The Electrode Potential of Gaseous Bromine and of Liquid Bromine.
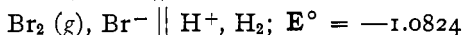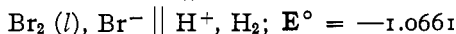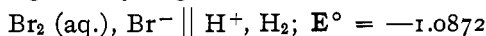
We have found that the normal electrode potential of aqueous bromine is —1.0872 v. against the normal hydrogen electrode. Now the vapor pressure of (hypothetical) molal bromine we have just seen to be 1.45 atmos. Hence, for bromine vapor at atmospheric pressure the normal potential will be numerically less by $0.05915 \times \log (1.45)^{1/2}$, and is, therefore, —1.0824 v.

The vapor pressure of liquid bromine at 25°, according to the measurements of Ramsay and Young,[1] is 213 mm. = 0.280 atmos. Therefore, the normal electrode potential of liquid bromine is $-1.0824 - 0.05915 \log (0.280)^{1/2} = -1.0661$ v.

Summary.

The potential of bromine in potassium bromide has been measured against the calomel electrode, and the potential of bromine in hydrobromic acid against the hydrogen electrode. In the latter case concordant measurements with variations in concentration of tenfold in hydrobromic acid, and of more than tenfold in bromine, fix the normal electrode potential of bromine within one- or two-tenths of a millivolt. The free energy of dilution of hydrobromic acid from 0.1 M and 0.03 M to 0.01 M has been measured and the corrected degrees of dissociation shown to be identical with those of hydrochloric acid. The distribution constant of bromine between carbon tetrachloride and slightly acidified water has been obtained, as well as the distribution constant between carbon tetrachloride and 0.1 M hydrobromic acid. The vapor pressure of bromine over solutions in carbon tetrachloride have been measured and found to be proportional to the mol fraction in the latter phase.

With the aid of these measurements we find the following normal electrode potentials against hydrogen at 25°:

$$\text{Br}_2 \text{ (aq.)}, \text{Br}^- \| \text{H}^+, \text{H}_2; \mathbf{E}^\circ = -1.0872$$
$$\text{Br}_2 \text{ (}l\text{)}, \text{Br}^- \| \text{H}^+, \text{H}_2; \mathbf{E}^\circ = -1.0661$$
$$\text{Br}_2 \text{ (}g\text{)}, \text{Br}^- \| \text{H}^+, \text{H}_2; \mathbf{E}^\circ = -1.0824$$

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THE ENTROPY OF THE ELEMENTS AND THE THIRD LAW OF THERMODYNAMICS.

BY GILBERT N. LEWIS AND G. E. GIBSON.

The concept of entropy as developed by Clausius, fundamental as it is, has always been regarded as an abstraction far less tangible than the concept of energy. The idea was rendered more concrete by Boltzmann

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[1] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

who showed the intimate relation between the entropy of a system and the probability of the particular state in which the system exists. If an isolated system is capable of passing from one state to another we may speak of the relative probability of the two states. Thus, if a certain amount of gas is distributed between two identical vessels connected with one another, it is almost certain, or, in other words, the chance is nearly unity, that the percentage of molecules in each vessel will be substantially the same. We may consider, however, the case where all of the molecules are in one vessel. The chance that any one molecule will be found in vessel A is one-half, and, therefore, the chance that all of the molecules will be in vessel A will be $(1/2)^n$, where n is the number of molecules. The relation between entropy and probability may then be stated as follows: If an isolated system is capable of existing in two different states, I and II, the difference in entropy is proportional to the difference in the logarithms of the chance, or probability, of I and II. The constant of proportionality depends upon the unit of entropy which is chosen. Thus in the case given above, where we considered the process in which a gas compressed in a single one of the two identical vessels is allowed to flow into the other empty vessel so as to equalize the pressure in the two, the increase in entropy, $\Delta S = S_2 - S_1$, is proportional to $\ln 1 - \ln(1/2)^n$, and if k is the proportionality factor when the unit of entropy is the calorie per degree,

$$\Delta S = nk\ln 2 = NR\ln 2,$$

where N is the number of mols and R the ordinary gas constant.

In general other factors besides spatial distribution, such, for example, as the distribution of velocities among the individual molecules, must also be considered, but often it remains possible to determine the relative chance of two mutually convertible states of an isolated system. Planck[1] has attempted to go farther and determine *a priori* the absolute probability of a system in any given state, but this attempt, stimulating and indeed promising as it has been, can not as yet be regarded as fully successful.

In recent years important discoveries relating to specific heat have also served in their turn to render the idea of entropy more acceptable as a working tool for common scientific use. When a substance is heated the relation between the entropy S and the heat capacity C is given by the thermodynamic equation, which we shall presently discuss more fully,

$$dS = Cd\ln T.$$

Now the integration of this equation shows that if C remains finite, or even if C approaches zero with the temperature, but less rapidly than the temperature, there is an infinite difference between the entropy at any finite temperature and the entropy at the absolute zero. Of course,

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[1] Planck, "Theorie der Wärmestrahlung."

in the thermodynamic definition of entropy there is left an arbitrary constant, or, in other words, we may assume arbitrarily the numerical value of the entropy of a system at some one state. It was formerly supposed that if the entropy of any substance at a given temperature should be assigned a positive finite value, then with diminishing temperature the entropy would pass through zero and on through negative values to —∞. This supposed fact doubtless helped to prevent the common adoption of the entropy concept.

However, after Dewar had found experimentally that the specific heat of diamond at low temperatures diminishes far more rapidly than the temperature itself, so that at low temperatures which are readily obtainable the specific heat does not differ measurably from zero, Einstein suggested that this would be found to be a common property of matter, and recent experiments upon the specific heat of many substances at low temperatures have fully substantiated this view. This means that the difference between the entropy of a system at a finite temperature and at the absolute zero is not infinite but finite. In other words, if we adopt the suggestion of Planck and take the entropy at the absolute zero as zero, the entropy at every finite temperature will have a finite positive value determined solely by the thermodynamic state of the system.

To the chemist entropy is of special significance because of its appearance in the fundamental equation of free energy[1]

$$\Delta F - \Delta H = -T\Delta S \qquad (1)$$

where ΔF is the increase in free energy, ΔH the increase in heat content, and ΔS the increase in entropy associated with any isothermal process or reaction.

In discussing this equation we must consider a theorem which was first clearly stated by Nernst, namely: In an isothermal process involving pure solids and liquids. the change in entropy approaches zero as the temperature approaches the absolute zero. Thus the entropy of a compound at the absolute zero would be the sum of the entropies of its elements, and therefore, following Planck, this principle may be stated in the more general form: The entropy of every actual substance in the pure state is zero at the absolute zero of temperature.[2] This principle, which evidently may be expressed in a number of different ways, has sometimes been called the *third law of thermodynamics*.

When Nernst first discussed the calculation of free energy from thermal data, he assumed the specific heat of solids and liquids to remain finite

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[1] We shall follow the notation of Lewis (THIS JOURNAL, **35**, 1 (1913)).

[2] The term "actual substance" is used in order to exclude a purely ideal substance, such as the perfect gas. Whether the qualifying phrase "in the pure state" is necessary can only be determined after more experimental material is available.

down to the absolute zero. It was not, however, this fact which caused confusion in what is called the Nernst heat theorem, but rather the inclusion of the "chemical constants" which were calculated for gaseous substances by a method first suggested by LeChatelier.[1] Unfortunately the greater part of the work on this subject, which has appeared in recent literature, has done more to obscure than to reveal the truth, since much of it has had too much the aspect of special pleading.

