured the specific heat of $PbSO_4$. Relying on Anderson's data alone, there is obtained $S_{298.1}=35.2\pm1.0$, of which 6.75 is extrapolation below 56.2°.

Basic sulfates.—From consideration of various equilibrium data, the author (*250*) has calculated $\Delta S_{298.1}=-3.5$ for the reaction $PbSO_4+PbO=PbSO_4\cdot PbO$, $\Delta S_{298.1}=-4.3$ for the reaction $PbSO_4+2PbO=PbSO_4\cdot 2PbO$, and $\Delta S_{298.1}=-5.8$ for the reaction $PbSO_4+3PbO=PbSO_4\cdot 3PbO$. These values lead to $S_{298.1}=48\pm2$ for $PbSO_4\cdot PbO$, $S_{298.1}=64\pm2.5$ for $PbSO_4\cdot 2PbO$, and $S_{298.1}=79\pm3$ for $PbSO_4\cdot 3PbO$.

LITHIUM

Element.—Simon and Swain (*373*) (15°–300°) have measured the specific heat of Li. From their data, $S_{298.1}=6.70\pm0.06$. Of this quantity, only 0.015 is extrapolation below 15°.

For Li (*g*), the Sackur equation, to which must be added $R\ ln\ 2$, yields $S_{298.1}=33.15\pm0.01$.

Using values from Allen and Longair's (*6*) table, $I=41.1\times10^{-40}$ and $\omega=351.6$ for Li_2 (*g*). These result in $S_{298.1}=47.0\pm0.5$.

Lithium ion.—Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=4.7\pm1.0$ for $^{-}Li^{+}$ (*aq.*) from data for the reaction $Li_2CO_3=2Li^{+}+CO_3^{--}$.

Chloride.—Niwa (*331*) has estimated $S_{298.1}=49.9\pm1.4$ for LiCl (*g*) from vapor pressure data. From residual ray data (*273, p. 758*), $S_{298.1}=9.7\pm0.5$ is computed for LiCl (*s*).

Iodide.—The vibration frequency of LiI (*g*) is reported as $\omega=450$ (*273, p. 2349*). Estimating 3.0×10^{-8} cm. as the interatomic distance there results $I=98\times10^{-40}$. Further calculation gives $S_{t+r,298.1}=55.70$, $S_{v,298.1}=0.80$, and $S_{298.1}=56.5\pm1.0$.

Hydrides.—The specific-heat data of Günther (*188*) (74°–293°) on a somewhat impure sample of LiH give $S_{298.1}=5.9\pm0.5$, the extrapolation below 70.8° being 0.21.

The values $I=3.75\times10^{-40}$ and $\omega=1{,}383$ have been reported for LiH (*g*) (*273, p. 2349*). From these, $S_{t+r,298.1}=40.80$ and $S_{v,298.1}=0.02$, making $S_{298.1}=40.8\pm0.2$.

Similarly, from $I=6.604\times10^{-40}$ and $\omega=1{,}042$ (*273, p. 2349*) for LiD (*g*), there are obtained $S_{t+r,298.1}=42.29$, $S_{v,298.1}=0.08$, and $S_{298.1}=42.4\pm0.2$.

Hydroxide.—The heat and free energy of formation from the elements of LiOH were obtained by Ueda (*402, 403*) as $\Delta H_{298.1}=-115{,}253$ and $\Delta F^{\circ}_{298.1}=-105{,}128$. These figures correspond to $\Delta S_{298.1}=-34.0$ and $S_{298.1}=12.8\pm1.0$ for LiOH.

Carbonate.—Brown and Latimer (*57*) (16°–301°) determined the specific heat of Li_2CO_3. From their data, $S_{16.8}=0.05$ (extrapolation) and $S_{298.1}-S_{16.8}=21.49$, making $S_{298.1}=21.5\pm0.2$.

MAGNESIUM

Element.—Clusius and Vaughen (*101*) (11°–228°), Eastman and Rodebush (*130*) (74°–289°), and Nernst and Schwers (*329*) (27°–94°) have measured the specific heat of Mg. Relying largely on the data of the first-named investigators, there is calculated $S_{298.1}=7.77\pm0.1$. The extrapolation is 0.004 below 11.3°.

The Sackur equation yields $S_{298.1}=35.51\pm0.01$ for Mg (*g*). Clusius and Vaughen (*101*) have obtained $S_{298.1}=35.3$, from the entropy of the solid, high-temperature specific-heat, and vapor-pressure data, in good agreement.

Magnesium ion.—Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=-31.6\pm3$ as the entropy of Mg^{++} (*aq.*) from data for the reaction $Mg(OH)_2+2H^{+}=Mg^{++}+2H_2O$.

Oxide.—Giauque and Archibald (*159*) (20°–301°), Günther (*187*) (39°–84°), and Parks and Kelley (*334*) (94°–291°) have measured the specific heat of MgO. In the earlier entropy compilations (*245, 249*) the data of Günther and Parks and Kelley were used to obtain $S_{298.1}=6.4\pm0.1$, with an extrapolation of 0.02 below 39.8°. The

measurements of Parks and Kelley were on a dense, macrocrystalline, translucent sample. This is mentioned because of the difference in specific heat found by Giauque and Archibald who studied a finely powdered material made by dehydrating $Mg(OH)_2$ at 573°–623°. Their results yield $S_{298.1}=6.66\pm0.02$, of which 0.007 is extrapolation below 20.3°. This difference in entropy, although amounting to 4 percent, is not great enough in magnitude to be of importance in most thermodynamic calculations and the mean, 6.55 ± 0.15, may be used without considering the physical characteristics of the material.

The moment of inertia and vibration frequency of the MgO (*g*) molecule have been given as $I=40.59\times10^{-40}$ and $\omega=662$ (*273, p. 2350*), respectively. From these figures $S_{t+r,298.1}=50.38$, $S_{v,298.1}=0.26$, and $S_{298.1}=50.7\pm0.3$.

Hydroxide.—Giauque and Archibald (*159*) (22°–321°) also measured the specific heat of $Mg(OH)_2$. Their calculation gives $S_{298.1}=15.09$, the extrapolation below 21.1° being 0.033. The error should not exceed ±0.03, as the result, in combination with other data, was shown to yield a correct value of the entropy of H_2O (*g*).

Carbonate.—The specific heat of $MgCO_3$, magnesite, was measured by Anderson (*17*) (56°–292°). The entropy corresponding to his data is $S_{298.1}=15.7\pm0.2$. The extrapolation below 56.2° is 0.57.

Silicate.—Wagner (*404*) (21°–36°) measured the specific heat of $MgSiO_3$. His results were joined in a C_p vs. $1/T$ plot to the value $C_p=19.4$ at 298.1°, the value given by high-temperature specific-heat data (*246*). The entropy extrapolation below 19.95° is 0.07, and $S_{298.1}=15.4\pm1.0$. The estimated error is large because of the absence of true specific-heat data at temperatures above 36°.

Sulfate.—From thermodynamic calculations of the author (*250*) pertaining to $MgSO_4$, it is estimated that $S_{298.1}=20$. This value seems reasonable in magnitude and probably is not in error by more than ±2 units.

MANGANESE

Element.—The specific heat of Mn was determined by Kelley (*252*) (53°–290°). The entropy is $S_{298.1}=7.61\pm0.06$, of which 0.52 is extrapolation below 53.1°.

The spectroscopic data (*273, p. 2348*) for Mn (*g*) show that only the lowest energy state, whose quantum weight is 6, need be considered in obtaining the entropy at 298.1°. The result is $S_{298.1}=41.50\pm0.01$.

Oxides.—Millar (*315*) (70°–301°) has measured the specific heat of MnO. His data give $S_{70.8}=2.22$ (extrapolation) and $S_{298.1}=14.4\pm0.6$.

An estimate of the entropy of MnO (*g*) may be made from $\omega=836$ (*273, p. 2353*) and a guess of the Mn–O distance, 2.2×10^{-8} cm. The latter corresponds to $I=99\times10^{-40}$. The result is $S_{298.1}=54.0\pm1.5$, of which 0.18 is vibrational entropy.

Specific-heat measurements of MnO_2 also were made by Millar (*315*) (72°–294°). The calculated entropy is $S_{298.1}=13.9\pm0.4$, of which 1.76 is extrapolation below 70.8°.

Kapustinsky and Bayuskina (*221*) have suggested $S_{298.1}=22.9$ for Mn_2O_3, calculated from dissociation-pressure studies of MnO_2.

In addition, Millar (*315*) (72°–306°) has measured the specific heat of Mn_3O_4. His data yield $S_{298.1}=35.5\pm0.7$, the extrapolation being 4.67 below 70.8°.

Sulfide.—Anderson (*13*) (59°–297°) has measured the specific heat of MnS. There is calculated $S_{298.1}=18.7\pm0.3$. The extrapolation below 56.2° is 2.14.

Selenide.—The specific heat of MnSe was determined by Kelley (*252*) (54°–287°). The data yield $S_{298.1}=21.7\pm0.5$, of which 2.78 is extrapolation below 53.1°.

Telluride.—Kelley (*252*) (54°–327°) also measured the specific heat of MnTe. There is obtained $S_{298.1}=22.4\pm0.5$, with an extrapolation below 53.1° of 3.35.

Chloride.—The specific heat of $MnCl_2$ was measured by Trapeznikova and Miljutin (*398*, *399*) (14°–131°). Their data lead to $S_{14.1}=0.16$ (extrapolation) and $S_{298.1}-S_{14.1}=25.75$, making $S_{298.1}=25.9\pm1.0$.

Carbonate.—Anderson (*17*) (55°–297°) has measured the specific heat of $MnCO_3$, rhodochrosite. His results give $S_{298.1}=20.5\pm0.3$. The extrapolation below 56.2° is 1.65.

Permanganate ion.—Latimer, Pitzer, and Smith (*286*) obtained $S_{298.1}=46.7\pm0.4$ for MnO_4^- (*aq.*) from data for the reaction $KMnO_4=K^+ + MnO_4^-$.

MERCURY

Element.—The heat capacity of Hg at low temperatures was studied by Carpenter and Stoodley (*70*) (197°–234°), Pollitzer (*341*, *342*) (31°–243°), and Simon (*368*, *369*) (3°–232°). Pollitzer has measured the heat of fusion as 554.5 calories, while Bridgeman (*52*) has obtained 560 calories per gram-atom. The mean value, 557.2, will be used. Henning (*194*) gave 234.2° as the melting point. The entropy calculations are $S_{3.16}=0.03$ (extrapolation), $S_{234.2}-S_{3.16}=14.47$ (crystals), $\Delta S_{234.2}=557.2/234.2=2.38$ (fusion), and $S_{298.1}-S_{234.2}=1.65$ (liquid). The sum is $S_{298.1}=18.5\pm0.2$ for Hg (*l*).

The Sackur equation gives $S_{298.1}=41.80\pm0.01$ for Hg (*g*). Only the lowest energy state, whose quantum weight is 1, is effective at 298.1°.

Hg_2^{++} ion.—Latimer, Pitzer, and Smith (*286*) have obtained $S_{298.1}=17.7\pm3$ for Hg_2^{++} (*aq.*) from data for the reaction $2Hg+2H^+=Hg_2^{++}+H_2$.

Oxides.—Günther (*187*) (25°–75°) has measured the specific heat of HgO (red). His data lead to $S_{298.1}=16.6\pm1.0$, the extrapolation below 25.1° being 0.83.

The cell measurements of Fried (*149*) give $\Delta S_{298.1}=-13.9$ for the reaction HgO (yellow)$+H_2=H_2O$ (*l*)$+$Hg. As the other entropies are known, there results $S_{298.1}=17.9$ for HgO (yellow). The same reaction was studied by Shibata and Murata (*366*) and Shibata, Kobayashi, and Furukawa (*367*). Their results yield $\Delta S_{298.1}=-13.25$, which corresponds to $S_{298.1}=17.3$ for HgO (yellow). The mean value, $S_{298.1}=17.6\pm0.5$, is adopted.

Mercurous bromide.—From cell measurements, Ishikawa and Ueda (*206*) gave $\Delta F^\circ_{298.1}=-21{,}350$ and $\Delta H_{298.1}=-24{,}470$ for the formation of HgBr from the elements. These figures result in $\Delta S_{298.1}=-10.5$, which, with the values for the constituent elements, yields $S_{298.1}=26.4\pm1.0$ for HgBr. This value appears reasonable, as it is 3 units

higher than that of HgCl, while for the analogous silver salts 2.6 units difference is observed.

Mercurous chloride.—Pollitzer (*341, 342*) (22°–199°) measured the specific heat of HgCl. His data give $S_{298.1}=23.0\pm0.7$. The extrapolation below 22.4° is 1.35.

Better values are obtainable from the cell measurements of Gerke (*154*), who reported $\Delta S_{298.1}=-21.8$ for the reaction $Hg+1/2\ Cl_2=HgCl$ and $\Delta S_{298.1}=7.8$ for the reaction $Ag+HgCl=AgCl+Hg$. The corresponding values for HgCl are $S_{298.1}=23.4\pm0.5$ and $S_{298.1}=23.6\pm0.5$. The mean, $S_{298.1}=23.5\pm0.5$, is adopted for HgCl.

Still another method of obtaining the entropy of HgCl is furnished by the residual ray data of Rubens (*352*). This method already has been discussed. The result in this instance is $S_{298.1}=24.7$ for HgCl.

Mercuric halides.—Data are available (*273, p. 2356*) for computing approximate entropy values for $HgBr_2$ (*g*), $HgCl_2$ (*g*), and HgI_2 (*g*).

For $HgBr_2$ (*g*), $I=1{,}500\times10^{-40}$, $\omega_1=64$ (2), $\omega_2=220$ (1), and $\omega_3=297$ (1). There are computed $S_{t+r,298.1}=62.70$ and $S_{v,298.1}=15.05$, making $S_{298.1}=74.7\pm2$.

The molecular constants reported for $HgCl_2$ are $I=607\times10^{-40}$, $\omega_1=71$ (2), $\omega_2=355$ (1), and $\omega_3=413$ (1). These yield $S_{t+r,298.1}=60.06$ and $S_{v,298.1}=10.32$. Therefore, $S_{298.1}=70.4\pm2$.

Similarly, for HgI_2 (*g*), $I=2{,}750\times10^{-40}$, $\omega_1=50$ (2), $\omega_2=153$ (1), and $\omega_3=233$ (1). There are obtained $S_{t+r,298.1}=64.60$, $S_{v,298.1}=14.13$, and $S_{298.1}=78.7\pm2$.

The above figures, when combined with the heat and free-energy-of-vaporization values of Kelley (*247*), lead to $S_{298.1}=38.9$ for $HgBr_2$ (*s*), $S_{298.1}=34.6$ for $HgCl_2$ (*s*), and $S_{298.1}=42.2$ for HgI_2 (*s*).

Sulfate.—The specific heat of Hg_2SO_4 was measured by Pollitzer (*341, 342*) (23°–203°) and Schutz (*358*) (14°–295°). The data of the former are erratic, and only those of Schutz will be used. His specific-heat curve breaks quite sharply and in peculiar fashion at the lower end, making extrapolation uncertain; results with a spread of 0.4 unit may be obtained, depending on the judgment of the calculator. The results given by Schutz are adopted, $S_{298.1}=48.0\pm0.5$, of which 1.23 is extrapolation below 15.90°. Before Schutz's work, the author (*249, 250*) computed $S_{298.1}=47.9$ from available thermodynamic data for Hg_2SO_4.

MOLYBDENUM

Element.—Simon and Zeidler (*374*) (15°–275°) measured the specific heat of Mo. From their results the value $S_{298.1}=6.83\pm0.05$ may be calculated, the extrapolation below 15.8° being only 0.01.

The lowest energy state of Mo (*g*), which is the only one effective at 298.1°, has the quantum weight 7 (*273, p. 2347*). The entropy is computed to be $S_{298.1}=43.47\pm0.01$.

Sulfides.—The specific heat of MoS_2 was measured by Anderson (*22*) (56°–293°). The entropy is $S_{298.1}=15.0\pm0.2$, of which 1.04 is extrapolation below 56.2°.

Kelley (250) has computed $\Delta S_{298.1}=-13.8$ for the reaction $Mo+3S(rh)=MoS_3$. This value leads to $S_{298.1}=15.9\pm1.0$ for MoS_3.

NEON

Element.—The Sackur equation leads to the value $S_{298.1}=34.96\pm0.01$ for Ne (*g*).

The heat capacity of Ne at low temperatures was measured by Clusius (*80*) (11°–53°). He has also determined the vapor pressure from which the heat of sublimation at the melting point, 24.59°, was calculated to be 510.6 calories. The entropy calculations give $S_{10.0}=0.58$ (extrapolation), $S_{24.59}-S_{10.0}=2.97$ (crystals), $\Delta S_{24.59}=510.6/24.59=20.76$ (sublimation at 323.5 mm. pressure), $\Delta S_{24.59}=-1.70$ (compression from 323.5 mm. to 1 atmosphere pressure), and $S_{298.1}-S_{24.59}=12.39$ (gas, $C_p=4.97$). The sum is $S_{298.1}=35.0\pm0.1$, in excellent agreement with the Sackur value.

NICKEL

Element.—The specific heat of Ni at low temperatures was measured by Bronson and Wilson (*56*) (203°–303°), Clusius and Goldmann (*96*) (10°–26°), Eucken and Werth (*144*) (15°–205°), Keesom and Clark (*226*) (1°–20°), Rodebush and Michalek (*350*) (67°–204°), and Simon and Ruhemann (*372*) (71°–83°). Calculation yields $S_{298.1}=7.12\pm0.05$, of which the extrapolation below 1.1° is ca. 6×10^{-4}.

In obtaining the entropy of Ni (*g*) at 298.1°, the following energy states are to be considered, $^3F_4$, $^3D_3$, $^3D_2$, $^3F_3$, $^3D_1$, and $^3F_2$. The term values are, respectively (*31*), 0, 204.82, 879.82, 1,332.15, 1,713.11, and 2,216.55, and the quantum weights are 9, 7, 5, 7, 3, and 5. These states add 5.391 to the translational entropy given by the Sackur equation, making $S_{298.1}=43.53\pm0.01$.

Oxide.—Seltz, DeWitt, and MacDonald (*362*) (68°–297°) measured the specific heat of NiO. Their data yield $S_{298.1}=9.2\pm0.1$, of which 0.65 is extrapolation below 68°. Kapustinsky and Silbermann (*222*), reported $\Delta S_{298.1}=1.52$ for the reaction $Ni+CO_2=NiO+CO$, which corresponds to $S_{298.1}=12.4$ for NiO. The latter result is given no weight in comparison with the third-law value.

Chloride.—The specific heat of $NiCl_2$ was measured by Trapeznikova, Shubnikov, and Miljutin (*401*) (12°–129°). Calculation gives $S_{12.6}=0.16$ (extrapolation) and $S_{298.1}-S_{12.6}=25.42$. The sum is $S_{298.1}=25.6\pm1.0$.

Carbonyl.—Crawford and Cross (*106*) have approximated the entropy of $Ni(CO)_4$ (*g*)) from molecular constants. They give 1.82×10^{-8} cm. as the Ni–C distance and 1.15×10^{-8} cm. as the C–O distance, the molecule being tetrahedral (symmetry number=12). These interatomic distances yield $I_1=I_2=I_3=795\times10^{-40}$. There is computed $S_{t+r,298.1}=66.42$. Crawford and Cross also report $\omega_1=380$ (1), $\omega_2=2{,}040$ (1), $\omega_3=70$ (2), $\omega_4=460$ (2), $\omega_5=90$ (3), $\omega_6=300$ (3), $\omega_7=540$ (3), $\omega_8=2{,}050$ (3), and $\omega_9=420$ (3). The vibrational entropy is computed as $S_{v,298.1}=30.65$. The sum is $S_{298.1}=97\pm2$.

NITROGEN

Element.—The heat capacity of N_2 at low temperatures was measured by Clusius (*76*) (10°–74°), Eucken (*136*) (16°–73°), Giauque and Clayton (*163*) (15°–78°), and Keesom and Onnes (*243*) (15°–77°). The calculations of Giauque and Clayton, which have been checked, are adopted. They find $S_{10}=0.46$ (extrapolation), $S_{35.61}-S_{10}=6.03$ (crystals II), $\Delta S_{35.61}=54.71/35.61=1.54$ (transition), $S_{63.14}-S_{35.61}$

$=5.59$ (crystals I), $\Delta S_{63.14}=172.3/63.14=2.73$ (fusion), $S_{77.32}-S_{63.14}=2.73$ (liquid), $\Delta S_{77.32}=1{,}332.9/77.32=17.24$ (vaporization), $\Delta S_{77.32}=0.22$ (correction to perfect gas state), and $S_{298.1}-S_{77.32}=9.73$ (gas). The sum is $S_{298.1}=45.9\pm0.1$. Giauque and Clayton also have calculated the entropy from spectroscopic data as $S_{298.1}=45.79\pm0.01$. This figure is the more accurate and is adopted.

The lowest energy state of N (g), which is the only state effective at 298.1°, has the quantum weight 4 (*273, p. 2346*). Adding $R\ ln\ 4$ to the Sackur equation results in $S_{298.1}=36.62\pm0.01$ for N (g).

Nitrous oxide.—The heat capacity of N_2O at low temperatures was measured by Blue and Giauque (*45*) (15°–188°), Clusius, Hiller, and Vaughen (*102*) (10°–61°), Eucken and Hauck (*137*) (90°–170°), and Eucken and Veith (*143*) (heat of fusion). The data and calculations of Blue and Giauque are adopted. They find $S_{14}=0.21$ (extrapolation), $S_{182.26}-S_{14}=16.79$ (crystals), $\Delta S_{182.26}=1{,}563/182.26=8.58$ (fusion), $S_{184.59}-S_{182.26}=0.22$ (liquid), $\Delta S_{184.59}=3{,}958/184.59=21.44$ (vaporization), $\Delta S_{184.59}=0.11$ (correction to perfect gas state), and $S_{298.1}-S_{184.59}=4.08$ (gas). The sum is $S_{298.1}=51.44\pm0.1$.