It will be shown in a later section that few, if any, of the tests of the third law of thermodynamics which have hitherto been made can be regarded as rigorous, but there are so many kinds of evidence which indicate the approximate validity of the law, and its inherent plausibility is such, that it has seemed desirable to assemble with some care the data which may be utilized in testing its validity and in applying it to the calculations of free energies, if it prove tenable.

If the entropy of a substance is known at one temperature and the specific heat is known over a range of temperatures, then it is possible to calculate the entropy at another temperature, by means of equations which we shall discuss presently. If for the entropies thus obtained we find the value of ΔS; and if ΔH, the heat of reaction, is known; ΔF, the free energy change, can be calculated at once from Equation 1. If this method is correct, then, in order to determine the free energy of formation of any compound from its elements, it will suffice to know the entropy of the substance, the entropy of the elements at the same temperature and the heat of formation of the compound. The entropies of the elements in their standard states, at the standard temperature of free-energy measurements, namely 25°, are therefore data of the greatest significance, and it will be the first object of this paper to obtain a comprehensive table of these important quantities.

Entropy and Specific Heat.

If any substance is heated, its increase in entropy is given by the equation $dS = dQ/T$. If S_o and S represent, respectively, the entropy at the absolute zero and at the chosen temperature T,

$$S - S_o = \int_o^T \frac{dQ}{T},$$ (2)

and making the assumption that $S_o = 0$,

$$S = \int_o^T \frac{dQ}{T}.$$ (3)

If, during the interval from zero to T, there occur no change of state,

[1] Aside from any other objection to the use of these chemical constants there is present the insuperable difficulty that two equally satisfactory empirical equations for the specific heat of a gas may lead to widely different values of the constant in the free energy equation. At least at present the chemical constant of a substance like carbon dioxide or water vapor cannot possess any real significance.

as from solid to liquid, or from one crystalline modification to another, $dQ = CdT$, where C is the heat capacity of the particular amount of the substance chosen. In dealing with the elements we may choose the gram atom as this unit, once for all. If the substance is heated throughout at constant volume or at constant pressure, $dQ = C_v dT$ or $dQ = C_p dT$. When not otherwise stated, we shall consider a constant pressure of one atmosphere as maintained, and may write for the entropy

$$S = C_p dT/T = C_p d \ln T. \qquad (4)$$

It will not be expedient, however, to deal exclusively with the specific heat at constant pressure, for it is the specific heat at constant volume which is apparently subject to simple and universal laws. It was shown by Lewis[1] that it is the atomic heat at constant volume which most nearly obeys the law of Dulong and Petit, and which possesses at higher temperatures the theoretical value $3/2R$ or 5.97 calories per degree. Moreover, at lower temperatures it is C_v for which Einstein,[2] Nernst and Lindemann,[3] and Debye[4] have made important generalizations.

The equations obtained by these investigators have one important idea in common, namely, that for all solid substances, or at least for a large class of solids, the heat capacity is the same function of the temperature, provided that the latter is divided by a constant which is characteristic of each substance; in other words, the heat capacity per gram atom may be expressed by the equation

$$C_v = f(T/\theta) \qquad (5)$$

where T is the absolute temperature, θ is a characteristic constant for each substance, and f is the same function for different substances.

The pioneer equation of Einstein was hardly expected to do more than give a theoretical explanation for the general trend of specific heat with the temperature, while the modifications introduced by Nernst and Lindemann only served to bring an equation of similar type into closer agreement with observation. The equation of Debye not only has a more satisfactory theoretical basis than the other two, but is also in remarkably close agreement with the experimental data which have been obtained for a certain class of solids. Debye's specific heat formula was in fact intended for those crystalline solids which belong to the regular system, and it is a corollary of his work that the validity of Equation 5 must be similarly restricted.

All substances which obey Equation 5, and of which the heat capacity is the same function of T/θ as the heat capacity of the characteristic isotropic metals like copper or lead, we shall call substances of Class 1.

[1] Lewis, THIS JOURNAL, **29**, 1165 (1907); Z. anorg. Chem., **55**, 200 (1907).

[2] Einstein, Ann. Phys., [4] **22**, 180 (1907).

[3] Nernst and Lindemann, Sitzb. Akad. Wiss. Berlin, **1911**, 494.

[4] Debye, Ann. Phys., [4] **39**, 789 (1912).

The equation of Debye is far from simple in form and not convenient for practical application, but at very low temperatures it approaches as a limit the simpler equation

$$C_v = a(T/\theta)^3 \qquad (6)$$

where a is a universal constant. There is reason to believe that this limiting equation represents an exact law of nature for substances of Class 1. So much can hardly be said of the general formula of Debye which rests upon ingenious but unproved hypotheses, and in particular is based upon the Planck radiation formula, of which the absolute validity is not yet certain. For this reason, instead of making any assumption as to the exact form of the heat capacity equation, we have employed a graphical method of calculating the entropy of solid substances, which, moreover, enables us to test by inspection the fundamental principle involved in Equation 5.

The Entropy of Solid Elements of Class I.

Replacing Equation 3 by the obvious identity,

$$S = \int_0^T C_p d \ln T = \int_0^T C_v d \ln T + \int_0^T (C_p - C_v) d \ln T, \qquad (7)$$

we may note that the last term is negligible at low temperatures, and at high temperatures is small and readily calculable. Hence we may focus our attention for the moment upon the term $\int_0^T C_v d \ln T$. If we plot the values of C_v as ordinates against those of $\ln T$ as abscissae, the area under the curve will be equal to this integral, which we may appropriately denote by S_v, since it is equal to the entropy change in heating from the absolute zero to the temperature in question, at constant volume. This area may be measured with sufficient accuracy either by a planimeter or by counting squares on coördinate paper. For the sake of convenience it is desirable to use the common logarithm, $\log T$, instead of the natural logarithm, $\ln T$, in which case the area between the absolute zero and a given temperature must be multiplied by 2.303 in order to give the value of S_v at that temperature.

This method of plotting has the further advantage that it enables us to test without further assumption the validity of Equation 5. For, if this equation is true for a certain class of solids, C_v for all will be the same function of $\log (T/\theta)$, or of $\log T - \log \theta$. In other words, the plots for two substances of Class I will be identical, except for a displacement along the $\log T$ axis, and this displacement will be equal to the difference between the two values of $\log \theta$. Since this method gives only the relative and not the absolute values of $\log \theta$, we may define θ for every substance as the temperature at which C_v is one-half of the Dulong and Petit constant. In other words, when $T = \theta$, $C_v = 3R/2$.