Blue and Giauque also computed the entropy from the values $I=66.0\times10^{-40}$, $\omega_1=1{,}285.4$ (1), $\omega_2=589.1$ (2), and $\omega_3=2{,}224.1$ (1). The result is $S_{298.1}=52.58\pm0.01$. The value from heat capacities is less than this by 1.14 units. The difference is of the order of $R\ ln\ 2$, which may be attributed to lack of orientation of the N_2O molecules in the crystal lattice of the solid (*45*). The value $S_{298.1}=52.58\pm0.01$ should be employed in connection with other values in this bulletin. Results identical with this also were computed by Badger and Woo (*35*) and Kassel (*224*). Rodebush (*349*) obtained a slightly lower figure but used a moment of inertia now known to be erroneous.

Nitric oxide.—Eucken and Karwat (*139*) (22°–117°) and Johnston and Giauque (*215*) (15°–121°) have studied the heat capacity of NO at low temperatures. The entropy calculations of Johnston and Giauque are repeated here. They find $S_{14.35}=0.27$ (extrapolation), $S_{109.49}-S_{14.35}=8.79$ (crystals), $\Delta S_{109.49}=549.5/109.49=5.02$ (fusion), $S_{121.36}-S_{109.49}=1.73$ (liquid), $\Delta S_{121.36}=3{,}292.6/121.36=27.13$ (vaporization), $\Delta S_{121.36}=0.09$ (correction to perfect gas state). The sum is $S_{121.36}=43.03\pm0.1$. At this temperature the spectroscopic calculations of Johnston and Giauque yield $S_{121.36}=43.75$. The discrepancy is 0.72, very nearly $1/2\ R\ ln\ 2=0.69$. The explanation offered by Johnston and Giauque is that, as the liquid is highly associated into N_2O_2 molecules, it appears reasonable that such effect would persist in the solid, and solid isomers would result if in the association process more than one type of pairing could occur between molecules which retained some of the electronic differences they possessed in the gaseous state. An equimolal mixture of two such isomers would explain the discrepancy. The correct entropy is that given by the spectroscopic data. At 298.1°, Johnston and Giauque calculated $S_{298.1}=50.43$. Johnston and Chapman (*213*) corrected an error in this value and gave $S_{298.1}=50.35$. An additional slight error was discovered by Witmer (*407*), who reduced the figure to $S_{298.1}=50.34$. This last value is adopted. The error should not be over ±0.01.

Dioxide.—To ascertain the entropy of N_2O_4 (g), Giauque and Kemp (*166*) found it necessary to compute the entropy of NO_2 (g) from molecular constant data. They derived $I_1I_2I_3=1.44\times10^{-116}\pm5$

percent from equilibrium data for the reaction $NO_2=NO+1/2\ O_2$. The vibration frequencies used are those given by Sutherland and Penney (*393*), $\omega_1=641$ (1), $\omega_2=1{,}373$ (1), and $\omega_3=1{,}615$ (1). The symmetry number is 2 and the quantum weight of the lowest electronic state is 2. There is obtained $S_{t+r,298.1}=57.05$ and $S_{v,298.1}=0.42$, making $S_{298.1}=57.47\pm0.1$ for NO_2 (g).

Tetroxide.—Giauque and Kemp (*166*) (16°–295°) have measured the heat capacity of N_2O_4 (that is, the equilibrium mixture of N_2O_4 and NO_2). Their calculations are repeated here. They give $S_{15}=0.34$ (extrapolation), $S_{261.90}-S_{15}=31.98$ (crystals), $\Delta S_{261.90}=3{,}502/261.90=13.37$ (fusion), $S_{294.25}-S_{261.90}=3.87$ (liquid), $\Delta S_{294.25}=9{,}110/294.25=30.96$ (vaporization), and $\Delta S_{294.25}=0.10$ (correction to perfect gas state). The sum is $S_{294.25}=80.62\pm0.15$ for the equilibrium mixture of NO_2 (g) and N_2O_4 (g).

At 294.25°, the boiling point, $S_{294.25}=57.35$ for NO_2 (g) is calculated from the data given previously. Giauque and Kemp find the degree of dissociation to be $\alpha=0.161$, from a careful study of available equilibrium data for the reaction $N_2O_4=2NO_2$. By substituting this value in the relationship, $S_{N_2O_4}=\frac{1}{1-\alpha}S\text{ mix.}-\frac{2\alpha}{1-\alpha}S_{NO_2}+R\,ln\frac{1-\alpha}{1+\alpha}+\frac{2\alpha R}{1-\alpha}\,ln\,\frac{2\alpha}{1+\alpha}$, they obtain $S_{294.25}=72.5$ for N_2O_4 (g). This value corresponds to $S_{298.1}=72.7\pm0.2$.

Pentoxide.—A rough value of the entropy of N_2O_5 (s) may be obtained from the specific-heat data of McGraw (*309*) (95°–245°). The extrapolation is large, as $C_p=14.27$ at 95° and is subject to a large uncertainty. There is calculated $S_{298.1}=36.6\pm2$, of which 8.68 is extrapolation below 89.1°.

An estimate of the entropy of N_2O_5 (g) may be made by adding the above result to the entropy of sublimation, $\Delta S_{298.1}=45.2$ (*247*). The result is $S_{298.1}=82$, which can be considered merely an order-of-magnitude calculation.

Nitrosyl bromide.—Blair, Brass, and Yost (*44*) have determined the heat and free energy of the reaction $2NO+Br_2$ (g)$=2NOBr$ (g). Their figures give $\Delta S_{298.1}=-28.98\pm0.3$, from which $S_{298.1}=65.2\pm0.2$ for NOBr (g).

Nitrosyl chloride.—The heat and free energy of the reaction $2NO+Cl_2=2NOCl$ (g) were obtained by Dixon (*119*). From his figures, $\Delta S_{298.1}=-33.6\pm1.0$, which leads to $S_{298.1}=60.2\pm0.6$ for NOCl (g). More recently, Beeson and Yost (*42*) have studied the same reaction and arrived at $\Delta S_{298.1}=-28.0\pm0.5$. This figure leads to $S_{298.1}=63.0\pm0.3$ for NOCl (g).

Jahn (*211*) has computed the entropy from the values $I_1I_2I_3=2.06\times10^{-115}$, $\omega_1=1{,}832$ (1), $\omega_2=633$ (1), and $\omega_3=923$ (1). Beeson and Yost suggested $\omega_2=346$ instead of 633. The results of Jahn are $S_{t+r,298.1}=60.77$ and $S_{v,298.1}=0.54$. To the sum of these he has added $R\ ln\ 4$ for the assumed quantum weight of 4 for the lowest electronic state and reported $S_{298.1}=64.06$.

Evidently more information would be desirable, but for the present the value $S_{298.1}=63.0\pm0.3$ is adopted.

Ammonia.—The heat capacity of NH_3 was determined at low temperatures by Clusius, Hiller, and Vaughen (*102*) (10°–135°), Eucken and Karwat (*139*) (24°–222°), and Overstreet and Giauque

(*332*) (15°–240°). The results obtained by the last-named workers are accepted. They give $S_{15}=0.06$ (extrapolation), $S_{195.36}-S_{15}=10.16$ (crystals), $\Delta S_{195.36}=1{,}351.6/195.36=6.92$ (fusion), $S_{239.68}-S_{195.36}=3.65$ (liquid), $\Delta S_{239.68}=5{,}581/239.68=23.29$ (vaporization), $\Delta S_{239.68}=0.07$ (correction to perfect gas state), and $S_{298.1}-S_{239.68}=1.81$ (gas). The sum is $S_{298.1}=45.94\pm0.1$.

Overstreet and Giauque (*332*) and Stephenson and McMahon (*383*) have computed the entropy from the same molecular constant data and have obtained, respectively, $S_{298.1}=45.91$ and $S_{298.1}=46.03$. The data used are $I_1=I_2=2.782\times10^{-40}$, $I_3=4.33\times10^{-40}$, $\omega_1=3{,}335$ (1), $\omega_2=3{,}540$ (2), $\omega_3=948$ (1), and $\omega_4=1{,}631$ (2). The simplest calculation gives $S_{t+r,298.1}=45.88$ and $S_{v,298.1}=0.13$. The sum is $S_{298.1}=46.01$, which agrees with Stephenson and McMahon. Their value is adopted, $S_{298.1}=46.03\pm0.1$.

Ammonium halides.—Simon (*368*) (20°–291°) has measured the specific heat of NH_4Cl, and Simon, von Simson, and Ruhemann (*375*) have measured the specific heats of NH_4Br (201°–277°), NH_4Cl (205°–276°), NH_4F (203°–284°), and NH_4I (199°–276°). In addition, Zlunitsyn (*418*) (230°–263°) has studied NH_4I. All these substances have temperature ranges in which the specific heat rises to very large values and then falls off abruptly on the high-temperature side. In no instance has the total energy under the "hump" been measured; consequently, it is virtually impossible to use the data in entropy calculations. Moreover, only in the case of NH_4Cl have data been obtained to temperatures low enough to permit reasonably certain extrapolation.

A graphic calculation of the entropy of NH_4Cl, including that under the "hump," gives $S_{298.1}=31.8$, with 0.11 extrapolation below 20°. The error in this value may be quite large as the entropy under the "hump" amounts to nearly one-third of the total. No attempt will be made to utilize the data for the other halides.

Ammonium bicarbonate.—From decomposition-pressure data $S_{298.1}=28.3$ was estimated for NH_4HCO_3 by Kelley and Anderson (*258*). The error in this value is estimated as ±2.0.

Ammonium bisulfide.—The value $S_{298.1}=27.1$ for NH_4HS was suggested by Kelley (*250*) from consideration of thermodynamic properties. The error in this value also is estimated as ±2.0.

Ammonium hydroxide.—Latimer, Pitzer, and Smith (*286*), from data for the reaction NH_3 $(g)+H_2O$ $(l)=NH_4OH$ (*aq.*), report $S_{298.1}=42.8\pm0.4$ for NH_4OH (*aq.*).

Other ammonium compounds.—Crenshaw and Ritter (*107*) have obtained specific-heat data for NH_4CN (203°–283°), NH_4NO_3 (183°–273°), and $(NH_4)_2SO_4$ (183°–283°). The data are insufficient for entropy calculations because of the large extrapolations involved, the difficulties being enhanced by transitions of the NH_4Cl type that occur in all three cases.

Ammonium ion.—The value $S_{298.1}=26.4\pm0.5$ for NH_4^+ (*aq.*) was reported by Latimer, Pitzer, and Smith (*286*). Data for the reaction $NH_4OH=NH_4^++OH^-$ form the basis of this value.

Nitrite ion.—Latimer, Pitzer, and Smith (*286*) gave $S_{298.1}=29.9\pm1.0$ for NO_2^- (*aq.*). This result was obtained from data for the reaction $AgNO_2=Ag^++NO_2^-$.

Nitrate ion.—The entropy of NO_3^- (*aq.*) also was reported by Latimer, Pitzer, and Smith (*286*), $S_{298.1}=35.0\pm0.2$. In this instance,

suitable data were available for two reactions, $KNO_3=K^+ + NO_3^-$ and $Ba(NO_3)_2=Ba^{++}+2NO_3^-$. The individual results were both 35.0 ± 0.3.

OSMIUM

Element.—The value of Lewis and Gibson (*292*) from Dewar's (*117*) data is $S_{298.1}=7.8\pm0.5$ for Os (*s*).

Oxide.—Anderson and Yost (*26*) have computed the entropy of OsO_4 (*g*) from molecular constants. They have taken the molecule as tetrahedral, symmetry number=12, and give 1.66×10^{-8} cm. Os–O distance, $\omega_1=971$ (1), $\omega_2=568$ (2), $\omega_3=1{,}187$ (3), and $\omega_4=688$ (3). The interatomic distance corresponds to $I_1=I_2=I_3=194\times10^{-40}$. There are computed $S_{t+r,298.1}=63.40$ and $S_{v,298.1}=2.25$, making $S_{298.1}=65.6\pm0.5$.

Anderson and Yost (*26*) report also $\Delta F°_{298.1}=-70{,}900$ and $\Delta H_{298.1}=-93{,}600$ for the reaction $Os+2O_2=OsO_4$ (*s*), corresponding to $\Delta S_{298.1}=-76.1$. This figure leads to $S_{298.1}=29.8$ for OsO_4 (*s*). An independent value for this substance may be obtained by subtracting the entropy of sublimation given by Kelley (*247*), $\Delta S_{298.1}=35.8$, from the entropy of the gas. This leads to $S_{298.1}=29.8$ for OsO_4 (*s*) (yellow variety). The close agreement between these values undoubtedly is fortuitous. The figure $S_{298.1}=29.8\pm1.0$ is adopted.

OXYGEN

Element.—Heat-capacity measurements of O_2 at low temperatures were made by Clusius (*76*) (10°–73°), Eucken (*136*) (17°–73°), and Giauque and Johnston (*165*) (12°–91°). The heat of vaporization only was determined by Frank and Clusius (*148*). The calculations of Giauque and Johnston, which have been checked, are repeated here. They find $S_{11.75}=0.32$ (extrapolation), $S_{23.66}-S_{11.75}=1.70$ (crystals III), $\Delta S_{23.66}=22.42/23.66=0.95$ (transition), $S_{43.76}-S_{23.66}=4.66$ (crystals II), $\Delta S_{43.76}=177.6/43.76=4.06$ (transition), $S_{54.39}-S_{43.76}=2.40$ (crystals I), $\Delta S_{54.39}=106.3/54.39=1.95$ (fusion), $S_{90.13}-S_{54.39}=6.46$ (liquid), $\Delta S_{90.13}=1{,}628.8/90.13=18.07$ (vaporization), $\Delta S_{90.13}=0.17$ (correction to perfect gas state), and $S_{298.1}-S_{90.13}=8.35$ (gas). The sum is $S_{298.1}=49.1\pm0.1$.

Giauque and Johnston also have calculated the entropy from spectroscopic data, obtaining $S_{298.1}=49.03$. This value has been checked approximately by Gordon and Barnes (*183*), who report $S_{300}=49.04$. The value $S_{298.1}=49.03\pm0.01$ is adopted for O_2.

The entropy of monatomic O (*g*) is obtainable from the Sackur equation and spectroscopic data. At 298.1°, the only states to be considered are $^2P_2$, $^2P_1$, and $^2P_0$, which have term values 0, 159, and 226, and quantum weights 5, 3, and 1, respectively. These add 4.212 units to the translational entropy, making $S_{298.1}=38.48\pm0.01$.

Ozone.—Stuart (*390*) has tabulated $\omega_1=1{,}046$ (1), $\omega_2=700$ (1), and $\omega_3=1{,}357$ (1) for the O_3 (*g*) molecule. The molecule is not linear, the angle being about 122° according to Stuart, who also gave 1.29×10^{-8} cm. as the distance between nuclear centers. These dimensions yield $I_1=74.2\times10^{-40}$, $I_2=67.3\times10^{-40}$, and $I_3=6.9\times10^{-40}$. There is calculated $S_{t+r,298.1}=56.69$ and $S_{v,298.1}=0.41$. The sum is $S_{298.1}=57.1\pm0.5$.

Neutral OH.—Johnston and Dawson (*214*) have computed $S_{298.1}=43.90\pm0.01$ for neutral OH (*g*) from spectroscopic data.

Hydroxyl ion.—The entropy of OH^- (*aq.*) was given by Latimer, Pitzer, and Smith (*286*) as $S_{298.1}=-2.49\pm0.06$, obtained from data for the reaction H_2O $(l)=H^++OH^-$.

PALLADIUM

Element.—The value given by Lewis and Gibson (*292*), $S_{298.1}=8.9\pm0.5$, for Pd (*s*) is repeated here, as no pertinent new data have appeared.

Spectroscopic data for Pd (*g*) show that only the lowest energy state, quantum weight=1, need be considered at 298.1°. The Sackur equation gives $S_{298.1}=39.92\pm0.01$.

PHOSPHORUS

Element.—Ashley (*30*) and Herzberg (*195*) have investigated the spectra of P_2 (*g*). They gave results yielding $I=90.4\times10^{-40}$ and $I=88.9\times10^{-40}$, respectively. Employing the former value, $S_{t+r,298.1}=51.87$ is computed. Almy (*7*) and Jakowlewa (*212*) gave $\omega=780.4$ and $\omega=776.4$, respectively, as the vibration frequency. Therefore, $S_{v,298.1}=0.23$. The sum is $S_{298.1}=52.1\pm0.3$. Yost and Anderson (*410*) have calculated a virtually identical result, $S_{298.1}=52.0$.

Anderson and Yost (*27*) have computed the entropy of P_4 (*g*) from molecular constants. For the tetrahedral molecule, symmetry number=12, they tabulate 2.21×10^{-8} cm. (*P–P* distance), $I_1=I_2=I_3=248\times10^{-40}$, $\omega_1=372$ (2), $\omega_2=463$ (3), and $\omega_4=607$ (1). These figures yield $S_{t+r,298.1}=61.99$ and $S_{v,298.1}=4.89$, making $S_{298.1}=66.8\pm0.5$ for P_4 (*g*).

The entropy of vaporization of P (*s*) (white) to P_4 (*g*) was given as $\Delta S_{298.1}=24.59$ by Kelley (*247*). Combining this result and the entropy of P_4 (*g*) leads to $S_{298.1}=10.6\pm1.0$ for P (*s*) white, virtually identical with the result of Anderson and Yost, $S_{298.1}=10.55$, whose calculation supersedes the earlier one of Yost and Anderson (*410*).

The entropy of monatomic P (*g*), obtained from the Sackur equation with $R\,ln\,4$ added (*273, p. 2346*), is $S_{298.1}=38.99\pm0.01$.

Tribromide.—Howard and Wilson (*198*) have given $\omega_1=380$ (1), $\omega_2=162$ (1), $\omega_3=400$ (2), and $\omega_4=116$ (2) for the PBr_3 (*g*) molecule. The atoms are at the corners of a pyramid, symmetry number=3, with a P–Br distance of 2.31×10^{-8} cm. and a valence angle of 104°. From these figures $I_1=1{,}740\times10^{-40}$ and $I_2=I_3=910\times10^{-40}$. There is calculated $S_{t+r,298.1}=71.58$ and $S_{v,298.1}=11.82$, making $S_{298.1}=83.4\pm2$ for PBr_3 (*g*).

Trichloride.—Yost and Anderson (*410*) have computed $S_{298.1}=74.7\pm2$ for PCl_3 (*g*). The data used are $I_1=558.3\times10^{-40}$, $I_2=I_3=314.7\times10^{-40}$, $\omega_1=510$ (1), $\omega_2=257$ (1), $\omega_3=480$ (2), and $\omega_4=190$ (2). The older calculation of Yost and Sherborne (*414*) is in error.

From values of the heat and free energy of vaporization (*247*) of PCl_3 (*l*), $\Delta S_{298.1}=22.5$ is computed. This leads to $S_{298.1}=52.2\pm3$ for PCl_3 (*l*). Anderson and Yost (*27*) have given substantially the same value, $S_{298.1}=52.8$.

Pentachloride.—Anderson and Yost (*27*), from data for the reactions PCl_3 $(g)+Cl_2=PCl_5$ (*s*) and PCl_5 $(s)=PCl_5$ (*g*), calculate $S_{298.1}=87.7$ for PCl_5 (*g*) and $S_{298.1}=40.8$ for PCl_5 (*s*). The errors are estimated tentatively as ±3 and ±4, respectively.

Trifluoride.—The entropy of PF_3 (g) also was computed by Yost and Anderson (*410*). The data used are $I_1=176.0\times10^{-40}$, $I_2=I_3=106.6\times10^{-40}$, $\omega_1=890$ (1), $\omega_2=531$ (1), $\omega_3=840$ (2), and $\omega_4=486$ (2). The result is $S_{298.1}=64.2\pm1.0$.

Phosphine.—Clusius and Frank (*94*) (11°–186°) and Stephenson and Giauque (*382*) (15°–186°) have measured the heat capacity of PH_3 at low temperatures. This substance undergoes transitions in the solid state at 88.10° and 49.43°, and it is possible to supercool the form stable between 49.43° and 88.10°. When this is done, however, the supercooled form itself undergoes a transition at 30.39°. Stephenson and Giauque have straightened out the energy relationships among these crystalline species very satisfactorily. The data of Clusius and Frank are quite unsatisfactory in this respect. The calculations of Stephenson and Giauque have been checked and are repeated here. For PH_3, supercooled below 49.43°, they find $S_{15}=0.495$ (extrapolation), $S_{30.29}-S_{15}=2.185$ (crystals III′), $\Delta S_{30.29}=19.6/30.29=0.647$ (transition), and $S_{49.43}-S_{30.29}=4.800$ (crystals II). The sum is $S_{49.43}=8.13$. For the variety stable below 49.43°, $S_{15}=0.338$ (extrapolation), $S_{49.43}-S_{15}=4.041$ (crystals III), and $\Delta S_{49.43}=185.7/49.43=3.757$ (transition). The sum for this path is $S_{49.43}=8.14$. The agreement between these two values of $S_{49.43}$ constitutes a good test of the third law of thermodynamics. The remaining calculations are $S_{88.10}-S_{49.43}=6.71$ (crystals II), $\Delta S_{88.10}=115.8/88.10=1.31$ (transition), $S_{139.35}-S_{88.10}=5.19$ (crystals I), $\Delta S_{139.35}=270.4/139.35=1.94$ (fusion), $S_{185.38}-S_{139.35}=4.14$ (liquid), $\Delta S_{185.38}=3{,}489/185.38=18.82$ (vaporization), $\Delta S_{185.38}=0.14$ (correction to perfect gas state), and $S_{298.1}-S_{185.38}=3.96$ (gas). The total is $S_{298.1}=50.35\pm0.1$.