We have, therefore, adopted the expedient of plotting upon transparent coördinate paper the data which have been accurately determined for a number of elements crystallizing in the regular system, and by sliding one curve over the other, keeping the two axes of abscissae together, we have observed how nearly the various curves can be brought into coincidence. The extraordinary confirmation of Equation 5 which is thus obtained is shown in Fig. 1, in which the atomic heats[1] of aluminum, copper, lead and carbon in the form of diamond are plotted against log (T/θ). It is evident that the four curves coincide well within the limits of experimental error.
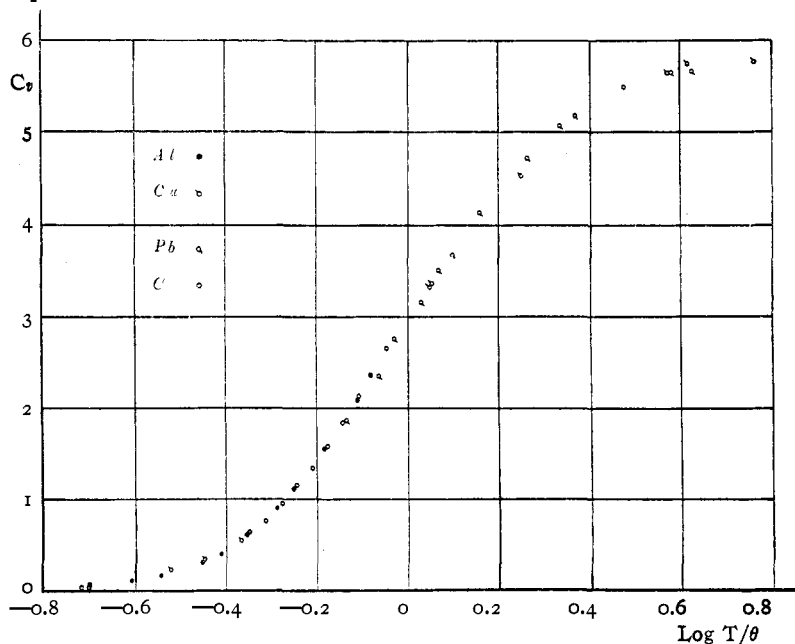
Fig. 1.

Five other metals for which accurate data have been furnished, silver, mercury, thallium, and zinc, are not included in the figure, but their curves also coincide fully with the others. This is especially interesting

[1] The points taken for lead are chosen at random from the numerous data of Eucken and Schwers (Verh. deut. physik. Ges., 15, 582 (1913)), which, moreover, agree within the limits of experimental error with those of Nernst (Ann. Phys., [4] 36, 395 (1911)) and of Kammerlingh Onnes (Akad. Wetensk., 23, 805 (1914)). For copper we have used the values of Nernst and Lindemann (Z. Elektrochem., 17, 817 (1911)); those for aluminum from Nernst and Schwers (Berl. akad., 1914, 355), and for diamond those of Nernst and Lindemann obtained chiefly from the measurements of Nernst and of Weber. In addition we have used data as follows: For silver and zinc from Nernst and Lindemann; for thallium from Nernst and Schwers; for mercury from Pollitzer (Z. Elektrochem., 19, 515 (1913)).

in the case of zinc, since this metal in its ordinary state is not composed of regular but chiefly of hexagonal crystals. This leads to the suspicion that Class I may include not only those elements which crystallize in the regular form but all those which are monatomic, if we use this term to indicate that the unit of the crystalline space-lattice is a single atom. In this sense a substance may be presumed to be monatomic in the solid state when in the vapor state it is known only in the monatomic form.

We may state, therefore, that there is a class of substances which obey Equation 5 within narrow limits of experimental error. The exact nature of the function which appears in this equation we need not discuss at this point, but we may assume with Debye that with diminishing temperature Equation 5 assumes the form of (6), an assumption which is also well substantiated by experimental observation, and this will simplify the calculation of entropy. Thus, in order to determine the change in entropy from the absolute zero up to the point where Fig. 1 begins, we may note that from Equations 4 and 6

$$S = C_v/3. \tag{8}$$

Using this equation for determining the entropy change up to a small value of C_v, and then finding the area under the curve from this point on, we obtain the values of S_v which are given in Table I at the several values of log T/θ. This table also gives the corresponding value of C_v.

TABLE I.

log T/θ.	C_v.	S_v.	log T/θ.	C_v.	S_v
—0.6	0.11	0.04	+0.40	5.26	5.59
—0.5	0.21	0.07	+0.50	5.49	6.82
—0.4	0.43	0.15	+0.60	5.65	8.08
—0.3	0.84	0.30	+0.70	5.72	9.41
—0.2	1.43	0.53	+0.80	5.76	10.74
—0.1	2.19	0.98	+0.90	5.78	12.07
0.0	2.98	1.62	+1.00	5.79	13.40
+0.10	3.78	2.41	+1.10	5.80	14.74
+0.20	4.43	3.37	+1.20	5.81	16.08
+0.30	4.91	4.42	....	....	.....

From this table, by interpolation, the values of S_v and C_v may be obtained at any temperature for any element of Class I when the value of log T/θ is known. Thus, for example, an element with $\theta = 40$, that is, an element for which $C_v = 3R/2$ at 40° A. will, at 400° A. where log $T/\theta = 1$, have an atomic heat at constant volume of about 5.79 and an entropy (S_v) of 13.40, both being expressed, as they will be throughout this paper, in calories per degree.

If we know in advance, from the crystalline form or otherwise, that a substance belongs to Class I, we may find the value of log θ, and of S_v at any temperature, from a single measurement of C_v, provided that the

measurement is made at a low enough temperature so that C_v is considerably lower than $3R$.

Unfortunately detailed specific heat curves have been obtained for very few elements. On the other hand, Dewar[1] has measured for a large number of elements the average atomic heat between the boiling points of hydrogen and nitrogen, and from these we may obtain, by a somewhat laborious calculation, the values of log θ, in those cases in which the element may be assumed to belong to Class I.

Taking the boiling points of nitrogen and hydrogen as $77.4°$ A. and $20.0°$ A., then log $(77.4/20.0) = 0.587$. The problem consists in finding two points of the characteristic curve of Fig. 1 such that the difference in abscissae is 0.587, and the average C_v between these limits is that obtained by Dewar. If we take any point on the curve and a point whose abscissa is 0.587 higher, and if we divide the intermediate range by points which are equally spaced, not with respect to log T/θ, but with respect to T/θ, the average of the corresponding ordinates gives the average value of C_v. If the value so obtained is identical with one obtained by Dewar for some element, then the lower value of log T/θ, which we have chosen, is equal to log $(20.0/\theta)$, and log θ for that element is obtained directly. For convenience in utilizing Dewar's values we have made a table by carrying out the above calculation for different portions of the characteristic curve. Table II shows the value of log θ for any element whose mean C_v, between the boiling points of hydrogen and nitrogen, is given in the second column.

TABLE II.

log θ.	C_v.	log θ.	C_v.	log θ.	C_p.
2.20	0.30	1.85	1.69	1.50	4.00
2.15	0.37	1.80	2.00	1.45	4.29
2.10	0.50	1.75	2.32	1.40	4.51
2.05	0.68	1.70	2.68	1.35	4.75
2.00	0.88	1.65	3.04	1.30	4.95
1.95	1.11	1.60	3.39	1.25	5.11
1.90	1.39	1.55	3.71	1.20	5.26

Before making our final calculation from Dewar's values some comments are necessary. He did not, of course, measure C_v but C_p, but at these low temperatures, in all the cases where we have used his measurements, the difference is doubtless well within the experimental error. A more serious source of error is due to the fact that the measurements were made by means of a hydrogen calorimeter, and Dewar's value for the heat of vaporization of hydrogen is undoubtedly too high. It cannot be stated at present how much too high it is, since the two most recent determinations of this quantity, both made in the Leiden[2] laboratory, are

[1] Dewar, *Proc. Roy. Soc. London*, **89A**, 158 (1913).