Yost and Anderson (*410*) and Stephenson and Giauque (*382*) have calculated the entropy of PH_3 (g) from molecular constants. The values $I_1=8.26\times10^{-40}$ and $I_2=I_3=6.221\times10^{-40}$ are used in both calculations. Yost and Anderson used $\omega_1=2{,}306$ (1), $\omega_2=979$ (2), and $\omega_3=1{,}115$ (2), while Stephenson and Giauque employed Fung and Barker's (*150*) assignment, $\omega_1=2{,}327$ (1), $\omega_2=990$ (2), $\omega_3=1{,}121$ (1), and an estimated value $\omega_4=2{,}340$ (2). Both sets of values lead to virtually the same values of $S_{v,298.1}$. The computed entropy is $S_{298.1}=50.5\pm0.3$.

In this instance, it appears better to accept the result from heat-capacity data, $S_{298.1}=50.35\pm0.1$.

Phosphonium iodide.—Crenshaw and Ritter (*107*) (93°–283°) measured the specific heat of PH_4I. At 93° the specific heat is 11.97, making extrapolation both difficult and uncertain. There is estimated $S_{89.1}=10.92$ as the extrapolation and $S_{298.1}-S_{89.1}=21.14$ is computed from the data. The result is $S_{298.1}=32.1\pm2$.

Nitride.—Curry, Herzberg, and Herzberg (*113*) have obtained $I=35.16\times10^{-40}$ and $\omega=1{,}330.3$ for the PN (g) molecule, and Ghosh and Datta (*155*) have given $\omega=1{,}337$. These figures yield $S_{t+r,298.1}=50.42$ and $S_{v,298.1}=0.02$, making $S_{298.1}=50.44\pm0.1$. According to Moreau and Rocquet (*320*), PN (g) is a decomposition product of P_3N_5 obtained when the latter is heated in vacuo to 700° C.

Phosphoric acid.—The entropy of H_3PO_4 ($aq.$) was given as $S_{298.1}=44.0\pm1.5$ by Latimer, Pitzer, and Smith (*286*). The data employed are for the reaction $H_2PO_4^-+H^+=H_3PO_4$ ($aq.$).

Phosphate ions.—Latimer, Pitzer, and Smith (*286*) obtained $S_{298.1}=28.0\pm1.5$ for $H_2PO_4^-$ (*aq.*) from data for the reaction $HPO_4^{--}+H^+=H_2PO_4^-$.

The same investigators reported $S_{298.1}=-2.3\pm1.5$ for HPO_4^{--} (*aq.*) from data for the reaction $Pb_3(PO_4)_2+2H^+=3Pb^{++}+2HPO_4^{--}$.

They also list $S_{298.1}=-45\pm2$ for PO_4^{---} (*aq.*) obtained from data for the reaction $HPO_4^{--}=H^+ + PO_4^{---}$.

PLATINUM

Element.—Kok and Keesom (*262*) (1°–21°)and Simon and Zeidler (*374*) (17°–209°) have measured the specific heat of Pt. Calculation gives $S_{298.1}=10.0\pm0.1$. The extrapolation is about 6×10^{-4} below 1.1°.

Spectroscopic data for Pt (*g*) show that three states are effective at 298.1°—D_3, D_2, and one unlabeled (*273, p. 2349*). The term values are 0, 776, and 824 and the quantum weights are 7, 5, and 9, respectively. It is computed that 4.256 is to be added to 41.72, the Sackur value, making $S_{298.1}=45.98\pm0.2$.

Sulfides.—From thermodynamic data, Kelley (*250*) has computed $S_{298.1}=12.2$ for PtS and $S_{298.1}=17.4$ for PtS_2. The errors in these figures are not readily determinable and may be large.

POTASSIUM

Element.—Eastman and Rodebush (*130*) (68°–287°) and Simon and Zeidler (*374*) (14°–277°) have studied the specific heat of K at low temperatures. Relying entirely on the data of the latter investigators, there is obtained $S_{298.1}=15.2\pm0.2$, of which the extrapolation below 14.1° is 0.45.

For K (*g*), the Sackur equation, with $R\ ln\ 2$ added, gives $S_{298.1}=38.30\pm0.01$.

The moment of inertia and vibration frequency of K_2 (*g*) are $I=492\times10^{-40}$ and $\omega=92.6$, according to Allen and Longair (*6*). These figures give $S_{t+r,298.1}=55.93$ and $S_{v,298.1}=3.62$, making $S_{298.1}=59.5\pm0.5$.

Potassium ion.—Latimer, Pitzer, and Smith (*286*) report $S_{298.1}=24.2\pm0.2$ for K^+ (*aq.*). Data for two reactions, $KCl=K^+ + Cl^-$ and $KBr=K^+ + Br^-$, were employed, and the individual results obtained were 24.2 ± 0.2 and 24.3 ± 0.8.

Bromide.—Nernst (*325, 328*) (78°–90°) made a few specific-heat measurement of KBr. The specific heat at 78.7° is 9.48, so only a rough entropy calculation is possible. The result is $S_{298.1}=22.4\pm1.0$. Residual-ray data of Rubens (*352*) and Rubens and von Wartenburg (*354*) give $S_{298.1}=22.6\pm0.5$. The latter value is the more reliable.

The vibration frequency of KBr (*g*) has been given as $\omega=231$ (*273, p. 2349*). From results of crystal-structure studies, it is estimated that the K–Br distance is 3.3×10^{-8} cm., making $I=472\times10^{-40}$. These figures give $S_{t+r,298.1}=58.48$ and $S_{v,298.1}=1.88$, making $S_{298.1}=60.4\pm1.0$. Niwa (*331*) has estimated $S_{298.1}=58.2\pm1.5$.

Chloride.—Feodosiev (*146*) (86°–298°), Keesom and Clark (*227*) (3°–18°), Lindemann and Schwers (*297*) (22°–90°), Nernst (*325, 328*) (22°–235°), and Southard and Nelson (*381*) (16°–288°) have measured the specific heat of KCl. There is obtained $S_{298.1}=19.76\pm0.1$, of which about 3×10^{-4} is extrapolation below 3°.

The residual-ray data of Rubens (*352*) and Rubens and Hollnagel (*353*) give $S_{298.1}=19.5\pm0.5$, in good agreement with the more reliable value given above.

The vibration frequency of KCl (*g*) is $\omega=280$ (*273, p. 2349*). The interatomic distance is estimated as 3.1×10^{-8} cm., corresponding to $I=295\times10^{-40}$. These figures yield $S_{t+r,298.1}=56.15$, $S_{v,298.1}=1.54$, and $S_{298.1}=57.7\pm1.0$. Another value was computed by the author (*247*) from vapor-pressure data and the entropy of the solid, $S_{298.1}=57.6$, which is in excellent agreement with the above result. Niwa (*331*) has obtained $S_{298.1}=56.0\pm1.4$, also from vapor-pressure data.

Fluoride.—Niwa (*331*) has estimated $S_{298.1}=56.7\pm1.8$ for KF (*g*).

Iodide.—From Rubens and von Wartenberg's (*354*) residual-ray data, $S_{298.1}=24.1\pm0.5$ is computed for KI.

Hydride.—The moment of inertia and vibration frequency of KH (*g*) have been reported as $I=8.18\times10^{-40}$ and $\omega=969$, respectively (*273, p. 2349*). There is calculated $S_{t+r,298.1}=47.18$, $S_{v,298.1}=0.11$, and $S_{298.1}=47.3\pm0.1$.

Bromate.—Ahlberg and Latimer (*4*) (15°–297°) have measured the specific heat of $KBrO_3$. Their results give $S_{298.1}=35.7\pm0.2$, of which 0.23 is extrapolation below 14.13°.

Chlorate.—The specific heat of $KClO_3$ was measured by Latimer, Schutz, and Hicks (*288*) (13°–294°). There is computed $S_{298.1}=34.2\pm0.2$, with an extrapolation below 12.59° of 0.14.

Perchlorate.—Latimer and Ahlberg (*279*) (12°–299°) have studied the specific heat of $KClO_4$. Calculation gives $S_{298.1}=36.1\pm0.3$. The extrapolation is 0.29 below 12.6°.

Iodate.—The specific heat of KIO_3 also was measured by Ahlberg and Latimer (*4*) (17°–295°). The results of the entropy calculations are $S_{15.85}=0.36$ (extrapolation) and $S_{298.1}=36.2\pm0.2$.

Nitrate.—Southard and Nelson (*381*) (15°–296°) have investigated the specific heat of KNO_3. From these data, $S_{14.13}=0.22$ (extrapolation) and $S_{298.1}=31.8\pm0.2$.

Permanganate.—The specific heat of $KMnO_4$ was measured by Brown, Smith, and Latimer (*60*) (14°–296°). Their results yield $S_{15}=0.63$ (extrapolation) and $S_{298.1}-S_{15}=40.46$, making $S_{298.1}=41.1\pm0.2$.

Sulfate.—From consideration of the thermodynamic properties of K_2SO_4, Kelley (*250*) computed $S_{298.1}=44.8$. No attempt is made to estimate the error in this value. However, it appears reasonable compared with the result for Ag_2SO_4, $S_{298.1}=47.9$, allowance being made for the smaller mass of the potassium atom.

RADON

Element.—The Sackur equation gives $S_{298.1}=42.10\pm0.01$ for Rn (*g*).

RHENIUM

Element.—Spectroscopic data show that the lowest energy state of Re (*g*) has the quantum weight 6 (*273, p. 2348*). No other states are occupied at 298.1°. Therefore, from the Sackur equation plus $R\ ln\ 6$, $S_{298.1}=45.14\pm0.01$.

RHODIUM

Element.—A revision of the entropy of Rh (*s*) is not possible, as no new pertinent data have appeared. The result of Lewis and Gibson (*292*), $S_{298.1}=7.6\pm0.5$, is therefore repeated.

According to the data assembled by Bacher and Goudsmit (*31*), the only energy levels of Rh (*g*) to be considered at 298.1° are $^4F_{9/2}$, $^4F_{7/2}$, and $^4F_{5/2}$, which have the term values 0, 1,530, and 2,598 and quantum weights 10, 8, and 6, respectively. These states add 4.584 to the translational entropy computed from the Sackur equation, 39.81, making $S_{298.1}=44.40\pm0.1$.

RUBIDIUM

Element.—The Sackur equation, with *R ln* 2 added, gives $S_{298.1}=40.64\pm0.01$ for Rb (*g*).

From vapor-pressure data and the above entropy value of the gas, $S_{298.1}=16.6\pm1.0$ was computed for Rb (*s*) by Kelley (*247*).

Rubidium ion.—Latimer, Pitzer, and Smith (*286*) have reported $S_{298.1}=28.7\pm0.7$ for Rb^+ (*aq.*). Two reactions were considered, $RbClO_3=Rb^++ClO_3^-$ and $RbClO_4=Rb^++ClO_4^-$. The individual values obtained are 28.9 ± 0.8 and 28.5 ± 1.0.

Halides.—Niwa (*331*) has estimated $S_{298.1}=57.9\pm2.0$ for RbCl (*g*) and $S_{298.1}=62.2\pm2.0$ for RbI (*g*). From residual-ray data (*271, p. 560*), $S_{298.1}=21.2\pm1.0$ is computed for RbCl (*s*).

Chlorate.—Ahlberg (*1*) (16°–291°) has measured the specific heat of $RbClO_3$. Calculation from his data yields $S_{16.8}=0.48$ (extrapolation) and $S_{298.1}=36.3\pm0.4$.

RUTHENIUM

Element.—Bacher and Goudsmit (*31*) give $^5F_5$, $^5F_4$, and $^5F_3$ as the lowest energy states of Ru (*g*). The term values and quantum weights are, respectively, 0, 1,191, and 2,092, and 11, 9, and 7. The translational entropy from the Sackur equation is $S_{t,298.1}=39.78$, to which must be added 4.802 for the above given states. The result is $S_{298.1}=44.58\pm0.1$.

The only available entropy figure for Ru (*s*) is that given by Lewis and Gibson (*292*): $S_{298.1}=6.9\pm0.5$.

Sulfide.—From thermodynamic data, Kelley (*250*) has given values corresponding to $S_{298.1}=13.2$ for RuS_2. The probable error is at least ±1.0.

SAMARIUM

Sulfate.—The specific heat of $Sm_2(SO_4)_3\cdot8H_2O$ was measured by Ahlberg and Freed (*3*) (17°–297°) and Ahlberg, Blanchard, and Lundberg (*5*) (2.5°–41°). The lowest energy state of Sm^{+++} is $^6H_{5/2}$, with quantum weight 6. In computing the entropy, $2R\ ln\ 6$ per gram-formula mass is added to the value calculated in the usual manner from the specific-heat data. The result is $S_{2.51}=0.09$ (ordinary extrapolation below 2.51°)$+(S_{298.1}-S_{2.51})=153.67$ (from measurements)$+7.12$ ($2R\ ln\ 6$, splitting of lowest energy level of Sm^{+++}) $=160.9=S_{298.1}$.

SCANDIUM

Available spectroscopic data (*31*) show that two states must be considered in calculating the entropy of Sc (*g*) at 298.1°—$^2D_{3/2}$ and $^2D_{5/2}$—separated by 168 cm.$^{-1}$ and having quantum weights 4 and 6, respectively. The translational entropy from the Sackur equation is 37.353 and these states add 4.417, making $S_{298.1}=41.77\pm0.1$.

SELENIUM

Element.—Anderson (*24*) (54°–297°) and DeVries and Dobry (*116*) (98°–279°) have measured the specific heat of Se (crystalline). Anderson also has made measurements on the glassy form (49°–300°). Calculation of the entropy will be based upon Anderson's data for the crystals. There is obtained $S_{298.1}=10.0\pm0.5$, of which 1.95 is extrapolation below 53.1°. This is 0.5 unit lower than the value calculated by Anderson but is in agreement with the findings of Slansky and Coulter (*376*), who have intercompared the available data for S, Se, and Te.

Bacher and Goudsmit (*31*) give the lowest energy levels of Se (*g*) as $^3P_2$, $^3P_1$, and $^3P_0$, with quantum weights 5, 3, and 1 and term values 0, 1,990, and 2,534, respectively. These states add 3.198 to the Sackur value, 39.02, making $S_{298.1}=42.22\pm0.1$.

The moment of inertia, $I=300\times10^{-40}$, vibration frequency, $\omega=387$, quantum weight of the lowest electronic level (3), and symmetry number (2) have been recorded for Se_2 (*g*) (*273, p. 2353*). Calculation gives $S_{t+r,298.1}=60.23$, $S_{v,298.1}=1.02$, making $S_{298.1}=61.2\pm0.3$.

Hexafluoride.—From data of Yost, Steffens, and Gross (*416*), Yost (*409*), and Sachsse and Bartholome (*356*), the following data are available, $I_1=I_2=I_3=362\times10^{-40}$, $\omega_1=708$ (1), $\omega_2=662$ (2), $\omega_3=405$ (3), $\omega_4=245$ (3), $\omega_5=461$ (3), $\omega_6=787$ (3), and symmetry number=24. There are computed $S_{t+r,298.1}=63.06$ and $S_{v,298.1}=12.14$. The sum is $S_{298.1}=75.2\pm2.0$.

SILICON

Element.—Anderson (*10*) (61°–297°) and Nernst and Schwers (*329*) (20°–90°) have measured the specific heat of Si at low temperatures. The data of Anderson were joined to the lower-temperature values of Nernst and Schwers and $S_{298.1}=4.50\pm0.05$ calculated. The extrapolation is 0.007 below 20.0°.

The entropy of Si (*g*) may be computed from the Sackur equation and spectroscopic data. At 298.1° the states to be considered are $^3P_0$, $^3P_1$, and $^3P_2$, having term values 0, 77, and 223 and quantum weights 1, 3, and 5, respectively (*273, p. 2345*). These states add 4.190 to the value for the translational entropy. The result is $S_{298.1}=40.13\pm0.01$.

Oxides.—Anderson (*20*) (53°–297°), Günther (*189*) (71°–89°), and Nernst (*325*) (25°–233°) have measured the specific heat of SiO_2, quartz. Anderson's data are given the most weight in obtaining $S_{298.1}=10.1\pm0.1$. The extrapolation below 50.1° is 0.76. The older data of Günther and Nernst, considered alone, give $S_{298.1}=9.9$.

The specific heat of SiO_2, cristobalite, was measured by Anderson (*20*) (54°–298°) and Simon (*368*) (28°–117°). The data of Simon yield $S_{298.1}=10.4\pm0.1$, of which 0.08 is extrapolation below 17.8°. Those of Anderson give $S_{298.1}=10.3\pm0.1$, with an extrapolation of 0.99 below 50.1°. The mean, $S_{298.1}=10.35\pm0.1$, is adopted.

Anderson (*20*) (54°–295°) also measured the specific heat of SiO_2, tridymite. For this substance $S_{298.1}=10.5\pm0.2$, and the extrapolation below 50.1° is 0.97.

Nernst (*325*) (26°–233°), Simon (*368*) (18°–288°), and Simon and Lange (*371*) (10°–13°) have measured the specific heat of SiO_2, glass. From the data of the two latter investigations, $S_{298.1}-S_0=10.35\pm0.1$ is calculated, with an extrapolation below 10° of only 0.02. Simon

and Lange have given the value $S_0=0.9\pm0.3$ for the entropy of SiO_2 glass at 0°. Adding this quantity, there is obtained $S_{298.1}=11.2\pm0.4$.

Tetrachloride.—Yost and Blair (*411*) have computed $S_{298.1}=79.2$ for $SiCl_4$ (*g*). This calculation has been checked. The data employed are $I_1=I_2=I_3=620\times10^{-40}$, $\omega_1=422$ (1), $\omega_2=148$ (2), $\omega_3=608$ (3), $\omega_4=220$ (3), and symmetry number=12. These values give $S_{t+r,298.1}=65.64$ and $S_{v,298.1}=13.52$, making $S_{298.1}=79.2\pm1.0$.

From vapor-pressure data, the entropy of vaporization at 298.1° is $\Delta S_{298.1}=21.8$ (*247*). This value and the above result for the gas yield $S_{298.1}=57.4$ for $SiCl_4$ (*e*). Latimer (*276*) has obtained $S_{298.1}=56.4$ for this substance, which agrees within the limits of error of either result. However, recalculation of Latimer's heat-capacity data yields the following: $S_{70.8}=10.30$ (extrapolation), $S_{203.3}-S_{70.8}=24.75$ (crystals), $\Delta S_{203.3}=1{,}845/203.3=9.08$ (fusion), and $S_{298.1}-S_{203.3}=13.11$ (liquid). The sum is $S_{298.1}=57.2$ for $SiCl_4$ (*e*). The value $S_{298.1}=57.3\pm2.0$ is adopted.

Tetrafluoride.—Yost (*409*) has recorded $\omega_1=297$ (1), $\omega_2=268$ (2), $\omega_3=1{,}000$ (3) (uncertain), $\omega_4=463$ (3), and 1.54×10^{-8} cm. Si–F distance for the SiF_4 (*g*) molecule. There are computed $I_1=I_2=I_3=198\times10^{-40}$, $S_{t+r,298.1}=60.80$, and $S_{v,298.1}=7.24$. The sum of the entropy figures is $S_{298.1}=68.0\pm1.0$. Yost gives 67.0, which the author was unable to check.

Monosilane.—Molecular constants recorded (*273, p. 2359*) for SiH_4 (*g*) are $I_1=I_2=I_3=8.9\times10^{-40}$, $\omega_1=910$ (3), $\omega_2=978$ (2), $\omega_3=2{,}187$ (1), $\omega_4=2{,}183$ (3), and symmetry number=12. There are calculated $S_{t+r,298.1}=48.05$ and $S_{v,298.1}=0.62$, making $S_{298.1}=48.7\pm0.1$.

Clusius (*78*) (11°–160°) has measured the specific heat and heats of transition and fusion of SiH_4. The heat of vaporization was computed by Kelley (*247*) from vapor-pressure data as 2,955 calories at the boiling point, 161.5°. In warming the gas from 161.5° to 298.1°, specific heats of the gas, computed from the above given molecular constants, were employed. The entropy calculations are $S_{11.22}=0.26$ (extrapolation), $S_{63.45}-S_{11.22}=7.77$ (crystals II), $\Delta S_{63.45}=147.1/63.45=2.32$ (transition), $S_{88.48}-S_{63.45}=4.00$ (crystals I), $\Delta S_{88.48}=159.5/88.48=1.80$ (fusion), $S_{161.5}-S_{88.48}=8.77$ (liquid), $\Delta S_{161.5}=2{,}955/161.5=18.30$ (vaporization), and $S_{298.1}-S_{161.5}=5.48$ (gas). The sum is $S_{298.1}=48.7\pm0.2$, which is identical with the value calculated from molecular constants.

Carbide.—The specific heat of SiC was measured by Nernst and Schwers (*329*) (52°–97°), Günther (*187*) (53°–76°), and Kelley (*257*) (54°–293°). Relying wholly on the last investigation, there is computed $S_{298.1}=3.95\pm0.02$. The extrapolation below 53.1° is only 0.043.

Nitride.—Kelley (*251*) estimated $S_{298.1}=22.8$ for Si_3N_4 from data for the reaction $3Si+2N_2=Si_3N_4$. The error in this value may be a few units.

SILVER

Element.—The specific heat of Ag at low temperatures was measured by Bronson and Wilson (*56*) (193°–303°), Eucken, Clusius, and Woitinek (*145*) (11°–206°), Keesom and Kok (*231, 236*) (1.35°–21°), Meads (*313*) (15°–298°), and Nernst (*325, 328*) (35–273°). The entropy computed is $S_{298.1}=10.20\pm0.05$. The extrapolation below 1.35° is virtually negligible, since $C_p=2.44\times10^{-4}$ calories per gram-atom at this temperature.

The entropy of Ag (g) may be obtained from the Sackur equation with $R \ln 2$ added (*273, p. 2345*). The result is $S_{298.1}=41.33\pm0.01$.

Silver ion.—Latimer, Pitzer, and Smith (*286*) reported $S_{298.1}=17.54\pm0.15$ for Ag^+ ($aq.$). Data for two reactions were considered, $Ag_2O+2H^+=2Ag^++H_2O$ and $AgCl=Ag^++Cl^-$, which give, respectively, the values 17.46 ± 0.2 and 17.62 ± 0.2. The result of Lingane and Larson (*298*), $S_{298.1}=16.7$, is not in good agreement with these values.

Oxide.—Pitzer and Smith (*339*) (12°–286°) have measured the specific heat of Ag_2O. They found a region between liquid-hydrogen and liquid-air temperatures in which the specific heat was not reproducible. Calculation gives $S_{298.1}=29.1\pm0.3$, with an extrapolation below 12.59° of 0.72. This value is adopted.

Two other values are to be mentioned. The free-energy equation of Lewis and Randall (*296*) results in $\Delta S_{298.1}=-17.3$ for the reaction $2Ag+1/2\ O_2=Ag_2O$, which makes $S_{298.1}=27.6\pm2.0$ for Ag_2O. Moreover, in a discussion of the properties of Ag_2CO_3, Kelley and Anderson (*258*) derived $S_{298.1}=29.7\pm2.0$ for Ag_2O.

Sulfide.—Kimura (*261*) has studied the reaction $2Ag+H_2S=H_2+Ag_2S$ (α). His results give $\Delta S_{298.1}=-3.83$, corresponding to $S_{298.1}=34.5$ for Ag_2S (α). Kelley (*247*), from a consideration of available thermodynamic data, has obtained $S_{298.1}=35.0$, in which the error is here estimated as ±1.0. The latter entropy value is adopted.

Bromide.—Eastman and Milner (*129*) (24°–290°) and Eucken, Clusius, and Woitinek (*145*) (11°–274°) have measured the specific heat of AgBr. The entropy calculated from the combined data is $S_{298.1}=25.60\pm0.1$, of which 0.27 is extrapolation below 11.22°. The residual-ray data of Rubens (*352*) lead to the value $S_{298.1}=26.1\pm0.5$.

The vibration frequency of AgBr (g) has been reported as $\omega=249$ (*273, p. 2350*). Estimating the Ag–Br distance as 3.1×10^{-8} cm. results in $I=730\times10^{-40}$. There is computed $S_{t+r,298.1}=60.70$, $S_{v,298.1}=1.41$, and $S_{298.1}=62.1\pm1.0$ for AgBr (g).

Chloride.—The specific heat of AgCl was studied by Clusius and Harteck (*97*) (10°–126°), Eastman and Milner (*129*) (15°–293°), Nernst and Schwers (*329*) (22°–92°), and Nernst (*325*) (23°–208°). From the data of Clusius and Harteck and of Eastman and Milner there is obtained $S_{298.1}=23.0\pm0.1$, of which 0.14 is extrapolation below 10°. The residual-ray data of Rubens (*352*) permit calculation of $S_{298.1}=22.5\pm0.5$.

The entropy of AgCl (g) may be estimated from that of the solid and vapor-pressure data (*247*). There is obtained $S_{298.1}=59.7\pm2.0$. Another calculation of this quantity may be made from the vibration frequency, $\omega=342$ (*273, p. 2350*), and an estimate of the Ag–Cl distance, 2.9×10^{-8} cm. The latter corresponds to $I=370\times10^{-40}$. The results are $S_{t+r,298.1}=58.55$, $S_{v,298.1}=1.21$, and $S_{298.1}=59.8\pm1.0$. The two values are in good agreement.

Iodide.—Nernst and Schwers (*329*) (17°–117°) and Nernst (*325*) (29°–80°) have made specific-heat measurements of AgI. Their data result in $S_{298.1}=27.1\pm1.0$, with 1.93 extrapolation below 17.8°.

A more reliable figure is obtainable from Gerke's (*154*) cell measurements, which give $\Delta S_{298.1}=-8.0$ for the reaction $Pb+2AgI=PbI_2+2Ag$. This value results in $S_{298.1}=27.6\pm0.4$ for AgI.

The entropy of AgI (g) is estimated from $\omega=206$ (*273, p. 2350*) and the assumed value, 3.3×10^{-8} cm., for the Ag–I distance, cor-

responding to $I=1{,}050\times10^{-40}$. The results are $S_{t+r,298.1}=62.09$, $S_{v,298.1}=2.09$, and $S_{298.1}=64.2\pm1.0$.

Hydrides.—For AgH (*g*) there have been reported (*273, p. 2350*) $I=4.355\times10^{-40}$ and $\omega=1{,}776$. These figures give $S_{t+r,298.1}=48.90$ and $S_{v,298.1}=0.004$, making $S_{298.1}=48.9\pm0.1$.

The value $I=8.486\times10^{-40}$ was reported (*273, p. 2350*) for AgD. The vibration frequency apparently is unknown, but the vibrational entropy should be small, probably of the order of 0.04. As $S_{t+r,298.1}=50.26$, the value $S_{298.1}=50.3\pm0.1$ may be taken for AgD (*g*).

Carbonate.—Anderson (*15*) (53°–291°) measured the specific heat of $AgCO_3$. His data yield $S_{298.1}=40.0\pm0.9$. The extrapolation below 56.2° is 7.86.

Chromate.—Smith, Pitzer, and Latimer (*379*) (15°–295°) measured the specific heat of Ag_2CrO_4. Recalculation of their data gives $S_{298.1}=52.0\pm0.3$, of which 1.29 is extrapolation below 15.85°.

Chlorite.—The specific heat of $AgClO_2$ also was measured by Smith, Pitzer, and Latimer (*378*). There is computed $S_{298.1}=32.2\pm0.3$, with 0.44 extrapolation below 14.13°.

Iodate.—The specific heat of $AgIO_3$ was measured by Greensfelder and Latimer (*186*) (16°–298°). The entropy calculation yields $S_{15.85}=0.56$ (extrapolation) and $S_{298.1}=37.5\pm1.0$.

Nitrite.—Brown, Smith, and Latimer (*61*) (14°–295°) measured the specific heat of $AgNO_2$. There is here computed $S_{298.1}=30.6\pm0.2$, the extrapolation below 14.1° being 0.58.

Nitrate.—Smith, Brown, and Pitzer (*377*) (13°–297°) investigated the low-temperature specific heat of $AgNO_3$. Their data yield $S_{298.1}=33.7\pm0.2$, the extrapolation being 0.38 below 12.59°.

Sulfate.—The specific heat of Ag_2SO_4 was determined by Latimer, Hicks, and Schutz (*284*) (14°–297°). There is computed $S_{298.1}=47.9\pm0.3$ from their data. The extrapolation below 14.13° is 0.79.

$Ag(NH_3)_2^+$ (aq.).—Latimer, Pitzer, and Smith (*286*) obtained $S_{298.1}=57.8\pm1.0$ for $Ag(NH_3)_2^+$ (*aq.*) from data for the reaction $Ag^+ + 2NH_3$ (*aq.*) $= Ag(NH_3)_2^+$.

SODIUM

Element.—The specific heat of Na at low temperatures was measured by Eastman and Rodebush (*130*) (64°–294°), Günther (*188*) (87°–124°), and Simon and Zeidler (*374*) (16°–118°). Relying largely on the data of the last-mentioned investigators, $S_{298.1}=12.2+0\ 1$ is obtained. The extrapolation below 12.6° is 0.09.

For Na (*g*) at 298.1°, the Sackur equation with $R\ ln\ 2$ added gives $S_{298.1}=36.72\pm0.01$.

Allen and Longair (*6*) have recorded $I=179.5\times10^{-40}$ and $\omega=159$ for the Na_2 (*g*) molecule. These figures yield $S_{t+r,298.1}=52.35$, $S_{v,298.1}=2.58$, and $S_{298.1}=54.9\pm0.3$.

Sodium ion.—Latimer, Pitzer, and Smith (*286*) report $S_{298.1}=14.0\pm0.4$ for Na^+ (*aq.*). This value is based upon thermal data for the reactions $NaCl=Na^+ + Cl^-$, $NaNO_3=Na^+ + NO_3^-$, and $Na+H^+=Na+1/2H_2$, from which they calculated, respectively, the values 14.1 ± 0.5, 14.3 ± 0.5, and 13.7 ± 0.5.

Oxide.—From low-temperature specific-heat data for three sodium silicates and the approximately additive properties of silicates, Kelley

(*253*) has suggested $S_{298.1}=17$ for Na_2O. The error in this value is taken tentatively as ± 1.0.

Bromide.—The entropy of NaBr (*g*) may be estimated from $\omega=315$ (*273, p. 2349*) and the assumption of 2.9×10^{-8} cm. as the Na–Br distance, the latter corresponding to $I=250\times10^{-40}$. There results $S_{t+r,298.1}=56.77$ and $S_{v,298.1}=1.34$, making $S_{298.1}=58.1\pm1.0$. Niwa (*331*) has estimated $S_{298.1}=57.8\pm2.0$ from vapor-pressure data and an assumed entropy of NaBr (*s*).

Chloride.—The specific heat of NaCl was measured by McGraw (*309*) (95°–245°) and Nernst (*325, 328*) (25°–84°). The data of the former are very poor and are given no weight. From Nernst's work, $S_{298.1}=17.3\pm0.5$, the extrapolation being 0.20 below 25.1°. The residual-ray data of Rubens (*352*) and Rubens and Hollnagel (*353*) lead to $S_{298.1}=17.2\pm0.5$, a good agreement.

The entropy of NaCl (*g*) may be approximated from $\omega=380$ (*273, p. 2349*) and the estimate 2.8×10^{-8} as the Na–Cl distance. The latter figure makes $I=180\times10^{-40}$. There are computed $S_{t+r,298.1}=54.44$, $S_{v,298.1}=1.04$, and $S_{298.1}=55.5\pm1.0$. From vapor-pressure data, Kelley (*247*) obtained $S_{298.1}=56.4$, which was reported as 46.4, owing to a typographical error. Niwa (*331*) from his own more recent vapor-pressure data has estimated $S_{298.1}=55.4\pm1.4$.

Fluoride.—Niwa (*331*) estimated $S_{298.1}=53.8\pm1.8$ for NaF (*g*). Residual-ray data (*273, p. 758*) lead to $S_{298.1}=13.1\pm0.5$ for NaF (*s*).

Iodide.—The entropy of NaI (*g*) is estimated from $\omega=286$ (*273, p. 2349*) and the assumption of 3.2×10^{-8} cm. as the K–I distance. The corresponding moment of inertia is $I=330\times10^{-40}$. The results are $S_{t+r,298.1}=58.45$, $S_{v,298.1}=1.51$, and $S_{298.1}=60.0\pm1.0$.

Hydrides.—The values $I=5.725\times10^{-40}$ and $\omega=1{,}152$ have been reported (*273, p. 2349*) for NaH (*g*). These lead to $S_{t+r,298.1}=44.94$ and $S_{v,298.1}=0.05$, making $S_{298.1}=45.0\pm0.1$.

Similarly, $I=10.93\times10^{-40}$ and $\omega=826$ have been reported (*273, p. 2349*) for NaD (*g*). There are computed $S_{t+r,298.1}=46.35$, $S_{v,298.1}=0.19$, and $S_{298.1}=46.5\pm0.1$.

Hydroxide.—Shibata (*364, 365*) has obtained $\Delta F^\circ_{298.1}=-111{,}155$ and $\Delta H_{298.1}=-114{,}932$ for the reaction $2Na+HgO+H_2O=2NaOH+Hg$. The entropy of reaction is $\Delta S_{298.1}=-12.7$, which leads to $S_{298.1}=14.2\pm1.5$ for NaOH (*s*).

Carbonate.—Anderson's (*15*) (54°–290°) specific-heat measurements result in $S_{298.1}=32.5\pm0.6$ for Na_2CO_3. The extrapolation below 56.2° is 4.10.

Bicarbonate.—Anderson (*15*) (54°–296°) also measured the specific heat of $NaHCO_3$. The data lead to $S_{298.1}=24.4\pm0.4$, of which 2.19 is extrapolation below 56.2°.

Nitrate.—The specific heat of $NaNO_3$ was measured by Southard and Nelson (*381*) (16°–287°). There is calculated $S_{298.1}=27.8\pm0.1$, with an extrapolation of 0.15 below 15.85°.

Silicates.—Kelley (*253*) has measured the specific heats of Na_4SiO_4 (54°–299°), Na_2SiO_3 (53°–295°), and $Na_2Si_2O_5$ (54°–295°). The following results are obtained from these data:

For Na_4SiO_4, $S_{53.1}=2.48$ (extrapolation) and $S_{298.1}=46.8\pm0.6$;
For Na_2SiO_3, $S_{53.1}=1.39$ (extrapolation) and $S_{298.1}=27.2\pm0.3$; and
For $Na_2Si_2O_5$, $S_{53.1}=3.43$ (extrapolation) and $S_{298.1}=39.4\pm0.6$.

Sulfates.—The specific heats of Na_2SO_4 (13°–314°) and $Na_2SO_4\cdot10H_2O$ (14°–299°) were measured by Pitzer and Coulter (*338*). There

are computed $S_{13.3}=0.05$ (extrapolation) and $S_{298.1}=35.7\pm0.1$ for Na_2SO_4, and $S_{14.1}=0.6$ (extrapolation) and $S_{298.1}=140.5\pm0.3$ for $Na_2SO_4\cdot10\ H_2O$.

NaK.—The values $I=287\times10^{-40}$ and $\omega=123.5$ have been reported (*273, p. 2349*) for NaK (*g*). The figure for I is given as questionable but it may be shown to lead to a reasonable entropy value. There are computed $S_{t+r,298.1}=55.55$ and $S_{v,298.1}=3.05$, making $S_{298.1}=58.6\pm0.5$. As a test of this value, the entropy may be computed as the mean of the values for Na_2 (*g*) and K_2 (*g*) with *R ln* 2 added to take care of the difference in symmetry number. Thus, $S_{298.1}=1/2\ (54.93+59.55)+1.38=58.6$.

STRONTIUM

Element.—The entropy of Sr (*g*) may be obtained directly from the Sackur equation, as only the lowest energy state, whose quantum weight is 1, is effective at 298.1°. The result is $S_{298.1}=39.33\pm0.01$.

Strontium ion.—Latimer, Pitzer, and Smith (*286*) obtained $S_{298.1}=-7.3\pm1.5$ for Sr^{++} (*aq.*) from data relating to the reaction $SrCO_3+2H^+=Sr^{++}+H_2O\ (l)+CO_2\ (g)$.

Oxide.—The specific heat of SrO was measured by Anderson (*18*) (57°–299°). From his data $S_{298.1}=13.0\pm0.2$. The extrapolation below 56.2° is 1.17.

Mahla (*303*) has reported $I=74.1\times10^{-40}$ and $\omega=633$ for SrO (*g*). These figures give $S_{t+r,298.1}=54.38$, $S_{v,298.1}=0.41$, and $S_{298.1}=54.8\pm0.5$.

Carbonate.—Anderson (*16*) (54°–292°) has measured the specific heat of $SrCO_3$, strontianite. There is calculated $S_{298.1}=23.2\pm0.4$, with an extrapolation of 2.11 below 56.2°.

Sulfate.—The thermodynamic properties of $SrSO_4$ were discussed by Kelley (*250*). His figures lead to $S_{298.1}=28.2$, in which the error may be a few units.

SULFUR

Element.—The specific heat of rhombic sulfur, S (*rh*), was measured by Eastman and McGavock (*128*) (12°–366°) and Nernst (*325*) (22°–202°). The more recent and more extensive data of the former investigators give $S_{298.1}=7.62\pm0.05$, of which 0.12 is extrapolation below 15°.

Eastman and McGavock (*128*) (64°–378°) and Nernst (*325*) (83°–201°) also measured the specific heat of monoclinic sulfur, S (*mon*). Again the values from Eastman and McGavock's work are adopted. They compute 0.16 as the difference in entropy between the monoclinic and rhombic modifications, making $S_{298.1}=7.78\pm0.1$ for S (*mon*).

The entropy of monatomic S (*g*) at 298.1° may be obtained from the Sackur equation and spectroscopic data. The energy states to be considered are $^3P_2$, $^3P_1$, and $^3P_0$, with term values 0, 398, and 572 and quantum weights 5, 3, and 1, respectively (*273, p. 2347*). These states add 3.759 to the translational contribution, making $S_{298.1}=40.10\pm0.01$.

Badger (*33*) has reinterpreted the spectroscopic data for S_2 (*g*) and has obtained 1.840×10^{-8} cm. as the S–S distance. This corresponds to $I=89.4\times10^{-40}$. According to Hubin (*199*) the vibration frequency is $\omega=728$. The quantum weight of the lowest electronic state is 3. These figures yield $S_{298.1}=54.41\pm0.1$. Cross (*110*) has computed a

virtually identical result, while a different but incorrect figure, 53.85, has been reported by Godnew and Sverdlin (*177*). The results of Montgomery and Kassel (*319*) are based on the older interpretation of the spectra in which the internuclear distance was taken as 1.60 $\times 10^{-8}$ cm.

From a recalculation (*250*) of the equilibrium data of Preuner and Schupp (*343*), values were obtained leading to $S_{298.1}=92$ for S_6 (*g*) and $S_{298.1}=109$ for S_8 (*g*). The errors in these figures undoubtedly are large but difficult to estimate.

Monoxide.—Montgomery and Kassel (*319*) have computed the free energy of SO (*g*). The basic data employed correspond to $I=39.1 \times 10^{-40}$ and $\omega=1{,}118$. The quantum weight of the lowest electronic state was taken as 3. These figures yield $S_{298.1}=53.07\pm0.1$. As a check, the entropy of SO (*g*) may be estimated as the mean of those of O_2 (*g*) and S_2 (*g*) plus $R\ ln\ 2$ or $S_{298.1}=1/2\ (49.03+54.41)+1.38 =53.10$.

Dioxide.—Giauque and Stephenson (*170*) (15°–264°) have measured the heat capacity of SO_2. Their entropy calculation has been checked to within 0.01 unit. The individual items are $S_{15}=0.30$ (extrapolation), $S_{197.64}-S_{15}=20.12$ (crystals), $\Delta S_{197.64}=1{,}769.1/197.64=8.95$ (fusion), $S_{263.08}-S_{197.64}=5.96$ (liquid), $\Delta S_{263.08}=5{,}960/263.08=22.65$ (vaporization), $\Delta S_{263.08}=0.09$ (correction to perfect gas state), and $S_{298.1}-S_{263.08}=1.17$ (gas). The sum is $S_{298.1}=59.24\pm0.10$. This value is adopted.

The molecular dimensions of Cross and Brockway (*112*) were used by Cross (*111*) and Giauque and Stephenson (*170*) in calculating the entropy. The I values are $I_1=13.3\times10^{-40}$, $I_2=86.2\times10^{-40}$, and $I_3=99.4\times10^{-40}$. Badger and Bonner (*34*) have reported $\omega_1=525$, $\omega_2=1{,}152$, and $\omega_3=1{,}361$. There are obtained $S_{t+r,298.1}=58.72$ and $S_{v,298.1}=0.68$, making $S_{298.1}=59.40\pm0.2$. In the older calculation of Gordon (*180*) the wrong moments of inertia were used.

Trioxide.—Kelley (*250*), from equilibrium data for the reaction SO_2 (*g*)$+1/2O_2$ (*g*)$=SO_3$ (*g*), has calculated $S_{298.1}=63.8\pm2.0$ for SO_3 (*g*).

Vapor-pressure data lead to the estimate $\Delta S_{298.1}=32.1$ (*247*) for the entropy of vaporization of SO_3 (*l*). The corresponding value is $S_{298.1}=31.7\pm3.0$ for SO_3 (*l*).

Sulfuryl chloride.—Kelley (*250*) also estimated $S_{298.1}=83.2\pm2$ for SO_2Cl_2 (*g*) and $S_{298.1}=60.5\pm3$ for SO_2Cl_2 (*l*) from equilibrium data for the reaction SO_2Cl_2 (*g*)$=SO_2+Cl_2$ and vapor pressures.

Hexafluoride.—Eucken and Schröder (*140*) (13°–230°) have measured the heat capacity of SF_6. Calculations from their data yield $S_{12.6}=1.08$ (extrapolation), $S_{94.30}-S_{12.6}=18.13$ (crystals II), $\Delta S_{94.30} =384.2/94.30=4.07$ (transition), $S_{186.0}-S_{94.30}=11.47$ (crystals I), $\Delta S_{186.0}=5{,}615/186.0=30.19$ (sublimation at 0.161 atmosphere pressure), and $\Delta S_{186.0}=-3.63$ (compression from 0.161 to 1 atmosphere). The entropy increment involved in warming the gas from 186.0° to 298.1° was computed graphically from specific-heat values, calculated from the molecular constants given below, as $S_{298.1}-S_{186.0}=8.96$ (gas). These quantities add to give $S_{298.1}=70.3\pm0.7$.

Yost, Steffens, and Gross (*416*) have calculated the entropy of SF_6 (*g*) as $S_{298.1}=70.5$, superseding the older calculations of Yost and Clausen (*412*). Similarly, Eucken and Schröder (*140*) calculated $S_{298.1}=69.2$. More recently, Yost (*409*) has reported a somewhat

different set of constants, 1.58×10^{-8} cm. S–F distance, $\omega_1=775$ (1), $\omega_2=645$ (2), $\omega_3=525$ (3), $\omega_4=363$ (3), $\omega_5=617$ (3), and $\omega_6=963$ (3). The assignment of the ω's agrees closely with that of Sachsse and Bartholome (*356*). The value of S–F distance yields $I_1=I_2=I_3=313\times10^{-40}$ and the symmetry number is 24. These figures give $S_{t+r,298.1}=61.80$, $S_{v,298.1}=7.80$, and $S_{298.1}=69.6\pm0.5$ for SF_6 (*g*). This figure is considered preferable to that obtained from the heat-capacity data.

H_2S (aq.).—The entropy of H_2S (*aq.*) was obtained by Latimer, Pitzer, and Smith (*286*) as $S_{298.1}=29.4\pm0.3$ from available data for the reaction H_2S (*g*)$=H_2S$ (*aq.*).

Bisulfide ion.—Latimer, Pitzer, and Smith (*286*) reported $S_{298.1}=14.9\pm1.0$ for HS^- (*aq.*), based upon data for the reaction H_2S (*aq.*) $=H^+ + HS^-$.