[2] Onnes and Keesom, Communication from Physik. Lab. Leiden, 137d and 137e.

not in complete accord.   Since there may have been some other constant sources of error in the measurements, we have compared the values given by Dewar for six elements with those obtained by other observers, and find that his values are too high, on the average, by the factor 1.085. We have, therefore, somewhat arbitrarily divided all of Dewar's values by this factor and thus obtained the numbers given in the second column of Table III, namely, the average atomic heats from 20.0 to 77.4°.   From these figures, by the aid of a curve corresponding to Table II, the values of log θ in the third column are found.   The fourth column gives the corresponding value of S_v at 298° A. obtained by means of Table I.

TABLE III.

	C_v mean.	log θ.	S_v298.		C_v mean.	log θ.	S_v298.
Lithium.............	1.24	1.928	7.41	Strontium, impure..	4.44	.....	.....
Beryllium..........	1.15	1.945	7.18	Zirconium...........	2.19	1.773	9.41
Boron..............	0.22	.....	.....	Molybdenum.......	1.25	1.925	7.45
Graphite (Acheson) .	0.15	.....	.....	Ruthenium.........	1.01	1.974	6.80
Diamond...........	0.03	.....	.....	Rhodium...........	1.27	1.921	7.49
Sodium............	3.22	1.622	11.43	Palladium..........	1.87	1.822	8.80
Magnesium.........	1.60	1.863	8.25	Silver.............	2.41	1.738	9.89
Aluminum..........	1.03	1.970	6.85	Cadmium...........	3.19	1.627	11.38
Silicon, I...........	0.79	.....	.....	Tin...............	3.14	1.632	11.30
Silicon, II..........	0.71	.....	.....	Antimony..........	2.66	.....	.....
Phosphorus (yellow).	2.21	.....	.....	Iodine.............	4.23	.....,	.....
Phosphorus (red)....	1.24	.....	.....	Tellurium..........	3.39	.....	.....
Sulphur (rhombic)....	1.61	.....	.....	Cesium.............	6.29	.....	.....
Chlorine...........	3.16	.....	.....	Barium, impure.....	4.42	.....	.....
Potassium..........	4.61	.....	.....	Lanthanum........	4.24	1.459	13.60
Calcium............	2.63	1.709	10.29	Cerium............	4.27	1.450	13.71
Titanium...........	0.91	1.994	6.57	"Didymium".......	4.27	.....	.....
Chromium..........	0.64	2.063	5.70	Tungsten..........	1.61	1.860	8.29
Manganese.........	1.16	1.944	7.19	Osmium...........	1.37	1.901	7.78
Iron...............	0.90	1.996	6.54	Iridium............	1.77	1.838	8.60
Nickel.............	1.12	1.950	7.11	Platinum..........	2.42	1.737	9.91
Cobalt.............	1.12	1.950	7.11	Gold..............	2.91	1.669	10.81
Copper.............	1.44	1.890	7.92	Mercury...........	4.29	1.449	13.73
Zinc...............	2.32	1.754	9.66	Thallium..........	4.42	1.421	14.10
Arsenic............	1.79	.....	.....	Lead..............	4.57	1.390	14.52
Selenium...........	2.63	.....	.....	Bismuth...........	4.18	.....	......
Bromine...........	3.33	.....	.....	Thorium...........	4.22	1.462	13.58
Rubidium..........	5.54	.....	.....	Uranium...........	3.04	1.650	11.07

We have assumed that all of the elements for which the calculations have been made belong approximately to Class I.   If in certain cases this should later prove to be untrue the table must be corrected accordingly. It will be noted also that the calculation has been omitted in the case even of certain elements which crystallize in the regular system.   In the region of Dewar's measurements the specific heat of diamond is too

low to give an accurate measure of log θ, while on the other hand the specific heat of potassium, rubidium and cesium are too high to permit the calculation.   The last three elements, moreover, present an anomaly of great theoretical significance.

It was shown by Lewis, in the paper previously cited, that at room temperature the atomic heats of most of the alkali metals are higher than 3R, not only at constant temperature but at constant volume.   As far as we can see, the only explanation of this striking fact is that the electrons, which in these metals are bound by weaker constraints than in any other metals, possess a part of that energy which would be ascribed to them by the classical kinetic theory.   It is interesting, therefore, to observe that in the case of cesium, in which the electrons possess the highest degree of freedom, the value of C_p and probably of C_v is higher than 3R even at the low temperature of Dewar's measurements.

In Table IV we give the values of log θ and of S_{v298} for the eight solid elements of Class I which have been subjected to the more detailed investigations to which we have already referred.   In each case the full specific heat curve has been plotted and the values given in the table have been obtained by the method already described.

TABLE IV.

	log θ.	S_{v298}.
Diamond.................	2.664	0.58
Aluminum.................	1.980	6.73
Copper....................	1.893	7.91
Zinc.....................	1.760	9.60
Silver....................	1.730	10.00
Mercury(s)...............	1.379	14.69
Thallium.................	1.396	14.44
Lead.....................	1.342	15.11

These more accurate determinations of the entropy agree with those obtained from Dewar's measurements as closely as could be expected.

Since the preceding paragraphs were written an experimental investigation has been carried on in this laboratory by Eastman and Rodebush[1] with the purpose of studying more completely the specific heat of those metals in which the known freedom of the electrons might lead us to expect that deviation from the normal specific heat curve (Fig. 1) to which we have already referred in the case of certain alkali metals. This investigation shows that the C_v curves for sodium, calcium and magnesium are coincident with the regular curve of Class I at low temperatures, but as room temperature is approached the specific heats become abnormally high, rising in the case of the first two elements to values considerably above the Dulong and Petit constant.   In the case of potassium the deviations are so great that with measurements down to 64° A.

[1] This investigation will be published in the near future.

it is impossible to fit the specific heat curve to the regular curve. It is not possible, therefore, to obtain for potassium the value of $\log \theta$, but for the other three elements this has been calculated and is given in Table V. This table also gives the values of S_{298}, obtained in this case by counting squares on the plot, on account of the deviations from the regular curve.

TABLE V.

	$\log \theta$.	S_{298}.
Na	1.604	12.24
Mg	1.885	8.27
Ca	1.708	10.98

The Entropy of Solid Elements of Class II.

The calculation of the entropy of substances which do not obey Equation 2 offers a problem of great difficulty. It is true that when the complete specific heat curve is known we may plot the heat capacity against $\log T$ and determine the entropy from the area under the curve, but this method fails if the heat capacity is known only at a few temperatures. We are going to propose for this class of elements a formula based upon rather meagre data, but which will at least suffice for the first approximation, in the absence of other information, and may later be found to represent a general law. We have seen that elements of Class I obey very accurately the equation $C_v = f(T/\theta)$, where f is a universal function. We propose now for all elements (possibly for all solids, crystalline or non-crystalline) the equation

$$C_v = f(T^n/\theta^n) \qquad (9)$$

where f is the same function as before and n is unity for substances of Class I, and less than unity for all other substances. The only existing data for elements not of Class I, are in agreement with Equation 9 within the limits of experimental error. The agreement in the case of graphite[1] may be seen from Fig. 2, in which the curve is the characteristic curve of substances of Class I, and the individual points are obtained by plotting the experimental values of C_v against $n \log T/\theta$, where n in this case is 0.789. In other words, our assumption, which in the case of graphite the figure shows to be well substantiated, is that the curve of any solid element becomes identical with the typical curve of Class I when C_v is plotted against $n \log T/\theta$.