H_2SO_3 (aq.).—From data for the reaction SO_2 (*g*)$+H_2O$ (*l*) $=H_2SO_3$ (*aq.*), Latimer, Pitzer, and Smith (*286*) also gave $S_{298.1}=54.7\pm1.0$ for H_2SO_3 (*aq.*).

Bisulfite ion.—There also was recorded (*286*) $S_{298.1}=32.6\pm1.5$ for HSO_3^- from data for the reaction H_2SO_3 (*aq.*)$=H^+ + HSO_3^-$.

Sulfite ion.—Data for the reaction $HSO_3^-=H^+ + SO_3^-$ served for obtaining $S_{298.1}=3\pm3$ for SO_3^- (*aq.*) (*286*).

Bisulfate ion.—Likewise, $S_{298.1}=30.6\pm0.2$ was obtained (*286*) for HSO_4^- (*aq.*). Data for the reaction $SO_4^{--}+H^+=HSO_4^-$ served as the basis.

Sulfate ion.—From data for five reactions, $Na_2SO_4\cdot10H_2O=2Na^+ + SO_4^{--}+10H_2O$ (*l*), $Ag_2SO_4=2Ag^+ + SO_4^{--}$, $CaSO_4\cdot2H_2O=Ca^{++} + SO_4^{--}+2H_2O$ (*l*), $PbSO_4+2H_2O=H_2$ (*g*)$+PbO_2+SO_4^{--}+2H^+$, and $Hg_2SO_4+H_2=2Hg+2H^+ + SO_4^{--}$, Latimer, Pitzer, and Smith (*286*) obtained, respectively, 4.4 ± 1.0, 4.5 ± 2, 2.5 ± 2, 3.2 ± 2, and 5.2 ± 2 for SO_4^{--} (*aq.*). Their selection, $S_{298.1}=4.4\pm1.0$, also is adopted here.

TANTALUM

Element.—The specific heat of Ta was determined by Kelley (*256*) (53°–295°) and Simon and Ruhemann (*372*) (71°–78°). The data are not in agreement, and the more recent and more extensive results of the former are used here. Calculation gives $S_{298.1}=9.94\pm0.1$, of which 1.40 is extrapolation below 53.1°.

Oxide.—Kelley (*255*) (53°–295°) has measured the specific heat of Ta_2O_5. The data yield $S_{298.1}=34.2\pm0.4$, with an extrapolation below 53.1° of 2.83 units.

Carbide.—The specific heat of TaC also was measured by Kelley (*255*) (54°–295°). The results of entropy calculations are $S_{53.1}=0.95$ (extrapolation) and $S_{298.1}=10.1\pm0.1$.

TELLURIUM

Element.—Anderson (*24*) (54°–292°) and Slansky and Coulter (*376*) (14°–302°) have measured the specific heat of the same sample of crystalline Te. The data are in fair agreement, but Slansky and Coulter showed that Anderson's extrapolation of his results is erroneous. A recalculation gives $S_{298.1}=11.9\pm0.1$, with an extrapolation below 14.1° of 0.19. This agrees with the calculations of Slansky and Coulter.

In calculating the entropy of Te (*g*), *R ln* 5 is to be added to the Sackur equation. The result is $S_{298.1}=43.65\pm0.01$.

The moment of inertia and vibration frequency of Te_2 (*g*) were reported (*273, p. 2353*) as $I=863\times10^{-40}$ and $\omega=250$. The quantum weight of the lowest electronic state is 3. From these values there is computed $S_{298.1}=64.5\pm0.5$ for Te_2 (*g*).

Hexafluoride.—Molecular constants of TeF_6 (*g*) have been reported by Yost, Steffens, and Gross (*416*) and more recently by Yost (*409*). The latter gave 1.84×10^{-8} cm. Te–F distance, $\omega_1=701$ (1), $\omega_2=674$ (2), $\omega_3=313$ (3), $\omega_4=165$ (3), $\omega_5=370$ (3), and $\omega_6=752$ (3). Virtually identical ω's were given by Sachsse and Bartholome (*356*). The interatomic distance yields $I_1=I_2=I_3=424\times10^{-40}$. The symmetry number is 24. There are calculated $S_{t+r,298.1}=64.20$, $S_{v,298.1}=16.56$, and $S_{298.1}=80.6\pm1.0$.

THALLIUM

Element.—The specific heat of Tl was measured by Clusius and Vaughen (*101*) (11°–249°), Nernst and Schwers (*329*) (22°–96°), Hicks (*197*) (14°–301°), and Keesom and Kok (*233, 234, 235*) (1.3°–4.2°). A recalculation gives $S_{298.1}=15.4\pm0.1$, of which the extrapolation is about 7×10^{-4} below 1.3°.

The entropy of Tl (*g*) from the Sackur equation, with *R ln* 2 added, is $S_{298.1}=43.23\pm0.01$.

Thallous ion.—The entropy of Tl^+ (*aq.*) was reported by Latimer, Pitzer, and Smith (*286*) as $S_{298.1}=30.5\pm0.4$. Data for two reactions were considered—$TlNO_3=Tl^++NO_3^-$ and $Tl+AgCl=Ag+Tl^++Cl^-$—from which the respective values are 31.0 ± 0.5 and 30.1 ± 0.5. The selected result and that reported by Hicks (*197*), $S_{298.1}=30.2$, are in good agreement.

Bromide.—Data given by Ishikawa and Terui (*203*) for the reaction $Tl+1/2Br_2$ (*l*)$=TlBr$ lead to $S_{298.1}=27.9$ for TlBr. The residual-ray data of Rubens and Hollnagel (*353*) furnish an independent means of obtaining the entropy. The result is $S_{298.1}=26.8\pm1.0$, which is adopted.

From vapor-pressure data and the entropy of the solid Kelley (*247*) has calculated $S_{298.1}=63.2$ for TlBr (*g*). An approximate value also is obtainable from $\omega=192$ (*273, p. 2351*) and an estimate of the Tl–Br distance, 3.4×10^{-8} cm. There are computed $S_{t+r,298.1}=62.74$, $S_{v,298.1}=2.22$, and $S_{298.1}=65.0\pm1.5$.

Chloride.—Pollitzer (*342*) (23°–94°) has measured the specific heat of TlCl. The data yield $S_{298.1}=25.9\pm0.6$, the extrapolation being 0.56 below 22.4°.

The cell measurements of Gerke (*154*) yield $\Delta S_{298.1}=-1.1$ for the reaction $Tl+AgCl=TlCl+Ag$. This value leads to $S_{298.1}=27.1$, in disagreement with the third-law result.

Still another value may be obtained from the residual-ray data of Rubens and Hollnagel (*353*), which yield $S_{298.1}=23.7$.

The exact reason for these discrepancies is not apparent, and none of the values is entirely free from objection. For the present the mean, $S_{298.1}=25.6\pm1.5$, is adopted.

The entropy of TlCl (*g*) was calculated by Kelley (*247*) from vapor pressures and the entropy of the solid. Correcting this figure to correspond to the value just given for the solid results in $S_{298.1}=60.0$. An estimate may be made from $\omega=284$ (*273, p. 2351*) and the assump-

tion of 3.3×10^{-8} as the Tl–Cl distance. There is computed $S_{t+r,298.1}=60.83$, $S_{v,298.1}=1.51$, and $S_{298.1}=62.3\pm1.5$.

Fluoride.—From $\omega=311$ (*273, p. 2351*) and the estimate of 2.9×10^{-8} cm. as the Tl–F distance, there is computed $S_{v,298.1}=1.37$, $S_{t+r,298.1}=59.01$, and $S_{298.1}=60.4\pm1.5$ for TlF (*g*).

Iodide.—Rubens and Hollnagel's (*353*) residual-ray data lead to $S_{298.1}=29.9\pm1.0$ for TlI (*s*).

Kelley (*247*) has estimated $S_{298.1}=63.9$ for TlI (*g*) from vapor pressures and the entropy of the solid.

Nitrate.—Latimer and Ahlberg (*280*) (16°–291°) have measured the specific heat of $TlNO_3$. Entropy calculations give $S_{15.85}=1.39$ (extrapolation) and $S_{298.1}=38.4\pm0.2$.

THORIUM

Element.—Lewis and Gibson's (*292*) value with an estimate of the probable error will be listed, $S_{298.1}=13.6\pm0.8$. No other pertinent data are available.

TIN

Element.—The specific heat of ordinary or white Sn was measured by Keesom and van den Ende (*230*) (1.3°–20.3°), Keesom and Kok (*232*) (3.5°–3.9°), Keesom and van Laer (*238, 239, 240*) (1°–4°), Lange (*274*) (22°–286°), and Rodebush (*347*) (69°–101°). The entropy is computed as $S_{298.1}=12.3\pm0.1$. The extrapolation is virtually negligible, about 8×10^{-5} below 1.1°.

Lange (*274*) (15°–284°) also measured the specific heat of gray Sn. From his data, $S_{298.1}=10.7\pm0.1$, with an extrapolation below 12.6° of 0.25.

The entropy of Sn (*g*) is $S_{298.1}=40.24\pm0.01$, obtained from the Sackur equation.

Stannous ion.—Latimer, Pitzer, and Smith (*286*) give $S_{298.1}=-4.9\pm1.0$ for Sn^{++} (*aq.*), based upon data for the reaction $Sn+2H^{+}=Sn^{++}+H_2$.

Oxides.—Millar (*317*) has measured the specific heats of SnO (69°–293°) and SnO_2 (71°–290°). His data yield $S_{298.1}=13.5\pm0.3$ for SnO, and $S_{298.1}=12.5\pm0.3$ for SnO_2. The extrapolations are, respectively, 2.07 below 63.1° and 1.38 below 70.8°.

Tetrabromide.—The following data have been reported (*273, p. 2360*) for $SnBr_4(g)$: $I_1=I_2=I_3=2{,}160\times10^{-40}$, $\omega_1=64$ (2), $\omega_2=88$ (3), $\omega_3=220$ (1), $\omega_4=279$ (3), and symmetry number=12. These figures give $S_{t+r,298.1}=72.21$, $S_{v,298.1}=26.38$ and $S_{298.1}=98.6\pm2$.

Tetrachloride.—Yost and Blair (*411*) have computed $S_{298.1}=87.2$, to which may be assigned the error ±1.0 for $SnCl_4$ (*g*). This calculation was checked. The data employed are $I_1=I_2=I_3=828\times10^{-40}$, $\omega_1=367$ (1), $\omega_2=104$ (2), $\omega_3=401$ (3), $\omega_4=136$ (3), and symmetry number=12.

From the above value and the entropy of vaporization, $\Delta S_{298.1}=25.1$ (*247*), $S_{298.1}=62.1\pm1.5$ is calculated for $SnCl_4$ (*l*). Latimer (*276*) has obtained $S_{298.1}=61.8$ from heat-capacity measurements (89°–294°). The agreement is well within the limit of error of either result.

Telluride.—McAteer and Seltz (*307*) found $\Delta S_{298.1}=0.0$ for the reaction Sn+Te=SnTe. This leads to $S_{298.1}=24.2\pm1.0$ for SnTe.

TITANIUM

Element.—For Ti, in accordance with Lewis and Gibson (*292*), $S_{298.1}=6.6\pm0.4$ is listed.

At 298.1°, three energy states are to be considered in deriving the entropy of Ti (*g*), $^3F_2$, $^3F_3$, and $^3F_4$ (*31*). The term values are 0, 170, and 387, and the quantum weights are 5, 7, and 9, respectively. There is added 5.541 to the translational entropy, 37.532, to make $S_{298.1}=43.07\pm0.1$.

Oxide.—The specific heat of TiO_2, rutile, was measured by McDonald and Seltz (*308*) (68°–292°). Their data yield $S_{298.1}=12.4\pm0.2$, of which 1.19 is extrapolation below 66.8°.

Tetrachloride.—Yost and Blair (*411*) have computed $S_{298.1}=84.4\pm1.0$ for $TiCl_4$ (*g*). This calculation was repeated with an identical result. The data employed are $I_1=I_2=I_3=744\times10^{-40}$ $\omega_1=386$ (1), $\omega_2=118$ (2), $\omega_3=491$ (3), $\omega_4=139$ (3), and symmetry number=12.

The entropy of vaporization of $TiCl_4$ (*l*), $\Delta S_{298.1}=24.0$, was obtained (*247*) from vapor-pressure data. From this and the entropy of the gas, $S_{298.1}=60.4\pm1.5$ is obtained for $TiCl_4$ (*l*). Latimer (*276*) found $S_{298.1}=59.5$ from heat-capacity data (86°–295°). Again, the agreement is within the limit of error of either value.

TUNGSTEN

Element.—Lange (*274*) (26°–92°) and Zwikker and Schmidt (*419*) (92°–290°) have measured the specific heat of W. From the data of the former, which are more reliable, $S_{298.1}=8.0\pm0.1$. The extrapolation below 25.1° is 0.07.

Spectroscopic data for W (*g*) show that the occupied states at 298.1° are $^5D_0$, $^5D_1$, and $^5D_3$. The term values are 0, 1,670, and 3,325, and the quantum weights are 1, 3, and 5, respectively (*273, p. 2348*). These states add 0.017 to the translational entropy, 41.54, making $S_{298.1}=41.56\pm0.01$.

URANIUM

Element.—Lewis and Gibson (*292*), from Dewar's (*117*) data, give $S_{298.1}=11.1\pm0.6$ for U.

VANADIUM

Element.—Anderson (*21*) (54°–297°) has measured the specific heat of V. Calculation gives $S_{298.1}=7.0\pm0.1$, of which 0.48 is extrapolation below 56.2°.

In computing the entropy of V (*g*) the energy states to be considered are (*31*) $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4F_{9/2}$, $^6D_{1/2}$, $^6D_{3/2}$, $^6D_{5/2}$, $^6D_{7/2}$, and $^6D_{9/2}$. These states have term values 0, 137.4, 323, 553, 2,112, 2,153, 2,220, 2,311, and 2,425 cm.$^{-1}$, respectively, and quantum weights 4, 6, 8, 10, 2, 4, 6, 8, and 10. The result is that 5.838 must be added to the Sackur entropy, making $S_{298.1}=43.55\pm0.1$.

Oxides.—Anderson (*21*) also measured the specific heats of V_2O_3 (56°–288°), V_2O_4 (61°–280°), and V_2O_5 (56°–290°). From his data there are obtained $S_{298.1}=23.5\pm0.3$ for V_2O_3, $S_{298.1}=24.5\pm0.3$ for V_2O_4, and $S_{298.1}=31.3\pm0.5$ for V_2O_5. The extrapolations below 56.2° are, respectively, 1.03, 1.23, and 2.47.

XENON

Element.—The Sackur equation gives $S_{298.1}=40.54\pm0.01$ for Xe (*g*). Clusius and Roccoboni (*100*) (10°–166°) have measured the heat capacity of Xe at low temperatures. The entropy calculation from their data is made somewhat uncertain by the large amount of premelting, indicating lack of purity. The results are $S_{10}=0.82$ (extrapolation), $S_{161.3}-S_{10}=14.82$ (crystals), $\Delta S_{161.3}=548.5/161.3=3.40$ (fusion), $S_{165.1}-S_{161.3}=0.25$ (liquid), $\Delta S_{165.1}=3{,}020/165.1=18.29$ (vaporization), $\Delta S_{165.1}=0.14$ (correction to perfect gas state), and $S_{298.1}-S_{165.1}=2.94$ (gas, $C_p=4.97$). The sum is $S_{298.1}=40.7\pm0.3$, which agrees with the more certain value given above.

YTTRIUM

The entropy of Y (*g*) is obtainable from the Sackur equation and spectroscopic data (*31*). At 298.1° the states $^2D_{3/2}$ and $^2D_{5/2}$, separated by 530 cm.$^{-1}$ and having quantum weights 4 and 6, are to be considered. They add 3.507 to the Sackur-equation result, giving $S_{298.1}=42.88\pm0.1$.

ZINC

Element.—Bronson and Wilson (*56*) (193°–303°), Clusius and Harteck (*97*) (12°–202°), Keesom and van den Ende (*230*) (1.3°–22°), Nernst (*325*) (33°–274°), and Pollitzer (*341*) (67°–210°) have measured the specific heat of Zn. Giving the most weight to the data of Clusius and Harteck and Keesom and van den Ende, $S_{298.1}=9.95\pm0.05$ is computed. The extrapolation is negligible—about 8×10^{-5} below 1.3°.

At 298.1° the Sackur equation yields $S_{298.1}=38.46\pm0.1$ for Zn (*g*). No addition to this value is necessary, as only the lowest energy state, of unit quantum weight, need be considered.

Zinc ion.—Latimer, Pitzer, and Smith (*286*) have reported $S_{298.1}=-25.7\pm1.0$ for Zn^{++} (*aq.*). Data for the reaction $Zn+2H^+=Zn^{++}+H_2$ form the basis of their calculation. Excellent agreement exists between this value and that reported by Bates (*39*), $S_{298.1}=-25.9\pm0.5$.

Oxide.—Specific-heat measurements of ZnO were made by Clusius and Harteck (*97*) (30°–200°), Maier, Parks, and Anderson (*306*) (88°–295°), and Millar (*316*) (81°–298°). The combined results yield $S_{298.1}=10.4\pm0.1$, the extrapolation being 0.17 below 28.2°.

Another result may be calculated from heat and free-energy-of-formation data. The mean of the better values (*270, p. 826; 271, p. 1509*) of the former is $\Delta H_{298.1}=-83{,}170$ and Maier (*304*) has obtained $\Delta F^\circ_{298.1}=-75{,}930$ from oxide cell measurements and from equilibrium measurements of the reaction $ZnO+CO=Zn\ (g)+CO_2$. These figures give $S_{298.1}=10.2$ for ZnO.

An approximate value of the entropy of ZnO (*g*) may be calculated. It is estimated that the Zn–O distance is about 2.0×10^{-8} cm., corresponding to $I=85\times10^{-40}$. The vibration frequency was reported (*273, p. 2351*) as $\omega=818$. There are computed $S_{t+r,298.1}=53.93$ and $S_{v,298.1}=0.20$, making $S_{298.1}=54.1\pm1.0$.

Sulfide.—Clusius and Harteck (*97*) (18°–197°) and Günther (*187*) (21°–59°) measured the specific heat of ZnS. Employing only the more recent and more reliable data of the former investigators, $S_{298.1}=13.8\pm0.2$ is calculated, with only 0.09 extrapolation below 17.8°.

Telluride.—McAteer and Seltz (*307*) obtained $\Delta S_{298.1}=-2.9$ for the reaction $Zn+Te=ZnTe$. This leads to $S_{298.1}=19.0\pm1.0$ for ZnTe.

Bromide.—Ishikawa and Yoshida (*207*) obtained $\Delta F^\circ_{298.1}=-31{,}442$ and $\Delta H_{298.1}=-29{,}530$ for the reaction $Zn+2HgBr=ZnBr_2+2Hg$. The entropy of reaction if therefore $\Delta S_{298.1}=6.41$. For $ZnBr_2$, then, $S_{298.1}=32.2\pm1.5$. More recently, Bates (*40*), from cell measurements and thermal data, reported $S_{298.1}=32.95$. The agreement is satisfactory, and the rounded figure corresponding to the result of Bates, $S_{298.1}=33.0\pm1.0$, is adopted.

Chloride.—Elliott and Yost (*133*) have given the heat and free energy of formation of $ZnCl_2$ as $\Delta H_{298.1}=-99{,}950$ and $\Delta F^\circ_{298.1}=-87{,}990$. The entropy of formation is $\Delta S_{298.1}=-38.8$, and the corresponding entropy of $ZnCl_2$ is $S_{298.1}=24.5$.

Ishikawa, Kimura, and Murooka (*208*) have studied the reaction $Zn+2HgCl=ZnCl_2+2Hg$. Their results yield $\Delta S_{298.1}=6.68$, corresponding to $S_{298.1}=26.5$ for $ZnCl_2$.

More recently, Bates (*40*) has obtained $S_{298.1}=25.9$ from all measurements and thermal data. This value, which intermediates the two above given results, is adopted and the error is estimated as ±1.0.

Iodide.—Bates (*40*) also has reported $S_{298.1}=38.5$ for ZnI_2, from cell measurements and thermal data. Again, ±1.0 is estimated as the error.

Carbonate.—The specific heat of $ZnCO_3$, smithsonite, was measured by Anderson (*17*) (58°–299°). His data give $S_{298.1}=19.7\pm0.3$, of which 1.45 is extrapolation below 56.2°.

Sulfate.—Pollitzer (*341, 342*) (27°–208°) has measured the specific heat of $ZnSO_4\cdot7H_2O$. The data, however, obviously are not suitable for an entropy calculation.

The reaction $Zn+Hg_2SO_4=ZnSO_4+2Hg$ was investigated by Ishikawa and Murooka (*201*), who obtained $\Delta H_{298.1}=-56{,}332$ and $\Delta F^\circ_{298.1}=-59{,}209$, making $\Delta S_{298.1}=9.68$. This result leads to $S_{298.1}=30.7\pm2$ for $ZnSO_4$.

Antimonides.—DeWitt and Seltz (*118*) have reported $S_{298.1}=21.4$ for ZnSb, $S_{298.1}=63.6$ for Zn_3Sb_2, and $S_{298.1}=73.5$ for Zn_4Sb_3. These values are based on e. m. f. measurements. The errors are here estimated as ±1.4, ±1.8, and ±2.1, respectively.

ZIRCONIUM

Element.—For Zr, in accordance with Lewis and Gibson (*292*), $S_{298.1}=9.5\pm0.6$.

In obtaining the entropy of Zr (*g*) at 298.1° the states to be considered are (*31*) $^3F_2$, $^3F_3$, and $^3F_4$, with term values 0, 570, and 1,241 and quantum weights 5, 7, and 9, respectively. The figure to be added to the Sackur value is 3.880, making $S_{298.1}=43.33\pm0.1$.

ELECTRON GAS

The application of the Sackur equation (with $R\ ln\ 2$ added for electron spin) to electron gas gives $S_{298.1}=4.98$. The molecular weight is taken as 5.454×10^{-4} gram in this calculation.

TABLES OF LOW-TEMPERATURE SPECIFIC HEATS, ENTROPIES AT 298.1° K., AND DATA CONCERNING CHANGES IN STATE

The following tables summarize the available low-temperature specific-heat data, entropy data, and data concerning changes in state occurring in the temperature range 0° to 298.1° for the elements and inorganic compounds.

Table 7 lists values of the specific heats read from the smooth curves used in calculating the third-law entropies. These values are given at 10°, 25°, 50°, 100°, 150°, 200°, and 298.1° K. Specific-heat figures for gases are those obtained by calculation from spectroscopically determined energy levels or molecular constants. Values in parentheses are extrapolations below or above the temperature range of the actual measurements. The asterisk is used to denote substances having "humps" in their specific-heat curves in the range 0° to 298.1° K. The dagger marks substances undergoing one or more changes in state—sharp transition, fusion, sublimation, and vaporization. The letters *s*, *l*, and *g* denote respectively the crystalline, liquid, and gaseous states, and the symbol *aq.*, placed after chemical formulas of ions and a few other substances, refers to hypothetical, ideal solutions of 1 molal concentration. Table 7 also gives the entropy values at 298.1° obtained by the several methods indicated. The column marked "Miscellaneous" contains the results calculated from residual-ray data and those estimated by procedures mentioned in the previous section of this bulletin.

Table 8 gives values of the temperatures of changes in state, together with the accompanying heat absorption in calories per mole. This table includes all the substances marked by the dagger in table 7. The data given are those selected previously in computing the third-law entropies.

TABLE 7.—*Low-temperature specific heats and entropies at 298.1° K.*

Substance	Specific heats, calories per formula mass							Entropies at 298.1° K.				
	10° K.	25° K.	50° K.	100° K.	150° K.	200° K.	298.1° K.	Third law	Spectroscopic or molecular constants	$\Delta F°$ and ΔH	Misc.	Value recommended
Aluminum:												
Al (*s*)	0.01	0.115	0.92	3.11	4.45	5.15	5.82	6.75±0.05				6.75±0.05
Al (*g*)									39.31±0.01			39.31±0.01
Al^{+++} (*aq*)										−76±10		−76±10
Al_2O_3 (*s*)	(.01)	(.05)	.45	3.21	8.00	12.40	18.90	12.5±0.15				12.5±0.15
Al_2SiO_5(disthen)	(.01)	.19	1.10	6.07	13.15	19.68	(29.03)	20.7±0.5				20.7±0.5
Al_2SiO_5 (sillimanite)	(.03)	.47	2.58	8.44	15.22	21.65	30.45	27.0±0.5				27.0±0.5
Al_2SiO_5 (andalusite)	(.03)	.55	2.97	9.60	16.91	22.45	32.14	25.0±0.5				25.0±0.5
Antimony:												
Sb (*s*)	(.06)	(.80)	(2.99)	4.92	5.55	5.82	6.03	10.5±0.3				10.5±0.3
Sb (*g*)									43.07±0.01			43.07±0.01
Sb_2 (*g*)									60.9±0.5			60.9±0.5
Sb_2O_3 (*s*)	(.23)	(2.16)	(5.50)	12.02	16.79	20.26	24.23	29.4±0.6				29.4±0.6
Sb_4O_6 (*g*)								102				102
Sb_2O_4 (*s*)	(.26)	(2.31)	(5.49)	11.16	17.27	21.75	27.39	30.4±0.7				30.4±0.7
Sb_2O_5 (*s*)	(.08)	(1.03)	(3.94)	12.67	18.48	22.73	28.11	29.9±1.2				29.9±1.2
Sb_2S_3 (*s*)										39.6		39.6
$SbCl_3$ (*g*)									80.9±2			80.9±2
$SbCl_3$ (*s*)										44.8±3		44.8±3
Argon: A (*g*)†	(.72)	3.75	6.20 (*s*)	4.97 (*g*)	4.97	4.97	4.97	37.0±0.2	36.99±0.01			36.99±0.01
Arsenic:												
As (*s*)	(.03)	(.35)	(1.88)	3.99	4.94	5.43	5.89	8.4±0.2				8.4±0.2
As (*g*)									41.62±0.01			41.62±0.01
As_2 (*g*)									57.3±0.5			57.3±0.5
As_4 (*g*)								69				69
As_2O_3 (*s*)	(.25)	(2.16)	(4.77)	9.72	14.45	18.26	22.86	25.6±0.5				25.6±0.5
As_4O_6 (*g*)								101				101
As_2O_5 (*s*)	(.03)	(.50)	(2.62)	9.45	15.87	20.93	27.85	25.2±0.4				25.2±0.4
$AsCl_3$ (*g*)									78.2±2			78.2±2
$AsCl_3$ (*l*)										55.8±3		55.8±3
AsF_3 (*g*)									69.2±2			69.2±2
AsF_3 (*l*)										50.1±3		50.1±3
Barium:												
Ba (*g*)									40.67±0.01			40.67±0.01
Ba^{++} (*aq*)										2.3±0.3		2.3±0.3
BaO (*s*)	(.07)	(1.06)	(3.81)	7.63	9.55	10.47	11.34	16.8±0.3				16.8±0.3
BaO (*g*)									56.0±0.5			56.0±0.5
$BaCl_2 \cdot 2H_2O$ (*s*)	(.37)	3.18	10.19	21.13	27.30	31.64	37.10	48.5±0.3				48.5±0.3
BaF_2 (*s*)	(.08)	1.09	4.31	10.56	13.97	15.78	17.02	23.01±0.1				23.0±0.1
$Ba(BrO_3)_2 \cdot H_2O$	(.65)	5.31	15.08	28.59	37.70	44.00	52.90	68.8±1.5				68.8±1.5

TABLE 7.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula mass							Entropies at 298.1° K.				
	10° K.	25° K.	50° K.	100° K.	150° K.	200° K.	298.1° K.	Third law	Spectroscopic or molecular constants	$\Delta F°$ and ΔH	Misc.	Value recommended
Barium—Continued.												
$BaCO_3$ (*s*) (witherite)	(0.13)	(1.62)	(5.40)	12.02	15.32	17.41	20.40	26.8±0.5				26.8±0.5
$Ba(NO_3)_2$ (*s*)	(.45)	4.02	12.27	22.73	27.38	30.60	36.07	51.1±0.4				51.1±0.4
$BaSO_4$ (*s*)	(.17)	1.98	7.16	13.75	17.30	20.12	24.32	31.6±0.3				31.6±0.3
Beryllium:												
Be (*s*)	.00	.01	.05	.41	1.26	2.38	4.26	2.28±0.02				2.28±0.02
Be (*g*)									32.56±0.01			32.56±0.01
BeO (*s*)	(.00)	(.02)	(.09)	.69	1.90	3.42	6.07	3.37±0.05				3.37±0.05
BeO (*g*)									47.2±0.5			47.2±0.5
Be_2SiO_4 (phenacite)	(.01)	(.10)	(.75)	4.47	9.55	14.48	22.84	15.4±0.1				15.4±0.1
Bismuth:												
Bi (*s*)	.52	2.43	4.27	5.46	5.83	5.98	6.10	13.6±0.6				13.6±0.6
Bi (*g*)									44.68±0.01			44.68±0.01
Bi_2 (*g*)									65.4±1.0			65.4±1.0
Bi_2O_3 (*s*)	(.49)	(2.95)	(7.33)	15.04	19.48	23.10	27.13	36.2±0.7				36.2±0.7
$BiCl_3$ (*g*)									85.5±3			85.5±3
$BiCl_3$ (*s*)										45.8±4		45.8±4
Boron:												
B (*s*)											1.7±0.2	1.7±0.2
B (*g*)									36.66±0.01			36.66±0.01
BBr_3 (*g*)									76.7±3			76.7±3
BCl_3 (*g*)									68.6±3			68.6±3
BF_3 (*g*)	(.75)	3.95	8.52	12.76 (*s*)	24.64 (*l*)	10.05 (*g*)	12.10	61.4±0.5	60.8±1.0			61.1±0.5
B_4C (*s*)	(.00)	(.00)	(.10)	1.22	3.51	6.57	12.55	6.47±0.04				6.47±0.04
Bromine:												
Br_2 (*l*)†	(.74)	4.12	8.14	10.51	11.75	12.87 (*s*)	8.5 (*l*)	36.6±0.5		36.8±0.4		36.7±0.4
Br_2 (*g*)									58.63±0.03			58.63±0.03
Br (*g*)									41.81±0.01			41.81±0.01
Br^- (*aq.*)										19.7±0.2		19.7±0.2
BrCl (*g*)									57.4±0.1	57.4	57.35	57.4±0.1
BrO_3^- (*aq.*)										38.5±1.0		38.5±1.0
Cadmium:												
Cd (*s*)	.22	1.71	3.90	5.32	5.73	5.93	6.19	12.3±0.1				12.3±0.1
Cd (*g*)									40.07±0.01			40.07±0.01
Cd^{++} (*aq.*)										−15.6±1.2		−15.6±1.2
CdO (*s*)	(.03)	(.51)	(2.38)	5.76	7.99	9.31	10.38	13.1±0.3				13.1±0.3
CdO (*g*)								46.9				46.9
CdS (*s*)										17±1		17±1
CdTe (*s*)										22.2±1.0		22.2±1.0
$CdBr_2$ (*s*)										32.0±1.0		32.0±1.0

$CdCl_2$ (*s*)										31.2±1.0		31.2±1.0
CdI_2 (*s*)										39.5±1.0		39.5±1.0
$Cd(OH)_2$ (*s*)										21		21
$CdCO_3$ (*s*)										25.2		25.2
$CdSO_4$ (*s*)										31.3		31.3
$CdSO_4 \cdot H_2O$ (*s*)										39.7		39.7
$CdSO_4 \cdot 8/3H_2O$ (*s*)										57.5		57.5
CdSb (*s*)										21.2±0.7		21.1±0.7
Cd_3Sb_2 (*s*)										78.9±2		78.9±2
Calcium:												
Ca (*s*)	(.045)	.62	2.60	4.66	5.49	5.91	6.28	9.95±0.1				9.95±0.1
Ca (*g*)									37.00±0.01			37.00±0.01
Ca^{++} (*aq.*)										−11.4±0.3		−11.4±0.3
CaO (*s*)	(.00)	.08	.60	3.86	6.49	8.32	10.23	9.5±0.2				9.5±0.2
CaO (*g*)									52.3±0.5			52.3±0.5
CaS (*s*)	(.02)	(.34)	(2.02)	6.16	8.72	10.09	11.33	13.5±0.3				13.5±0.3
CaF_2 (*s*)	(.01)	.20	1.59	7.12	11.05	13.38	15.86	16.4±0.4				16.4±0.4
CaH_2 (*s*)	[1]							9.9±1.0				9.9±1.0
$Ca(OH)_2$ (*s*)	[2]							17.4±1.0				17.4±1.0
$CaCO_3$ (*s*) (calcite)	(.05)	.77	3.73	9.35	13.30	15.92	19.57	22.2±0.2				22.2±0.2
$CaCO_3$ (*s*) (aragonite)	(.04)	(.63)	(2.94)	9.40	13.46	16.01	19.42	21.1±0.3				21.2±0.3
$CaC_2O_4 \cdot H_2O$ (*s*)	(.11)	1.45	6.04	15.35	22.30	27.66	36.52	37.4±0.2				37.4±0.2
$Ca_3(PO_4)_2$ (*s*) (α)	(.08)	1.83	8.62	20.95	35.15	43.55	55.35	57.6±0.2				57.6±0.2
$Ca_3(PO_4)_2$ (*s*) (β)	(.10)	1.57	8.14	20.63	34.55	43.00	54.45	56.4±0.4				56.4±0.4
$CaSiO_3$ (*s*) (wollastonite)	.04	.47	2.70	7.29	11.81	16.05	20.38	19.6±0.2				19.6±0.2
$CaSiO_3$ (*s*) (pseudowollastonite)	.04	.55	2.57	8.57	13.41	16.78	20.67	20.9±0.2				20.9±0.2
$CaSO_4 \cdot 2H_2O$ (*s*) (selenite)	(.14)	1.60	7.60	19.10	27.52	34.36	44.46	46.4±0.2				46.4±0.2
$CaSO_4 \cdot \frac{1}{2}H_2O$ (*s*) (α)	(.09)	(1.08)	(5.24)	13.31	18.61	22.56	28.54	31.2±0.6				31.2±0.6
$CaSO_4 \cdot \frac{1}{2}H_2O$ (*s*) (β)	(.10)	(1.18)	(5.53)	13.57	19.01	23.10	29.69	32.1±0.6				32.1±0.6
$CaSO_4$ (*s*) (natural anhydrite)	(.05)	(.62)	(3.86)	11.06	15.64	19.11	23.82	25.5±0.4				25.5±0.4
$CaSO_4$ (*s*) (sol. α)	(.06)	(.66)	(4.13)	11.37	15.85	19.12	23.95	25.9±0.3				25.9±0.3
$CaSO_4$ (*s*) (sol. β)	(.03)	(.36)	(3.87)	11.55	15.97	19.18	23.67	25.9±0.3				25.9±0.3
Carbon:												
C (graphite)	(.00)	(.04)	.11	.40	.77	1.20	2.06	1.36±0.03				1.36±0.03
C (diamond)	(.00)	(.00)	(.00)	.06	.25	.58	1.45	0.585±0.005				0.585±0.005
C (*g*)									37.77±0.01			37.77±0.01
C_2 (*g*)									47.89			47.89
CO (*g*)†	(.78)	5.44	10.36 (*s*)	6.95 (*g*)	6.95	6.95	6.95	46.2	47.32±0.01			47.32±0.01
CO_2 (*g*)†	(.18)	2.14	6.09	9.51	11.39 (*s*)	7.74 (*g*)	8.90	51.1±0.1	51.08±0.01			51.08±0.01
CS (*g*)									50.3±0.2			50.3±0.2
CS_2 (*l*)†	(.60)	4.01	7.77	11.05	13.33 (*s*)	17.98 (*l*)	18.06	36.2±0.3				36.2±0.3
CS_2 (*g*)								57.1±0.5	56.84±0.3			56.84±0.3
COS (*g*)†	(.51)	3.81	7.71	10.51 (*s*)	17.26 (*l*)	16.94	9.92 (*g*)	55.27±0.1	55.37±0.1			55.37±0.1
CBr_4 (*g*)									85.5±1.0			85.5±1.0
CCl_4 (*g*)								74.35	74.2±0.5			74.2±0.5
CCl_4 (*l*)†	(.75)	6.78	11.32	16.68	20.94	25.70 (*s*)	30.99 (*l*)	52.2±0.3				52.2±0.3
CF_4 (*g*)†	(1.19)	6.50	12.07 (*s*)	18.64 (*l*)	9.59 (*g*)	11.24	14.51	62.8±0.5	62.7±0.5			62.7±0.5
$COCl_2$ (*g*)									67.2±1.0			67.2±1.0

[1] Specific-heat data exist only for the temperature range 69°–87°.
[2] Insufficient data. Entropy value based upon specific-heat measurements in the range 21°–86°.

TABLE 7.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula mass							Entropies at 298.1° K.				
	10° K.	25° K.	50° K.	100° K.	150° K.	200° K.	298.1° K.	Third law	Spectroscopic or molecular constants	$\Delta F°$ and ΔH	Misc.	Value recommended
Carbon—Continued.												
CH_4 (*g*)† *	(0.87)	4.99	7.81 (*s*)	12.91 (*l*)	7.95 (*g*)	8.00	8.55	44.5±0.2	44.5±0.1			44.5±0.1
CN (*g*)									48.42±0.01			48.42±0.01
C_2N_2 (*g*)†	(.29)	2.81	7.01	11.43	14.47	17.51 (*s*)	13.57 (*g*)	57.64	57.9±0.1			57.9±0.1
CNBr (*g*)									59.1±0.5			59.1±0.5
CNCl (*g*)									56.4±0.5			56.4±0.5
CNI (*g*)									61.3±0.5			61.3±0.5
CO_3—— (*aq.*)										−13.0±1.0		−13.0±1.0
HCO_3− (*aq.*)										22.2±0.8		22.2±0.8
H_2CO_3 (*aq.*)										45.1±0.7		45.1±0.7
CN− (*aq.*)										25±5		25±5
C_2O_4—— (*aq.*)										9.6±1.0		9.6±1.0
Cerium:												
Ce (*s*)	(3)							13.8±0.8				13.8±0.8
Ce (*g*)									48.1±0.1			48.1±0.1
Cesium:												
Cs (*g*)									41.95±0.01			41.95±0.01
Cs (*s*)										19.8±1.0		19.8±1.0
Cs^+ (*aq.*)										31.8±0.6		31.8±0.6
CsBr (*g*)											63.8±1.7	63.8±1.7
CsCl (*g*)											58.9±2.0	58.9±2.0
$CsClO_4$ (*s*)	(.87)	5.72	12.26	16.80	19.37	21.87	25.71	41.9±0.2				41.9±0.2
$CsAl(SO_4)_2 \cdot 12H_2O$ (*s*)	(1.97)	11.96	32.2	62.6	87.0	110.7	148.1	163±5				163±5
Chlorine:												
Cl_2 (*g*)†	(.32)	2.91	7.01	10.09	12.19 (*s*)	15.93 (*l*)	8.08 (*g*)	53.31±0.1	53.31±0.01	53.0±0.4		53.31±0.01
Cl (*g*)									39.47±0.01			39.47±0.01
Cl^- (*aq.*)										13.5±0.1		13.5±0.1
Cl_2O (*g*)									63.7±0.5	67.4		63.7±0.5
ClO_2 (*g*)									59.6±0.5			59.6±0.5
ClO^- (*aq.*)										10.0±2.0		10.0±2.0
ClO_2^- (*aq.*)										24.1±0.5		24.1±0.5
ClO_3^- (*aq*)										39.4±0.5		39.4±0.5
ClO_4^- (*aq.*)										43.6±0.5		43.6±0.5
Chromium:												
Cr (*s*)	(.01)	(.06)	(.47)	2.39	3.94	4.81	5.58	5.68±0.07				5.68±0.07
Cr (*g*)									41.64±0.01			41.64±0.01
Cr_2O_3 (*s*)	(.02)	(.14)	(1.10)	5.78	12.20	18.00	28.38	19.4±0.3				19.4±0.3
$CrCl_2$ (*s*)	(.77)	(3.73)	(6.65)	11.17	13.98	15.55	16.87	27.7±0.7		27.3		27.7±0.7
$CrCl_3$ (*s*)*			(4.93)	11.98	16.52	19.22	21.53	31.4		31.0		31.0±1.5
CrO_4——(*aq.*)										10.5±1.0		10.5±1.0

Cobalt:												
Co (*s*)	[4].02							6.8±0.2				6.8±0.2
Co (*g*)									42.89±0.01			42.89±0.01
$CoCl_2$ (*s*)	(.29)	3.77	4.68	11.04	(14.39)	(16.42)	(18.76)	25.4±1.0				25.4±1.0
Columbium: Cb (*g*)									44.46±0.01			44.46±0.01
Copper:												
Cu (*s*)	.01	.24	1.50	3.86	4.91	5.42	5.86	7.97±0.05				7.97±0.05
Cu (*g*)									39.75±0.01			39.75±0.01
Cu_2 (*g*)											58.9	58.9
Cu^{++} (*aq.*)										−26.5±1.0		−26.5±1.0
Cu_2O (*s*)	(.57)	(3.46)	(6.54)	9.50	11.32	12.80	14.69	24.1±1.5				24.1±1.5
CuO (*s*)	(.02)	(.28)	1.51	3.99	6.25	8.45	10.09	10.4±0.2				10.4±0.2
Cu_2S (*s*)	(.55)	(3.05)	(6.96)	11.94	14.81	16.45	18.24	28.9±0.8				28.9±0.8
CuS (*s*) (covellite)	(.09)	(1.26)	(3.63)	6.78	8.88	10.12	11.43	15.9±0.4				15.9±0.4
CuBr (*s*)										22.8±1.0		22.8±1.0
CuBr (*g*)									59.9±1.0			59.9±1.0
CuCl (*s*)										20.8±1.0		20.8±1.0
CuCl (*g*)									57.3±1.0			57.3±1.0
CuF (*g*)									54.9±1.0			54.9±1.0
CuI (*s*)	(.40)	2.90	6.54	9.99	11.26	11.89	12.92	23.1±0.3		24.0±1.0		23.1±0.3
CuI (*g*)									61.6±1.0			61.6±1.0
CuH (*g*)									46.9±0.1			46.9±0.1
CuD (*g*)									48.3±0.1			48.3±0.1
$CuCO_3$ (*s*)										17.7		17.7
$CuSO_4$ (*s*)										25.3		25.3
$CuO \cdot CuSO_4$ (*s*)										34.1		34.1
$CuSO_4 \cdot H_2O$ (*s*)										33.0		33.0
$CuSO_4 \cdot 3H_2O$ (*s*)										52.4		52.4
$CuSO_4 \cdot 5H_2O$ (*s*)										70.2		70.2
Fluorine:												
F_2 (*g*)									48.58±0.1			48.58±0.1
F (*g*)									37.93±0.01			37.93±0.01
F^- (*aq.*)										−2.3±2		−2.3±2
F_2O (*g*)									58.95±0.5			58.95±0.5
Gadolinium: $Gd_2(SO_4)_3 \cdot 8H_2O$*	(.60)	7.24	25.6	58.9	84.6	107.0	140.5	155.8±0.4				155.8±0.4
Gallium:												
Ga (*s*)	(.15)	.84	2.50	4.66	5.48	5.87	(6.21)	10.2±0.5				10.2±0.5
Ga (*g*)									40.39±0.01			40.39±0.01
Germanium:												
Ge (*s*)*	(.08)	1.12	3.02	3.96	4.83	5.45	6.24	10.1±0.2				10.1±0.2
Ge (*g*)									40.12±0.01			40.12±0.01
Gold:												
Au (*s*)	(.12)	1.23	3.50	5.10	5.68	5.89	6.03	11.4±0.1				11.4±0.1
Au (*g*)									43.13±0.01			43.13±0.01
AuH (*g*)									50.5±0.1			50.5±0.1
Hafnium:												
Hf (*s*)*	(.025)	.31	3.90	5.40	5.80	6.00	6.15	13.1±0.2				13.1±0.2
Hf (*g*)									44.65±0.01			44.65±0.01

[3] C_p=4.27 at 48.5°; C_p=6.13 at 71.6°.