For later reference we also have included in Fig. 2 values of C_v (per atom) for lead chloride plotted against 0.796 $\log T$. Here, also, we find perfect agreement with Equation 9. Indeed, all available data for the heat capacity (per atom) of compound substances, with the possible exception of one compound (ice) which we shall discuss later, corroborate Equation 9 within the limits of experimental error.

[1] Nernst, *Ann. Phys.*, [4] **36**, 345 (1911).

Whenever we have for a substance of Class II two values of C_v which are not too near to each other, nor to zero, nor to 3R, we may calculate the value of n as follows: If T_1 and T_2 are the temperatures at which
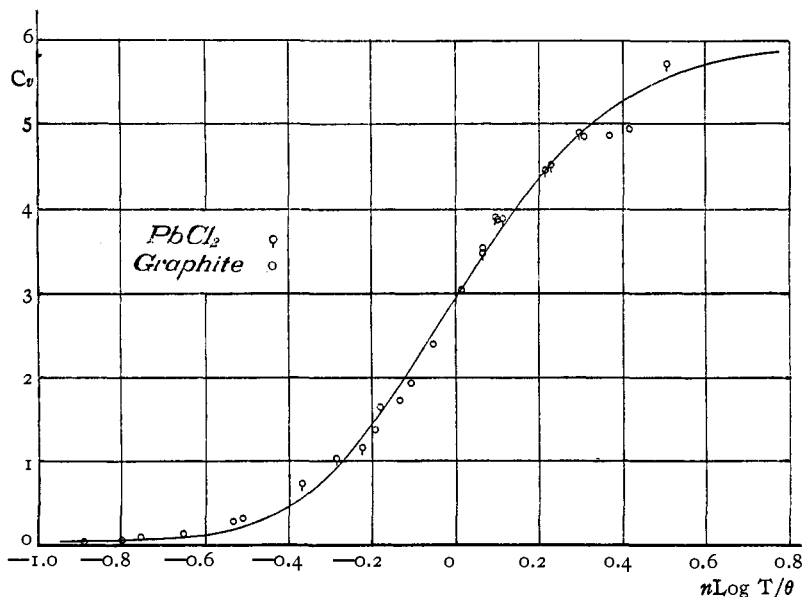

Fig. 2.

C_{v_1} and C_{v_2} are measured, if α_1 and α_2 are the two values of log (T/θ) on the typical curve of Class I corresponding to these values, C_{v_1} and C_{v_2}, then

$$n = \frac{\alpha_1 - \alpha_2}{\log T_1 - \log T_2}. \tag{10}$$

Similarly we may determine the temperature at which $C_v = 3R/2$, for if $C_{v_2} = 3R/2$, then in Equation 10

$$T_2 = \theta, \quad \alpha_2 = 0, \quad \text{and} \quad \log \theta = \log T_1 - \alpha_1/n. \tag{11}$$

In order to calculate the entropy at a given temperature it may first be observed that the entropy of a substance of the class under considera-tion is $1/n$ times as great as that of a substance of Class I at the same C_v. If we designate by θ' the value of θ for a curve of Class I which co-incides with the given curve at 298° A., the value of log θ' may be obtained immediately from Equation 7, for it is evident from the derivation of this equation that it is true for any value of T_1. If then for our present pur-pose we write $T_1 = 298$, then by definition $\alpha_1 = $ log $298/\theta'$, and by sub-stitution in Equation 11 we find

$$\log (298/\theta') = n \log (298/\theta). \tag{12}$$

Having thus obtained log $(298/\theta')$ we may, by Table I, calculate the value of S_{v298} for the substance of Class II in question.

The preceding calculations are based on the assumption that only two values of C_v are obtainable. If more data are at hand the method can be generalized by familiar methods. Thus if a large number of data are given, the best curve may be drawn through the individual points, and then, two points being taken from this curve in such locations as to give the highest degree of precision, the preceding calculation may be carried out.

In this way we have calculated the entropy of several non-metallic elements for which suitable data were obtainable, namely graphite, sulfur, silicon, iodine, bromine and chlorine.

Graphite.—The data for this substance have already been discussed. From them we find

$$n = 0.789, \log \theta = 2.594, \log (298/\theta') = -0.095.$$

The value corresponding to this taken from the curve of Table I is 1.00 and $S_{v298} = 1.00/0.789 = 1.27$.

Sulfur.—From the values of C_p for rhombic sulfur obtained by Nernst[1] at low temperatures and by Wiegand[2] at room temperature we have calculated the values of C_v by the method discussed in a later section, and from these we obtain the values $n = 0.653, \log \theta = 1.964, \log (298/\theta') = $ ·0.333, and $S_{v298} = 4.87/0.653 = 7.31$. The available data for monoclinic sulfur hardly suffice for a direct calculation, but they would lead to a value for the entropy not very different from the one which we shall calculate later by an indirect method.

Silicon (metallic).—The measurements of Nernst and Schwers[3] extend only from 20 to 90° A., but fall on a smooth curve from which we calculate $n = 0.79, \log \theta = 2.19$ and $S_{v298} = 4.6$.

Iodine.—From the meagre data of Nernst we find $C_v = 3.86$ when $\log T = 1.500$ and $C_v = 5.26$ when $\log T = 1.882$. Hence, $n = 0.763$, $\log \theta = 1.353, \log (298/\theta') = 0.854$ and $S_{v298} = 11.48/0.763 = 15.1$.

Owing to the incompleteness of the specific heat data this figure must be regarded as an approximate one.

Bromine and Chlorine.—Dewar found the average atomic heats of bromine and chlorine between the boiling points of hydrogen and nitrogen. A few other values have been obtained by Regnault, Koref and Estreicher and Staniewski.[4] From these scanty and perhaps not very accurate determinations of average atomic heats we have obtained, by a series of laborious calculations, rough values for the entropy of the two solids at their melting points. These calculations are analogous to those which we have already discussed in using Dewar's values, and we will not re-

[1] Nernst, *Ann. Physik*, [4] **36**, 345 (1911).

[2] Wiegand, *Ibid.*, [4] **22**, 64 (1907).

[3] Nernst and Schwers, *Ber.*, **47**, 355 (1914).

[4] Abegg, "Handbuch anorg. Chem."

produce them here, especially since the results are of only approximate validity. We may remark, however, that the value of n appears to be approximately the same for these two elements as for iodine. The entropies obtained were for bromine $S_{266} = 12.7$ and for chlorine $S_{171} = 9.1$. The entropy of liquid bromine and of gaseous chlorine at $25°$ will be considered in a later section.

The Difference between S and S_v at $298°$ A.