[4] Entropy value based on C_p=1.94 at 71.4°; specific heat has also been measured in the range 2°–18°.

TABLE 7.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula mass							Entropies at 298.1° K.				
	10° K.	25° K.	50° K.	100° K.	150° K.	200° K.	298.1° K.	Third law	Spectroscopic or molecular constants	$\Delta F°$ and ΔH	Misc.	Value recommended
Helium: He (*g*)									30.13±0.01			30.13±0.01
Hydrogen:												
H_2 (*g*)								31.3±0.1	31.23±0.01			31.23±0.01
HD (*g*)								34.45±0.15	34.39±0.1			34.39±0.1
D_2 (*g*)								34.63±0.1	34.62±0.1			34.62±0.1
H (*g*)									27.40±0.01			27.40±0.01
H^+ (*aq.*)											0.00	0.00
H_2O (*l*)†	0.066	0.74	1.90	3.80	5.26	6.74 (*s*)	18.04 (*l*)	16.75±0.03	16.79			16.75±0.03
H_2O (*g*)								45.09±0.1	45.13±0.01	45.1		45.13±0.01
D_2O (*l*)†	(.03)	.80	1.96	4.05	6.09	8.04 (*s*)	19.70 (*l*)	18.08±0.1				18.08±0.1
D_2O (*g*)								47.42±0.1	47.38±0.1			47.38±0.1
H_2S (*g*)†	(.19)	1.88	4.58	9.37	13.46 (*s*)	16.26 (*l*)	8.12 (*g*)	49.10±0.1	49.15±0.1			49.15±0.1
HBr (*g*)†*	(.63)	3.39	5.63	10.39	11.24 (*s*)	14.27 (*l*)	6.95 (*g*)	47.6±0.15	47.48±0.01			47.48±0.01
HCl (*g*)†	(.235)	2.13	4.57	9.47	11.42 (*s*)	6.95 (*g*)	6.95	44.5±0.15	44.66±0.01			44.66±0.01
HF (*g*)									41.53±0.01			41.53±0.01
HI (*g*)†*	(1.00)	4.03	6.64	10.47	10.83	11.42 (*s*)	6.95 (*g*)	49.5±0.15	49.36±0.01			49.36±0.01
$(HCN)_4$ (*l*)†*	(.12)	1.33	4.23	8.03	10.06	11.95 (*s*)	16.96 (*l*)	26.96±0.1				26.96±0.1
HCN (*g*)								47.92±0.2	48.23±0.1			48.23±0.1
DCN (*g*)									49.18±0.1			49.18±0.1
H_2Se (*g*)									52.9±1.0			52.9±1.0
D_2Se (*g*)									55.2±1.0			55.2±1.0
HDSe (*g*)									55.4±1.0			55.4±1.0
Indium: In (*g*)									41.51±0.01			41.51±0.01
Iodine:												
I_2 (*s*)	.93	5.12	8.79	10.96	11.86	12.42	13.14	27.9±0.1				27.9±0.1
I_2 (*g*)									62.29±0.01			62.29±0.01
I (*g*)									43.19±0.01			43.19±0.01
I^- (*aq.*)										25.3±0.5		25.3±0.5
IBr (*g*)									61.84±0.1	62.0	61.84	61.84±0.1
IBr (*s*)										33.0±1.4		33.0±1.4
ICl (*g*)									59.11±0.1	59.15	59.18	59.11±0.1
ICl_3 (*s*)										41.1±0.5		41.1±0.5
IO_3^- (*aq.*)										28.0±1.0		28.0±1.0
Iridium:												
Ir (*s*)	(s)							8.7±0.5				8.7±0.5
Ir (*g*)									45.25±0.1			45.25±0.1
Iron:												
Fe (*s*)	.01	.09	.71	2.82	4.33	5.17	6.03	6.47±0.1				6.47±0.1
Fe (*g*)									43.12±0.01			43.12±0.01
Fe^{++} (*aq.*)										−25.9±1.0		−25.9±1.0

Fe^{+++} (*aq.*)										−61±5		−61±5
FeO (*s*)*	(.02)	(.24)	(1.45)	5.85	10.00	11.73	12.43	14.2±2.0		13.4±1.0		13.4±1.0
Fe_2O_3 (*s*)	(.05)	(.77)	(2.86)	7.65	13.42	18.27	25.04	21.5±0.5				21.5±0.5
Fe_3O_4 (*s*)*	(.06)	(.85)	(3.72)	13.53	22.17	27.85	34.28	35.0±0.7				35.0±0.7
FeS (*s*)	(.05)	(.73)	(2.82)	7.15	9.85	11.33	13.06	16.1±0.3				16.1±0.3
FeS_2 (*s*) (pyrite)	(.01)	.09	.72	4.50	8.77	11.77	14.84	12.7±0.2				12.7±0.2
$FeCl_2$ (*s*)*	(.83)	2.94	5.89	12.07	(15.56)	(17.57)	(19.87)	29.4±0.7				29.4±0.7
Fe_3C	(.04)	(.47)	(3.20)	10.42	15.92	21.04	25.33	25.7±1.0		23.8		24.2±1.5
$FeCO_3$ (*s*) (siderite)	(.05)	(1.01)	(3.66)	9.57	13.33	16.08	19.63	22.2±0.4				22.2±0.4
Fe_4N										37.4		37.4
Krypton: Kr (*g*)	(1.46)	4.43	6.01	7.55 (*s*)	4.97 (*g*)	4.97	4.97	39.0±0.3	39.20±0.01			39.20±0.01
Lanthanum:												
La (*s*)	[6]							13.7±0.8				13.7±0.8
La (*g*)									43.57±0.1			43.57±0.1
Lead:												
Pb (*s*)	.66	3.36	5.11	5.83	6.06	6.20	6.39	15.49±0.05				15.49±0.05
Pb (*g*)									41.90±0.01			41.90±0.01
Pb^{++} (*aq.*)										3.9±0.9		3.9±0.9
PbO (*s*) (yellow)	(.23)	1.95	3.99	6.75	8.55	9.84	11.60	16.6±0.5		17.8±1.0		16.6±0.5
PbO (*g*)								55.9	57.4±0.5			57.4±0.5
PbO_2 (*s*)	(.08)	(1.04)	(3.64)	7.56	10.42	12.56	15.45	18.3±0.5				18.3±0.5
Pb_3O_4 (*s*)				20.84	26.98	31.29	35.14	50.5±1.6				50.5±1.6
PbS (*s*)	(.37)	(2.88)	(6.18)	9.41	10.65	11.25	11.83	21.8±0.6				21.8±0.6
PbS (*g*)								64.3	61.2±1.5			61.2±1.5
PbTe (*s*)										26.4±1.0		26.4±1.0
$PbBr_2$ (*s*)	(1.11)	5.41	12.00	16.30	17.61	18.31	19.15	38.6±0.5		33.7		38.6±0.5
$PbBr_2$ (*g*)								78.6				78.6
$PbCl_2$ (*s*)	(.77)	4.37	10.09	14.32	16.24	17.29	18.35	34.0±1.0		32.6±0.6		32.6±0.6
$PbCl_2$ (*g*)										75.9		75.9
PbI_2 (*s*)	[7]							41.3		42.2±0.5		42.2±0.5
PbI_2 (*g*)										86.9		86.9
$PbCO_3$ (*s*) (cerussite)	(.59)	(3.43)	(7.52)	13.19	16.08	17.88	20.89	31.3±0.8				31.3±0.8
$PbO \cdot PbCO_3$ (*s*)										48.5±1.5		48.5±1.5
$Pb_3(PO_4)_2$ (*s*)	(1.20)	7.88	20.09	34.70	44.30	51.65	61.25	84.5±0.5				84.5±0.5
$PbSO_4$ (*s*)	(.36)	(3.48)	(8.82)	14.62	18.02	20.70	24.93	35.2±1.0				35.2±1.0
$PbSO_4 \cdot PbO$ (*s*)										48±2		48±2
$PbSO_4 \cdot 2PbO$ (*s*)										64±2.5		64±2.5
$PbSO_4 \cdot 3PbO$ (*s*)										79±3		79±3
Lithium:												
Li (*s*)	(.03)	.16	.99	3.07	4.26	4.94	5.65	6.70±0.06				6.70±0.06
Li (*g*)									33.15±0.01			33.15±0.01
Li_2 (*g*)									47.0±0.5			47.0±0.5
Li + (*aq.*)										4.7±1.0		4.7±1.0
LiCl (*g*)											49.9±1.4	49.9±1.4
LiF (*s*)											9.7±0.5	9.7±0.5
LiI (*g*)									56.5±1.0			56.5±1.0
LiH (*s*)	(.00)	(.03)	(.23)	1.66	4.03	5.79	8.28	5.9±0.5				5.9±0.5
LiH (*g*)									40.8±0.2			40.8±0.2

[5] C_p=1.77 at 48.5°.
[6] C_p=4.24 at 48.5°.
[7] Insufficient data; entropy based on specific-heat measurements in the range 22°–96°.

TABLE 7.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula mass							Entropies at 298.1° K.				
	10° K.	25° K.	50° K.	100° K.	150° K.	200° K.	298.1° K.	Third law	Spectroscopic or molecular constants	$\Delta F°$ and ΔH	Misc.	Value recommended
Lithium—Continued.												
LiD (*g*)									42.4±0.2			42.4±0.2
LiOH (*s*)										12.8±1.0		12.8±1.0
Li_2CO_3	(0.04)	0.46	2.78	8.33	13.31	17.32	23.28	21.5±0.2				21.5±0.2
Magnesium:												
Mg (*s*)	.01	.19	1.41	3.77	4.90	5.38	5.71	7.77±0.1				7.77±0.1
Mg (*g*)								35.3	35.51±0.01			35.51±0.01
Mg^{++} (*aq.*)										−31.6±3		−31.6±3
MgO (*s*)	(.00)	.03	.22	2.04	4.48	6.52	9.03	6.55±0.15				6.55±0.15
MgO (*g*)									50.7±0.3			50.7±0.3
$Mg(OH)_2$ (*s*)	(.02)	.18	1.18	5.15	9.80	13.60	18.43	15.09±0.03				15.09±0.03
$MgCO_3$ (*s*) (magnesite)	(.01)	(.17)	(1.14)	5.93	10.50	13.85	18.05	15.7±0.2				15.7±0.2
$MgSiO_3$ (*s*)	(.04)	.39	2.02	5.26	8.61	12.56	19.40	15.4±1.0				15.4±1.0
$MgSO_4$ (*s*)										20±2		20±2
Manganese:												
Mn (*s*)	(.01)	(.17)	(1.17)	3.57	4.79	5.62	6.26	7.61±0.06				7.61±0.06
Mn (*g*)									41.50±0.01			41.50±0.01
MnO (*s*)*	(.04)	(.54)	(2.50)	7.88	7.98	9.10	10.27	14.4±0.6				14.4±0.6
MnO (*g*)									54.0±1.5			54.0±1.5
MnO_2 (*s*)*	(.03)	(.37)	(1.94)	5.96	8.02	10.34	13.67	13.9±0.4				13.9±0.4
Mn_2O_3 (*s*)										22.9		22.9
Mn_3O_4 (*s*)	(.06)	(.99)	(5.18)	14.41	21.95	27.37	33.29	35.5±0.7				35.5±0.7
MnS (*s*)*	(.05)	(.74)	(3.46)	9.41	11.91	11.39	11.94	18.7±0.3				18.7±0.3
MnSe (*s*)*	(.08)	(1.22)	(5.05)	10.48	11.85	12.62	12.20	21.7±0.5				21.7±0.5
MnTe (*s*)*	(.15)	(1.69)	(5.47)	10.07	12.05	13.34	17.40	22.4±0.5				22.4±0.5
$MnCl_2$ (*s*)	(.20)	1.58	5.28	11.80	(14.94)	(16.76)	(18.98)	25.9±1.0				25.9±1.0
$MnCO_3$ (rhodochrosite)	(.03)	(.60)	(2.86)	8.64	12.82	15.61	19.48	20.5±0.3				20.5±0.3
MnO_4^- (*aq.*)										46.7±0.4		46.7±0.4
Mercury:												
Hg (*l*)†	1.10	3.15	5.02	5.90	6.27	6.57(*s*)	6.65 (*l*)	18.5±0.2				18.5±0.2
Hg (*g*)									41.80±0.01			41.80±0.01
Hg_2^{++} (*aq.*)										17.7±3		17.7±3
HgO (*s*) (red)	(.19)	1.94	4.31	6.89	8.39	9.46	10.93	16.6±1.0				16.6±1.0
HgO (*s*) (yellow)										17.6±0.5		17.6±0.5
HgBr (*s*)										26.4±1.0		26.4±1.0
HgCl (*s*)	(.48)	3.52	7.81	9.44	10.67	11.38	12.15	23.0±0.7		23.5±0.5	24.7	23.5±0.5
$HgBr_2$ (*g*)									74.7±2			74.7±2
$HgBr_2$ (*s*)										38.9		38.9
$HgCl_2$ (*g*)									70.4±2			70.4±2
$HgCl_2$ (*s*)										34.6		34.6

HgI_2 (g)									78.7±2			78.7±2
HgI_2 (s)										42.2		42.2
Hg_2SO_4 (s)	(.80)?	6.77	12.20	18.95	23.02	26.44	31.55	48.0±0.5		47.9		48.0±0.5
Molybdenum:												
Mo (s)	(.01)	.13	.94	3.19	4.49	5.10	5.61	6.83±0.05				6.83±0.05
Mo (g)									43.47±0.01			43.47±0.01
MoS_2 (s)	(.02)	(.33)	(1.85)	5.72	9.79	12.57	15.19	15.0±0.2				15.0±0.2
MoS_3 (s)										15.9±1.0		15.9±1.0
Neon: Ne (g)	1.48 (s)						4.97 (g)	35.0±0.1	34.96±0.01			34.96±0.01
Nickel:												
Ni (s)	.01	.13	.99	3.24	4.64	5.38	6.16	7.12±0.05				7.12±0.05
Ni (g)									43.53±0.01			43.53±0.01
NiO (s)	(.01)	(.11)	(.78)	3.43	5.87	8.04	10.60	9.2±0.1				9.2±0.1
$NiCl_2$ (s)	(.25)	1.53	5.40	11.50	(14.94)	(16.68)	(18.57)	25.6±1.0				25.6±1.0
$Ni(CO)_4$ (g)									97±2			97±2
Nitrogen:												
N_2 (g)†	(1.06)	6.50	9.92 (s)	6.95 (g)	6.95	6.95	6.95	45.9±0.1	45.79±0.01			45.79±0.01
N (g)									36.62±0.01			36.62±0.01
N_2O (g)†	(.23)	2.49	6.56	9.92	12.18 (s)	8.04 (g)	9.24	51.44±0.1	52.58±0.01			52.58±0.01
NO (g)†	(.28)	2.36	5.09	8.61 (s)	7.44 (g)	7.27	7.14	49.6	50.34±0.01			50.34±0.01
NO_2 (g)									57.47±0.1			57.47±0.1
N_2O_4 (g)	(.33)	3.20	8.70	14.53	18.35	21.92 (s)	33.96 (l)	72.7±0.2				72.7±0.2
N_2O_5 (s)				15.11	21.63	26.07	(34.2)	36.6±2				36.6±2
N_2O_5 (g)								82				82
NOBr (g)										65.2±0.2		65.2±0.2
NOCl (g)										63.0±0.3		63.0±0.3
NH_3 (g)†	(.06)	.66	2.66	6.25	9.31 (s)	17.58 (l)	8.49 (g)	45.94±0.1	46.03±0.1			46.03±0.1
NH_4Cl (s)*	(.05)	.64	3.67	9.00	12.32	16.39	20.71	31.8				31.8
NH_4HCO_3 (s)										28.3±2		28.3±2
NH_4HS (s)										27.1±2		27.1±2
NH_4OH (aq.)										42.8±0.4		42.8±0.4
NH_4^+ (aq.)										26.4±0.5		26.4±0.5
NO_2^- (aq.)										29.9±1.0		29.9±1.0
NO_3^- (aq.)										35.0±0.2		35.0±0.2
Osmium:												
Os (s)	[8]							7.8±0.5				7.8±0.5
OsO_4 (g)									65.6±0.5			65.6±0.5
OsO_4 (s) (yellow)									29.8±1.0	29.8±1.0		29.8±1.0
Oxygen:												
O_2 (g)†	(.60)	5.30	11.01(s)	6.95(g)	6.95	6.95	6.95	49.1±0.1	49.03±0.01			49.03±0.01
O (g)									38.48±0.01			38.48±0.01
O_3 (g)									57.1±0.5			57.1±0.5
OH (g)									43.90±0.01			43.90±0.01
OH^- (aq.)										−2.49±0.06		−2.49±0.06
Palladium:												
Pd (s)	[9]							8.9±0.5				8.9±0.5
Pd (g)									39.92±0.01			39.92±0.01
Phosphorus:												
P_2 (g)									52.1±0.3			52.1±0.3
P_4 (g)									66.8±0.5			66.8±0.5

[8] C_p=1.37 at 48.5°.

[9] C_p=1.87 at 48.5°.

TABLE 7.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula mass							Entropies at 298.1° K.				
	10° K.	25° K.	50° K.	100° K.	150° K.	200° K.	298.1° K.	Third law	Spectroscopic or molecular constants	$\Delta F°$ and ΔH	Misc.	Value recommended
Phosphorus—Continued.												
P (*s*) (white)										10.6±1.0		10.6±1.0
P (*g*)									38.99±0.01			38.99±0.01
PBr_3 (*g*)									83.4±2			83.4±2
PCl_3 (*g*)									74.7±2			74.7±2
PCl_3 (*l*)										52.2±3		52.2±3
PCl_5 (*g*)										87.7±3		87.7±3
PCl_5 (*s*)										40.8±4		40.8±4
PF_3 (*g*)									64.2±1.0			64.2±1.0
PH_3 (*g*)†	(0.32)	2.66	10.80	11.18(*s*)	14.53(*l*)	8.11(g)	8.87	50.35±0.1	50.5±0.3			50.35±0.1
PH_3 (*g*)†* (unstable)	(.53)	3.85										
PH_4I (*s*)				12.74	16.57	19.07	26.16	32.1±2				32.1±2
PN (*g*)									50.44±0.1			50.44±0.1
H_3PO_4 (*aq.*)										44.0±1.5		44.0±1.5
$H_2PO_4^-$ (*aq.*)										28.0±1.5		28.0±1.5
HPO_4^{--} (*aq.*)										−2.3±1.5		−2.3±1.5
PO_4^{---} (*aq.*)										−45±2		−45±2
Platinum:												
Pt (*s*)	.05	.65	2.54	4.70	5.52	5.93	6.35	10.0±0.1				10.0±0.1
Pt (*g*)									45.98±0.2			45.98±0.2
PtS (*s*)										12.2		12.2
PtS_2 (*s*)										17.4		17.4
Potassium:												
K (*s*)	(.49)	3.01	4.98	5.88	6.24	6.49	6.97	15.2±0.2				15.2±0.2
K (*g*)									38.30±0.01			38.30±0.01
K_2 (*g*)									59.5±0.5			59.5±0.5
K^+ (*aq.*)										24.2±0.2		24.2±0.2
KBr (*s*)			8.34	10.08	11.10	11.82	12.82	22.4±1.0			22.6±0.5	22.6±0.5
KBr (*g*)									60.4±1.0		58.2±1.5	60.4±1.0
KCl (*s*)	.10	1.30	5.04	9.38	10.89	11.58	12.31	19.76±0.1			19.5±0.5	19.76±0.1
KCl (*g*)								57.6	57.7±1.0		56.0±1.4	57.7±1.0
KF (*g*)											56.7±1.8	56.7±1.8
KI (*s*)											24.1±0.5	24.1±0.5
KH (*g*)									47.3±0.1			47.3±0.1
$KBrO_3$ (*s*)	(.255)	2.74	8.69	15.53	19.19	21.70	25.07	35.7±0.2				35.7±0.2
$KClO_3$ (*s*)	(.21)	2.74	8.79	15.11	17.96	20.34	23.96	34.2±0.2				34.2±0.2
$KClO_4$ (*s*)	(.46)	2.94	9.41	15.52	18.55	21.13	26.33	36.1±0.3				36.1±0.3
KIO_3 (*s*)	(.295)	2.89	8.75	15.68	19.63	22.18	25.42	36.2±0.2				36.2±0.2
KNO_3 (*s*)	(.18)	2.08	7.71	14.46	16.15	19.10	23.01	31.8±0.2				31.8±0.2