We have calculated for many of the solid elements the increase in entropy which would be produced by heating from 0 to $298°$ A. at constant volume. This differs ordinarily very little from the corresponding change when the substance is heated at constant pressure. The difference at any temperature T is given by the equation

$$S - S_v = \int_0^T (C_p - C_v) d \ln T. \qquad (13)$$

Now while we are able, from existing data, to calculate $C_p - C_v$ for a number of elements at a single temperature, we have no data for calculating the change of this difference with the temperature. However, there is no doubt that $C_p - C_v$ falls with falling temperature and in the average case more rapidly than the temperature. Since $S - S_v$ is in no case large we shall produce no considerable error by adopting the rough empirical rule expressed by Lindemann and Magnus[1] in the equation

$$C_p - C_v = aT^{1/4}. \qquad (14)$$

Combining (13) and (14) we find by simple integration, that for any temperature,

$$S - S_v = {}^2/_3(C_p - C_v). \qquad (15)$$

The values of $C_p - C_v$ for a number of elements at room temperature were calculated by Lewis[2] from the thermodynamic equation

$$C_p - C_v = T\beta^2 V/41.8\alpha, \qquad (16)$$

where V is the atomic volume, and α and β are, respectively, the coefficients of cubical compressibility and thermal expansion. In addition to the values there given we may use the same equation to obtain values for lithium, silicon, sulfur (rhombic), arsenic and selenium from the data of Richards, Stull, Brink and Bonnet.[3]

The values of $C_p - C_v$ or of $S - S_v$ for the various elements, when plotted against the atomic numbers, show the same interesting kind of periodicity as is shown by other similar quantities such as atomic volume. Hence, even when data are lacking for the applications of Equations 15 and 16, we may still closely estimate the value of $C_p - C_v$ or $S - S_v$ for an element, when these quantities are known for neighboring elements

[1] Z. Elektrochem., 16, 269 (1910).
[2] Lewis, THIS JOURNAL, 29, 1165 (1907).
[3] THIS JOURNAL, 31, 154 (1909).

In Table VI we give the values of $C_p — C_v$ at room temperature, for a number of solid elements. Except in the cases marked with an asterisk the values have been obtained directly from the thermodynamic formula. These values multiplied by $^2/_3$ and added to the values of S_v in previous tables give the values of S_{298}.

TABLE VI, $C_p — C_v$.

Li	0.3	K	0.6	Zn	0.3	Cd	0.3	Pt	0.2
Be*	0.2	Ca*	0.3	As	0.0	Sn	0.3	Au	0.3
C*(Di.)	0.0	Ti*	0.1	Se	0.3	Sb	0.1	Tl	0.3
C*(Gr.)	0.0	Cr*	0.1	Zr*	0.1	I	0.9	Pb	0.4
Na	0.5	Mn*	0.1	Mo*	0.1	La*	0.1	Bi	0.1
Mg	0.2	Fe	0.1	Ru*	0.1	Ce*	0.1	Th*	0.1
Al	0.2	Co*	0.1	Rh*	0.1	W*	0.1	U*	0.1
Si	0.1	Ni	0.2	Pd	0.2	Os*	0.1	....	...
S	0.4	Cu	0.2	Ag	0.3	Ir*	0.2	....	...

The Entropy of Liquid and Gaseous Elements.

Whenever a substance undergoes a change of phase at its transition point, that is, at the temperature of equilibrium between the two phases, the increase in entropy is obviously equal to $\Delta H/T$, where ΔH is the heat absorbed in the transition and T is the transition temperature. Thus, if we wish to determine the entropy of liquid mercury at $25°$ C., we must know, for the solid, $\int_0^{T_1} C_p d \ln T$, where T_1 is the melting point, also $\Delta H/T_1$, the heat of fusion divided by the fusion temperature and $\int_{T_1}^{298} C_p d \ln T$ for liquid mercury.

Mercury.—The melting point of this element is approximately $234.1°$ A. and the latent heat of fusion is 560 cal. per gram atom as the mean of the closely concordant measurements of Person, Pollitzer, and Koref.[1] Hence, ΔS during fusion is 2.39. The entropy of solid mercury, which belongs to Class I and for which $\log \theta = 1.377$, can readily be obtained from Table I, whence $S_{v234.1} = 13.31$. At the higher temperatures the specific heat of solid mercury falls above the regular curve of Class I owing to the difference between C_p and C_v. From the area between the observed and the regular curve (Fig. 1) we find at $234.1°$ A. $S — S_v = 0.49$. We have, therefore, for the entropy of liquid mercury $S_{234.1} = 13.31 + 0.49 + 2.39 = 16.19$. The specific heat of liquid mercury between the melting point and room temperature is nearly constant, and the average value 6.7 multiplied by $\ln 298/234.1$ gives 1.62 as the increase in entropy in bringing liquid mercury to $25°$. We thus find for Hg(l), $S_{298} = 17.81$.

Liquid Bromine and Gaseous Chlorine.—We have found in a previous section rough values for the entropies of solid bromine and chlorine at their melting points $S_{266} = 12.7$ and $S_{171} = 9.1$, respectively.

[1] Landolt, Börnstein, Roth, "Tabellen."

The heat of fusion of bromine was found by Regnault to be 1290 cal. per gram atom, while Lewis and Randall[1] show that nearly the same value is obtained from the curve of vapor pressure. We have then $\Delta S = 1290/266 = 4.85$, for the entropy change in melting. Regnault found for the heat capacity per gram atom of liquid bromine, $C_p = 8.4$. In changing from the melting point to $25°$ C., $\Delta S = 8.4 \ln 298/266 = 0.95$, therefore, for liquid bromine $S_{298} = 12.7 + 4.85 + 0.95 = 18.5$.

The heat of fusion per gram atom of solid chlorine was found by Estreicher and Staniewski[2] to be 817 cal. Hence, $\Delta S = 817/171 = 4.77$. The atomic heat of liquid chlorine, according to the same authors, is about 7.8 between the melting point and the boiling point ($239.4°$ A.). Hence, in this range $\Delta S = 7.8 \ln 239.4/171 = 2.63$. For the heat of vaporization per gram atom the value obtained from the vapor-pressure measurements[3] is 2500 cal. Hence, for vaporization $\Delta S = 10.43$. The heat capacity of gaseous chlorine per atom[4] is $3.25 + 0.002T$. Hence, from the boiling point to $25°$ C., $\Delta S = 3.25 \ln 298/239.4 + 0.002(298 - 239.4) = 0.83$. Adding all these numbers to the entropy of the solid at its melting point, gives for the atomic entropy of chlorine gas $S_{298} = 27.8$.

These values for bromine and chlorine are only approximations. In the case of chlorine we shall discuss later other methods of calculating the entropy.

Oxygen, Nitrogen, Hydrogen, Argon, Helium (Carbon Monoxide).— Certain gases, when cooled, not only change from gas to liquid and from liquid to solid, but the solid itself on further cooling undergoes one or more transformations, and sometimes these transitions are accompanied by heat changes greater even than the heat of fusion. In the case of oxygen three solid forms occur. Fortunately, however, these systems have been very thoroughly studied by Eucken,[5] who has determined not only the specific heats of the various phases over a wide temperature interval, but also the transition points and the heats of transition. His specific heat data we have plotted against log T and thus have determined, from a measurement of the area, the entropy change from one transition point to the next. His measurements extend for several degrees below the boiling point of hydrogen and since his experimental curves at the lowest temperatures coincide (per gram atom) fairly well with the curve of Class I, we have assumed that this holds true down to the absolute zero, in estimating the small amount of entropy change between o and $17°$ A.

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[1] This Journal, **38**, 2348 (1916).

[2] Abegg's "Handbuch," IV, 2, 99.

[3] This calculation will be given in a paper shortly to be published by Lewis and Randall.

[4] Lewis and Randall, This Journal, **34**, 1128 (1912).

[5] *Ber. deut. physik. Ges.*, **18**, 4 (1916).

Since space would not permit a reproduction of our detailed calculations we shall merely give in Table VII a summary of the results obtained.

TABLE VII.   (Entropies per mol.)