$KMnO_4$ (*s*)	(.59)	4.32	10.38	16.83	20.94	23.99	28.10	41.1±0.2				41.1±0.2
K_2SO_4 (*s*)										44.8		44.8
Radon: Rn (*g*)									42.10±0.01			42.10±0.01
Rhenium: Re (*g*)									45.14±0.01			45.14±0.01
Rhodium:												
Rh (*s*)	[10]							7.6±0.5				7.6±0.5
Rh (*g*)									44.40±0.1			44.40±0.1
Rubidium:												
Rb (*g*)									40.64±0.01			40.64±0.01
Rb (*s*)										16.6±1.0		16.6±1.0
Rb^+ (*aq.*)										28.7±0.7		28.7±0.7
RbCl (*g*)											57.9±2.0	57.9±2.0
RbCl (*s*)											21.2±1.0	21.2±1.0
RbI (*g*)											62.2±2.0	62.2±2.0
$RbClO_3$ (*s*)	(.33)	3.01	9.53	15.81	18.81	21.12	24.66	36.3±0.4				36.3±0.4
Ruthenium:												
Ru (*g*)									44.58±0.1			44.58±0.1
Ru (*s*)	[11]							6.9±0.5				6.9±0.5
RuS_2 (*s*)										13.2		13.2
Samarium: $Sm_2(SO_4)_3 \cdot 8H_2O$	(.70)	7.67	27.4	62.3	88.0	109.2	144.9	160.9				160.9
Scandium: Sc (*g*)									41.77±0.1			41.77±0.1
Selenium:												
Se (*s*)	(.18)	(1.11)	(2.52)	4.36	5.19	5.61	5.92	10.0±0.5				10.0±0.5
Se (*g*)									42.22±0.1			42.22±0.1
Se_2 (*g*)									61.2±0.3			61.2±0.3
SeF_6 (*g*)									75.2±2			75.2±2
Silicon:												
Si (*s*)	(.00)	.06	.48	1.74	2.87	3.74	4.73	4.50±0.05				4.50±0.05
Si (*g*)									40.13±0.01			40.13±0.01
SiO_2 (quartz)	(.03)	.38	1.38	3.72	5.97	7.82	10.62	10.1±0.1				10.1±0.1
SiO_2 (cristobalite)	(.05)	.58	1.56	3.80	6.03	7.86	10.56	10.35±0.1				10.35±0.1
SiO_2 (tridymite)	(.05)	(.58)	(1.60)	3.90	6.14	7.97	10.66	10.5±0.2				10.5±0.2
SiO_2 (glass)	.06	.56	1.63	3.86	5.89	7.75	10.60	11.20±0.4				11.2±0.4
$SiCl_4$ (*g*)									79.2±1.0			79.2±1.0
$SiCl_4$ (*l*)†				20.65	26.21	31.94 (*s*)	34.73 (*l*)	57.2±2		57.4±2		57.3±2
SiF_4 (*g*)									68.0±1.0			68.0±1.0
SiH_4 (*g*)†	(.56)	3.27	8.41 (*s*)	14.46 (*l*)	14.77	8.50 (*g*)	10.26	48.7±0.2	48.7±0.1			48.7±0.1
SiC (*s*)	(.00)	(.00)	(.10)	1.02	2.42	3.89	6.37	3.95±0.02				3.95±0.02
Si_3N_4 (*s*)										22.8		22.8
Silver:												
Ag (*s*)	.05	.70	2.77	4.84	5.49	5.80	6.10	10.20±0.05				10.20±0.05
Ag (*g*)									41.33±0.01			41.33±0.01
Ag^+ (*aq.*)										17.54±0.15		17.54±0.15
Ag_2O (*s*)*	(1.08)	5.26	8.44	10.75	12.47	13.93	15.75	29.1±0.3		29.7±2.0		29.1±0.3
Ag_2S (α)										35.0±1.0		35.0±1.0
AgBr (*s*)	.56	3.72	8.02	10.83	11.68	12.10	12.52	25.60±0.1			26.1±0.5	25.60±0.1
AgBr (*g*)									62.1±1.0			62.1±1.0
AgCl (*s*)	.405	2.95	6.59	10.00	11.22	11.88	12.14	23.0±0.1			22.5±0.5	23.0±0.1
AgCl (*g*)									59.8±1.0	59.7±2.0		59.8±1.0
AgI (*s*)	(1.46)	4.41	7.53	10.94	11.98	12.49	13.01	27.1±1.0		27.6±0.4		27.6±0.4

[10] C_p=1.27 at 48.5°.

[11] C_p=1.01 at 48.5°.

TABLE 7.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula mass							Entropies at 298.1° K.				
	10° K.	25° K.	50° K.	100° K.	150° K.	200° K.	298.1° K.	Third law	Spectroscopic or molecular constants	$\Delta F°$ and ΔH	Misc.	Value recommended
Silver—Continued.												
AgI (*g*)									64.2±1.0			64.2±1.0
AgH (*g*)									48.9±0.1			48.9±0.1
AgD (*g*)									50.3±0.1			50.3±0.1
Ag_2CO_3 (*s*)	(0.49)	(3.90)	(10.22)	16.95	20.79	23.20	26.83	40.0±0.9				40.0±0.9
Ag_2CrO_4 (*s*)	(1.11)	6.04	12.83	21.10	26.28	29.92	34.00	52.0±0.3				52.0±0.3
$AgClO_2$ (*s*)	(.46)	3.25	8.15	13.82	16.58	18.50	20.87	32.2±0.3				32.2±0.3
$AgIO_3$ (*s*)	(.45)	3.30	8.38	14.91	18.97	21.72	24.60	37.5±1.0				37.5±1.0
$AgNO_2$ (*s*)	(.64)	3.46	7.73	12.89	15.45	17.17	19.17	30.6±0.2				30.6±0.2
$AgNO_3$ (*s*)	(.57)	3.61	8.56	14.35	17.02	18.91	22.24	33.7±0.2				33.7±0.2
Ag_2SO_4 (*s*)	(.88)	5.63	12.63	19.78	23.70	26.89	31.40	47.9±0.3				47.9±0.3
$Ag(NH_3)_2^+$ (*aq.*)										57.8±1.0		57.8±1.0
Sodium:												
Na (*s*)	(.14)	1.44	3.82	5.40	5.93	6.25	6.79	12.2±0.1				12.2±0.1
Na (*g*)									36.72±0.01			36.72±0.1
Na_2 (*g*)									54.9±0.3			54.9±0.3
Na^+ (*aq.*)										14.0±0.4		14.0±0.4
Na_2O (*s*)											17±1	17±1
NaBr (*g*)									58.1±1.0		57.8±2.0	58.1±1.0
NaCl (*s*)	(.04)	.58	3.82	8.44	10.15	11.09	12.14	17.3±0.5			17.2±0.5	17.3±0.5
NaCl (*g*)								56.4	55.5±1.0		55.4±1.4	55.5±1.0
NaF (*s*)											13.1±0.5	13.1±0.5
NaF (*g*)											53.8±1.8	53.8±1.8
NaI (*g*)									60.0±1.0			60.0±1.0
NaH (*g*)									45.0±0.1			45.0±0.1
NaD (*g*)									46.5±0.1			46.5±0.1
NaOH (*s*)										14.2±1.5		14.2±1.5
Na_2CO_3 (*s*)	(.16)	(1.84)	(6.17)	14.43	19.52	22.49	26.41	32.5±0.6				32.5±0.6
$NaHCO_3$ (*s*)	(.05)	(.75)	(4.06)	11.01	14.85	17.40	20.94	24.4±0.4				24.4±0.4
$NaNO_3$ (*s*)	(.115)	1.54	5.81	12.45	15.81	18.07	22.24	27.8±0.1				27.8±0.1
Na_4SiO_4 (*s*)	(.04)	(.68)	(6.37)	20.30	29.82	36.24	43.79	46.8±0.6				46.8±0.6
Na_2SiO_3 (*s*)	(.04)	(.45)	(3.33)	11.52	17.51	21.47	26.72	27.2±0.3				27.2±0.3
$Na_2Si_2O_5$ (*s*)	(.17)	(1.84)	(5.60)	15.87	23.89	29.69	37.41	39.4±0.6				39.4±0.6
Na_2SO_4 (*s*)	(.07)	1.22	6.36	15.92	21.42	25.27	30.42	35.7±0.1				35.7±0.1
$Na_2SO_4 \cdot 10H_2O$ (*s*)	(.70)	7.35	24.75	56.20	79.55	99.0	141.3	140.5±0.3				140.5±0.3
NaK									58.6±0.5		58.6	58.6±0.5
Strontium:												
Sr (*g*)									39.33±0.01			39.33±0.01
Sr^{++} (*aq.*)										−7.3±1.5		−7.3±1.5
SrO (*s*)	(.03)	(.38)	(2.09)	5.78	8.17	9.55	10.76	13.0±0.2				13.0±0.2

SrO (*g*)									54.8±0.5				54.8±0.5
$SrCO_3$ (strontianite)	(.04)	(.72)	(3.92)	10.58	14.25	16.47	19.46	23.2±0.4					23.2±0.4
$SrSO_4$ (*s*)										28.2			28.2
Sulfur:													
S (*rh*)	(.19)	.86	1.77	3.06	3.96	4.64	5.40	7.62±0.05					7.62±0.05
S (*mono*)			1.77	3.10	4.06	4.80	5.65	7.78±0.1					7.78±0.1
S (*g*)									40.10±0.01				40.10±0.01
S_2 (*g*)									54.41±0.1				54.41±0.1
S_6 (*g*)										92			92
S_8 (*g*)										109			109
SO (*g*)									53.07±0.1			53.10	53.07±0.1
SO_2 (*g*)†	(.28)	2.73	7.35	11.45	13.80 (*s*)	20.98 (*l*)	9.52 (*g*)	59.24±0.1	59.40±0.2				59.24±0.1
SO_3 (*g*)										63.8±2.0			63.8±2.0
SO_3 (*l*)										31.7±3.0			31.7±3.0
SO_2Cl_2 (*g*)										82.3±2.0			83.2±2.0
SO_2Cl_2 (*l*)										60.5±3.0			60.5±3.0
SF_6 (*g*)†	(1.56)	7.09	11.52	13.94	17.96	24.88 (*s*)	23.05 (*g*)	70.3±0.7	69.6±0.5				69.6±0.5
H_2S (*aq.*)										29.4±0.3			29.4±0.3
HS^- (*aq.*)										14.9±1.0			14.9±1.0
H_2SO_3 (*aq.*)										54.7±1.0			54.7±1.0
HSO_3^- (*aq.*)										32.6±1.5			32.6±1.5
SO_3^{--} (*aq.*)										3±3			3±3
HSO_4^- (*aq.*)										30.6±0.2			30.6±0.2
SO_4^{--} (*aq.*)										4.4±1.0			4.4±1.0
Tantalum:													
Ta (*s*)	(.05)	(.59)	(2.60)	4.78	5.47	5.77	6.05	9.94±0.1					9.94±0.1
Ta_2O_5 (*s*)	(.09)	(1.21)	(5.29)	13.87	20.68	25.70	32.30	34.2±0.4					34.2±0.4
TaC (*s*)	(.03)	(.37)	(1.96)	4.45	5.78	6.97	8.79	10.1±0.1					10.1±0.1
Tellurium:													
Te (*s*)	(.21)	1.55	3.55	5.16	5.66	5.90	6.14	11.9±0.1					11.9±0.1
Te (*g*)									43.65±0.01				43.65±0.01
Te_2 (*g*)									64.5±0.5				64.5±0.5
TeF_6 (*g*)									80.6±1.0				80.6±1.0
Thallium:													
Tl (*s*)	.81	3.21	5.01	5.84	6.06	6.16	6.29	15.4±0.1					15.4±0.1
Tl (*g*)									43.23±0.01				43.23±0.01
Tl^+ (*aq.*)										30.5±0.4			30.5±0.4
TlBr (*s*)										27.9	26.8±1.0		26.8±1.0
TlBr (*g*)									65.0±1.5	63.2			65.0±1.5
TlCl (*s*)	(.62)	4.30	8.04	10.67	11.58	12.07	12.60	25.9±0.6		27.1		23.7	25.6±1.5
TlCl (*g*)									62.3±1.5	60.0			62.3±1.5
TlF (*g*)									60.4±1.5				60.4±1.5
TlI (*s*)											29.9±1.0		29.9±1.0
TlI (*g*)										63.9			63.9
$TlNO_3$ (*s*)	(1.25)	5.10	10.53	15.58	17.83	19.68	23.78	38.4±0.2					38.4±0.2
Thorium: Th	(12)							13.6±0.8					13.6±0.8
Tin:													
Sn (white)	.22	1.65	3.68	5.35	5.85	6.08	6.30	12.3±0.1					12.3±0.1
Sn (gray)	.30	1.24	2.69	4.67	5.44	5.81	6.16	10.7±0.1					10.7±0.1
Sn (*g*)									40.24±0.01				40.24±0.01
Sn^{++} (*aq.*)										−4.9±1.0			−4.9±1.0

[12] C_p=4.22 at 48.5°.

TABLE 7.—*Low-temperature specific heats and entropies at 298.1° K.—Continued*

Substance	Specific heats, calories per formula mass							Entropies at 298.1° K.				
	10° K.	25° K.	50° K.	100° K.	150° K.	200° K.	298.1° K.	Third law	Spectroscopic or molecular constants	$\Delta F°$ and ΔH	Misc.	Value recommended
Tin—Continued.												
SnO (*s*)	(0.05)	(0.66)	(2.69)	5.86	7.93	9.31	10.59	13.5±0.3				13.5±0.3
SnO_2 (*s*)	(.02)	(.25)	(1.55)	4.98	7.86	10.10	12.57	12.5±0.3				12.5±0.3
$SnBr_4$ (*g*)									98.6±2.0			98.6±2.0
$SnCl_4$ (*g*)									87.2±1.0			87.2±1.0
$SnCl_4$ (*l*)†				24.12	28.66	31.60 (*s*)	39.49 (*l*)	61.8		62.1±1.5		62.1±1.5
SnTe (*s*)										24.2±1.0		24.2±1.0
Titanium:												
Ti (*s*)	(13)							6.6±0.4				6.6±0.4
Ti (*g*)									43.07±0.1			43.07±0.1
TiO_2 (rutile)	(.02)	(.25)	(1.52)	4.59	7.63	10.35	13.49	12.4±0.2				12.4±0.2
$TiCl_4$ (*g*)									84.4±1.0			84.4±1.0
$TiCl_4$ (*l*)†				22.77	27.14	30.12 (*s*)	37.53 (*l*)	59.5		60.4±1.5		60.4±1.5
Tungsten:												
W (*s*)	(.02)	.21	1.47	3.90	5.00	5.51	5.97	8.0±0.1				8.0±0.1
W (*g*)									41.56±0.01			41.56±0.01
Uranium: U (*s*)	(14)							11.1±0.6				11.1±0.6
Vanadium:												
V (*s*)	(.01)	(.13)	(.96)	3.23	4.61	5.28	5.90	7.0±0.1				7.0±0.1
V (*g*)									43.55±0.1			43.55±0.1
V_2O_3 (*s*)*	(.03)	(.34)	(1.86)	6.86	14.58	19.27	24.67	23.5±0.3				23.5±0.3
V_2O_4 (*s*)	(.03)	(.40)	(2.32)	8.80	15.88	21.45	27.96	24.5±0.3				24.5±0.3
V_2O_5 (*s*)	(.05)	(.78)	(4.54)	12.43	19.24	24.16	30.51	31.3±0.5				31.3±0.5
Xenon: Xe (*g*)†	(1.94)	4.73	5.99	6.75	8.04 (*s*)	4.97 (*g*)	4.97	40.7±0.3	40.54±0.01			40.54±0.01
Yttrium: Y (*g*)									42.88±0.1			42.88±0.1
Zinc:												
Zn (*s*)	.05	.77	2.65	4.59	5.38	5.70	6.07	9.95±0.05				9.95±0.05
Zn (*g*)									38.46±0.01			38.46±0.01
Zn^{++} (*aq.*)										−25.7±1.0		−25.7±1.0
ZnO (*s*)	(.02)	(.36)	1.86	4.24	6.18	7.72	9.62	10.4±0.1		10.2		10.4±0.1
ZnO (*g*)									54.1±1.0			54.1±1.0
ZnS (*s*)	(.05)	.72	2.76	5.88	8.23	9.48	(11.00)	13.8±0.2				13.8±0.2
ZnTe (*s*)										19.0±1.0		19.0±1.0
$ZnBr_2$ (*s*)										33.0±1.0		33.0±1.0
$ZnCl_2$ (*s*)										25.9±1.0		25.9±1.0
ZnI_2 (*s*)										38.5±1.0		38.5±1.0
$ZnCO_3$ (smithsonite)	(.03)	(.50)	(2.60)	8.21	12.41	15.26	19.05	19.7±0.3				19.7±0.3
$ZnSO_4$ (*s*)										30.7±2.0		30.7±2.0
ZnSb (*s*)										21.4±1.4		21.4±1.4

Zn_3Sb_2 (*s*)										63.6±1.8		63.6±1.8
Zn_4Sb_3 (*s*)										73.5±2.1		73.5±2.1
Zirconium:												
Zr (*s*)	[15]							9.5±0.6				9.5±0.6
Zr (*g*)									43.33±0.1			43.33±0.1
Electron gas: E									4.98±0.01			4.98±0.01

[13] = Cp=0.91 at 48.5°.

[14] = C_p=3.04 at 48.5°.

[15] C_p=2.19 at 48.5°.

TABLE 8.—*Date for changes in state*

Substance	*T*, °K.	Type of change	Heat absorbed, cal. per mole
Argon: A	83.0	Fusion	267.8
Do	83.85	Sublimation at 516.3 mm. pressure	1,899
Do	87.3	Vaporization at 1 atm. pressure	1,557.5
Boron trifluoride: BF_3	144.46	Fusion	1,014
Do	154.5	Vaporization at 0.2185 atm. pressure	4,440
Bromine: Br_2	265.9	Fusion	2,580
Carbon monoxide: CO	61.55	Transition	151.3
Do	68.09	Fusion	199.7
Do	81.61	Vaporization at 1 atm. pressure	1,443.6
Carbon dioxide: CO_2	194.67	Sublimation at 1 atm. pressure	6,030
Carbon disulfide: CS_2	161.1	Fusion	1,049
Carbonyl sulfide: COS	134.31	do	1,229.8
Do	222.87	Vaporization at 1 atm. pressure	4,423
Carbon tetrachloride: CCl_4	225.4	Transition	1,080.8
Do	250.2	Fusion	577.2
Carbon tetrafluoride: CF_4	76.23	Transition	353.2
Do	89.47	Fusion	167.4
Do	122.0	Vaporization at 0.1365 atm. pressure	3,120
Methane: CH_4	90.6	Fusion	224.0
Do	99.54	Vaporization at 246.13 mm. pressure	2,036
Do	111.7	Vaporization at 1 atm. pressure	1,988
Cyanogen: C_2N_2	245.27	Fusion	1,938
Do	251.95	Vaporization at 1 atm. pressure	5,576
Chlorine: Cl_2	172.12	Fusion	1,531
Do	239.05	Vaporization at 1 atm. pressure	4,878
Hydrogen: H_2	13.95	Fusion	28.0
Do	13.95	Vaporization at 53.8 mm. pressure	217.8
HD	16.60	Fusion	38.0
Do	16.60	Vaporization at 95 mm. pressure	265
D_2	18.65	Fusion	47.0
Do	19.65	Vaporization at 194.5 mm. pressure	302.3
Water: H_2O	273.1	Fusion	1,435.7
Do	298.1	Vaporization at 23.76 mm. pressure	10,499
D_2O	273.1	Sublimation at 3.65 mm. pressure	12,636
Do	276.9	Fusion	1,501
Hydrogen sulfide: H_2S	103.52	Transition	368.0
Do	126.22	do	121.3
Do	187.61	Fusion	568.1
Do	212.77	Vaporization at 1 atm. pressure	4,463
Hydrogen bromide: HBr	89.2	Transition	63.4
Do	113.2	do	78.8
Do	116.8	do	85.7
Do	186.24	Fusion	575.1
Do	206.38	Vaporization at 1 atm. pressure	4,210
Hydrogen chloride: HCl	98.36	Transition	284.3
Do	158.91	Fusion	476.0
Do	188.07	Vaporization at 1 atm. pressure	3,860
Hydrogen fluoride: HF	190.09	Fusion	1,094
Hydrogen iodide: HI	70.1	Transition	18.6
Do	125.6	do	192.4
Do	222.31	Fusion	686.3
Do	237.75	Vaporization at 1 atm. pressure	4,724
Hydrogen cyanide: (HCN)*	170.37	Transition	3.8
Do	259.86	Fusion	2,009
Do	298.80	Vaporization at 1 atm. pressure	6,027
Krypton: Kr	115.95	Fusion	390.7
Do	119.93	Vaporization at 1 atm. pressure	2,158
Mercury: Hg	234.2	Fusion	557.2
Neon: Ne	24.59	Sublimation at 323.5 mm. pressure	510.6
Nitrogen: N_2	35.61	Transition	54.71
Do	63.14	Fusion	172.3
Do	77.32	Vaporization at 1 atm. pressure	1,332.9
Nitrous oxide: N_2O	182.26	Fusion	1,563
Do	184.59	Vaporization at 1 atm. pressure	3,958
Nitric oxide: NO	109.49	Fusion	549.5
Do	121 36	Vaporization at 1 atm. pressure	3,292.6
Nitrogen tetroxide: $N_2O_4+NO_2$	261.90	Fusion	3,502
Do	294.25	Vaporization at 1 atm. pressure	9,110
Ammonia: NH_3	195.36	Fusion	1,351.6
Do	239.68	Vaporization at 1 atm. pressure	5,581
Oxygen: O_2	23.66	Transition	22.42
Do	43.76	do	177.6
Do	54.39	Fusion	106.3
Do	90.13	Vaporization at 1 atm. pressure	1,628.8
Phosphine: PH_3	30.29	Transition	19.6
Do	49.43	do	185.7
Do	88.10	do	115.8
Do	139.35	Fusion	270.4
Do	185.38	Vaporization at 1 atm. pressure	3,489

TABLE 8.—*Date for changes in state*—Continued

Substance	*T*, °K.	Type of change	Heat absorbed, cal. per mole
Silicon tetrachloride: $SiCl_4$	203.3	Fusion	1,845
Monosilane: SiH_4	63.45	Transition	147.1
Do	88.48	Fusion	159.5
Do	161.5	Vaporization at 1 atm. pressure	2,955
Sulfur dioxide: SO_2	197.64	Fusion	1,769.1
Do	263.08	Vaporization at 1 atm. pressure	5,960
Sulfur hexafluoride: SF_6	94.30	Transition	384.2
Do	186.0	Sublimation at 0.161 atm. pressure	5,615
Tin tetrachloride: $SnCl_4$	239.9	Fusion	2,190
Titanium tetrachloride: $TiCl_4$	248.0	do	2,240
Xenon: Xe	161.3	do	548.5
Do	165.1	Vaporization at 1 atm. pressure	3,020

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