	O₂.	N₂.	H₂.	CO.	A.	He.
Sol. III	2.20	..	..	..	..	..
ΔH	17.5	..	..	..	..	..
T	23.5	..	..	..	..	..
ΔS	0.74	..	..	..	..	..
Sol. II	4.58	6.37	..	9.84	..	..
ΔH	167.4	53.8	..	144.1	..	..
T	42.5	35.5	..	60.4	..	..
ΔS	3.94	1.51	..	2.39	..	..
Sol. I	2.62	5.72	(0.5)	1.15	9.24	(o)
ΔH	105.5	168.7	32(?)	224.1	267.9	..
T	54.1	63.1	15	67.3	83.4	..
ΔS	1.95	2.67	2.13(?)	3.33	3.21	(o)
liq.	6.52	2.72	1.22	3.26	0.37	(o)
ΔH	1599	1363	218	1414	1501	..
T	90.3	77.4	20.3	83.0	86.2	..
ΔS	17.72	17.62	10.73	17.06	17.42	2.8 (at 1.48°)
Gas	7.96	8.98	14.80	8.52	6.19	26.4
S₂₉₈	48.23	45.59	29.4	45.55	36.43	29.2

In this table, under O_2, the first figure gives the entropy of form III of solid oxygen at its transition point, as calculated from the curve of C_p against log T, from the absolute zero to this temperature. The second figure is the heat of transition to solid II, the third the absolute transition temperature, and the fourth the ratio of the last two numbers. The fifth figure gives the value of ΔS for solid II calculated from the specific heat curve between the points where it is in equilibrium with solids III and I, respectively. Then in the same way comes the calculation of the entropy change in passing to solid I, in heating solid I to the melting point, in melting, in heating the liquid to the boiling point and in vaporization. These data are all calculated from Eucken's work. The next to the last figure is the increase in entropy in heating oxygen gas from the boiling point to 25°, and here we have assumed for O_2, N_2 and CO the specific heat equation given by Lewis and Randall, namely, $C_p = 6.50 + 0.0010T$. The last figure gives the sum of all the entropy changes, and is the entropy of one mol of oxygen gas at 25° and atmospheric pressure.

The figures given under N_2 are similarly obtained, except that here Eucken obtained only two solid forms.

In the case of hydrogen no measurements have been made of the specific heat of the solid. It is unquestionably small and we may roughly estimate the entropy of solid hydrogen at the melting point as 0.5. We have been able to find no reference to the heat of fusion, except that in Abegg's

Handbuch is given the value obtained in the table upon the authority of Dewar, but we have not been able to find in Dewar's papers any indication that he determined this quantity. Therefore, this figure and the corresponding value of ΔS are marked (?). The specific heat of the liquid and the gas are given by Eucken, who also determined the heat of vaporization as 229 cal., but he does not himself attribute a high degree of accuracy to this result. A direct determination by Keesom[1] gives 222, while Onnes and Keesom[2] obtain 212 from careful vapor-pressure measurements. We shall take 218 as the value which at present seems most probable. It is worth noting that while the change of entropy for oxygen gas can be obtained from a simple formula, the specific heat of hydrogen gas changes so rapidly at low temperatures, when it approaches that of a monatomic gas, that it is necessary here once more to have recourse to a plot of C_p against log T and a measurement of the area under the curve.

The calculation for carbon monoxide is identical with that for nitrogen, two solid forms having been obtained by Eucken. This gas, although not an element, has been introduced here for the sake of a calculation which we shall wish to make presently. Eucken also studied the specific heat of carbon dioxide, but we have not been able to use his values because a plot of his data gives very decided evidence of an undetected transition point in the neighborhood of $50°$ A.

All of the data for argon are taken from Eucken except the specific heat of the gas. We may, however, take without question for monatomic gases, in any region in which the gas laws apply, $C_p = 4.97$.

Concerning helium we know only the specific heat of the gas $C_p = 4.97$ and the vapor pressure at several temperatures determined accurately by Kammerlingh-Onnes[3] between $1.48°$ A. and $4.29°$ A. These, however, are extremely significant. If we plot the logarithm of the vapor pressure against the reciprocal of the temperature, instead of a straight line which would be obtained if the heat of vaporization were constant, we obtain a line of pronounced curvature. On the other hand, if we make the most probable assumption, that at these very low temperatures the specific heat of the liquid is negligible compared with that of the gas, and therefore that there is a difference in C_p of about 5, then the equation for the heat of vaporization becomes

$$\Delta H = \Delta H_0 + 5T,$$

and the vapor-pressure equation becomes

$$-R \ln p = \Delta H_0/T - 5 \ln T + I$$

where I is a constant. In other words, not $\ln p$ but $5 \ln T - R \ln p$

[1] Communication from *Phys. Lab. Leiden*, 137e.
[2] *Ibid.*, 137d.
[3] *Ibid.*, 119.

should be a linear function of $1/T$. We have plotted $5 \ln T - R \ln p$ against $1/T$ and in fact find that four of the five experimental points fall exactly upon a straight line. This corroborates our assumption of zero heat capacity for liquid helium, which involves the assumption that its entropy is also negligible. From the slope of the line we find at once $\Delta H_0 = 13.0$ and $\Delta H_{1.48} = 20.4$. Hence, $\Delta S_{1.48} = 13.8$ for the entropy change in passing from liquid helium to gas at the vapor pressure, namely, 3 mm. In changing[1] the gas from 3 mm. pressure to 760 mm. $\Delta S = R \ln 3/760 = -11.0$. Changing now the gas from $1.48°$ A. to $298°$ A., $\Delta S = 4.97 \ln 298/1.48 = 26.4$. The algebraic sum of these three numbers gives the value of S_{298}.

The Entropy of Compound Substances.

As in the case of the elements, the increase in entropy, when a compound substance passes from the absolute zero to any given temperature, may be readily ascertained when the specific heat curve is known, together with the heats of transition and transition temperatures. Such a calculation we have already made in the case of carbon monoxide. In this section we shall find the entropies of all the compounds for which data are available and which readily lend themselves to the calculations which we shall make in the following section:

Potassium Chloride, Sodium Chloride and Potassium Bromide.— Nernst and Lindemann[2] have made a very extensive investigation of the specific heat of KCl and also give a number of data for NaCl and KBr. Their points fall very satisfactorily upon the curve of elements of Class I when the heat capacity per gram atom, that is, one-half the molal heat capacity, is plotted against $\log T$. They assume for each of these substances that $C_p - C_v$ at room temperatures is about 0.2. We may, therefore, apply to the curves for these substances the same method of calculation which we have previously employed. Thus we find (per gram atom) for KCl, $\log \theta = 1.75$, $S_{v298} = 9.72$, $S_{298} - S_{v298} = 2/3 \ (0.20)$ $= 0.14$, $S_{298} = 9.86$; for NaCl, $\log \theta = 1.84$, $S_{v298} = 8.58$, $S_{298} = 8.72$; for KBr, $\log \theta = 1.65$, $S_{v298} = 11.07$, $S_{298} = 11.21$. Multiplying by 2 we find then S_{298} per mol; KCl, 19.7; NaCl, 17.4; KBr, 22.4.

Lead Chloride, Lead Iodide, Mercurous Chloride, Silver Chloride, Silver Iodide, Thallous Chloride, Mercurous Sulfate.[3]—For lead chloride

[1] In order to avoid the objection that at $1.48°$ and 760 mm. helium would not be a perfect gas we could of course reverse the procedure, heat the gas at 3 mm. to room temperature and compress to atmospheric pressure, with the same result.

[2] *Loc. cit.*

[3] For lead chloride and mercurous chloride we have used the data of Nernst and Lindemann (*Loc. cit.*) together with data in the neighborhood of room temperature taken from the tables of Landolt and Börnstein. For lead iodide, silver chloride and silver iodide we have taken the data of Nernst and Schwers (*Loc. cit.*), for thallous chloride and mercurous sulfate those of Pollitzer (*Loc. cit.*).

we have already shown in Fig. 2 the remarkable agreement with Equation 9, by plotting C_v against $n \log (T/\theta)$. Here n was found to be 0.796 and $\log \theta = 1.660$. In the case of all the substances of this group $C_p - C_v$ is doubtless negligible and we therefore find $S_{298} = S_{v298} = 11.06$ per atom, or 33.2 per mol. For lead iodide the measurements of Nernst and Schwers are less extensive but show clearly that n is the same as for lead chloride and $\log \theta = 1.447$, whence $S_{298} = 13.77$ per atom or 41.3 per mol. For mercurous chloride $n = 0.665$, $\log \theta = 1.634$, $S_{298} = 11.6$ per atom or 23.2 per mol. For silver chloride $n = 0.869$, $\log \theta = 1.603$, $S_{298} = 11.7$ per atom or 23.4 per mol. For silver iodide $n = 0.769$, $\log \theta = 1.480$ and $S_{298} = 13.4$ per atom or 26.8 per mol. For thallous chloride $n = 90$, $\log \theta = 1.52$ and $S_{298} = 14.3$ per atom or 28.6 per mol. For mercurous sulfate $n = 0.39$, $\log \theta = 2.07$, and $S_{298} = 7.5$ per atom or 52.5 per mol.

Water, Benzene.—As an example of substances which have not the .character of salts we may consider ice and solid benzene, both of which were studied by Nernst and Lindemann, and the former in more detail by Pollitzer. When we apply the, n-formula (Equation 9) to ice, we find that the agreement is complete at all temperatures except in the neighborhood of the freezing point, where the specific heats obtained by numerous observers all lie very noticeably above the calculated values. The sudden rise in the specific heat of a substance just below its transition of fusion temperature has caused comment for many years. Unquestionably this effect, as ordinarily observed, has been due largely to experimental error. Thus if ice contains a certain salt as an impurity then at any temperature above the eutectic point of that salt the apparent specific heat is increased by the fact that some of the ice melts to produce a solution of the salt. However, the question remains as to whether a substance which is free from impurity may not, on account of physical inhomogeneity, show this same effect. The evidence certainly favors such a supposition. The rise in specific heat which we have mentioned in the case of ice can hardly be attributed to experimental error. Nernst[1] mentions a similar sharp rise in the specific heat of silver iodide near its transition point, and considers it a general phenomenon. In Eucken's work on the various solid forms of condensed gases, which we have used in a preceding section, a similar abnormal increase in specific heat is to be found in almost every case, just below a transition point. It appears likely that this phenomenon would not be found in the case of a perfect crystal of a pure substance, but that in a pure substance which has been allowed to solidify in the ordinary way, and which contains crystals of various sizes in different orientation, perhaps cemented together by another modification of the substance, with different thermodynamic properties, certain portions may begin to undergo a transition before the true transition point is reached.

[1] *Ann. Phys.*, [4] 36, 428 (1911).

With the exception of a small range of temperature just below the melting point the data for ice agree with our formula when $n = 0.43$ and $\log \theta = 2.51$. Making a very slight correction for the rise in specific heat near the melting point and calculating the entropy to this point we find $S_{273} = 3.32$ per atom, or 9.96 per mol. The heat of fusion is 1436, dividing which by 273 gives $\Delta S = 5.26$. For liquid water $C_p = 18.0$ and, therefore, the increase in entropy between $0°$ and $25°$ C. is 18 ln $(298/273) = 1.58$. Adding these terms gives for the entropy per mol of water, $S_{298} = 16.8$.

For solid benzene $n = 0.31$, $\log \theta = 2.82$ and $S_{298} = 3.0$ per atom or 36.0 per mol. Of course, benzene melts before it reaches 298, but since the specific heat of solid and liquid are the same within the limits of experimental error, the calculation is simplified by taking the above value and adding the entropy change on fusion, namely, $2370/278.4 = 8.5$. Hence, for liquid benzene per mol $S_{298} = 44.5$.

Tests of the Third Law of Thermodynamics and Calculation of Entropies from this Law.

Numerous attempts have been made to test the third law, but unfortunately many of these attempts have been too obviously polemic in character, and nearly all have dealt with a certain type of reactions, namely, reactions between solid salts and solid elements (and liquid mercury), which are not altogether representative and in which the free-energy change can be calculated with a fair degree of approximation from Thomson's rule, which assumes that $\Delta S = 0$. Certain calculations have been vitiated by uncertainties due to liquid potentials as pointed out by Taylor[1] in discussing the reactions $Ag + I = AgI$ and $Pb + 2I = PbI_2$, studied by Fischer[2] and by Braune and Koref.[3] Taylor himself studied the combined reaction $Pb + 2AgI = PbI_2 + 2Ag$. Here, however, another source of uncertainty arises. The silver halides produced electrolytically by the method of Jahn differ greatly in appearance from the salt which is produced by chemical precipitation and which has been used in the measurements of specific heat. Recent measurements in this laboratory show that between the brown silver chloride obtained by electrolysis and the white substance obtained by chemical precipitation there may be a difference in free energy ranging from 0 to 100 calories. Brönsted's[4] measurements with the brown silver chloride show a higher heat of formation than the values obtained with white silver chloride by Thomsen and Berthelot. The latter values may be too low, but at present there is no proof that the silver halides produced in the two different ways are thermo-

[1] Taylor, THIS JOURNAL, 38, 2295 (1916).

[2] Z. anorg. allgem. Chem., 78, 41 (1912).

[3] Ibid., 87, 175 (1914).

[4] Brönsted, Z. physik. Chem., 50, 485 (1904); 56, 669 (1906).

dynamically identical. This criticism also affects the calculations of Fischer, Braune and Koref, and Pollitzer.

Pollitzer also studied two reactions which are independent of the silver halides. In the first of these, namely, $Pb + 2HgCl = PbCl_2 + 2Hg$, he finds a discrepancy in the application of the third law amounting to 7.7 entropy units or 2300 cal. His other reaction, namely, that of the Clark cell, $Zn + Hg_2SO_4 + 7H_2O(s) = ZnSO_4.7H_2O + 2Hg(s)$, furnished, on the other hand, complete agreement with the third law. A similar calculation with two cadmium cells has been made by Seibert, Hulett and Taylor.[1] In one case they found complete agreement with the third law, in the other case a discrepancy of about 1000 cal. or 3.3 entropy units. Unfortunately there were available no accurate measurements of the specific heat of cadmium, which were needed in both calculations.

We shall now consider a number of tests of the third law which are made possible by our preceding calculations of entropy.

$C_G + {}^1/_2O_2 = CO.$—Of the numerous tests of the third law for which experimental data are available there is one which stands out from the others because of the extreme reliability of all the experimental data needed in the calculation. The free energy of formation of carbon monoxide from graphite and oxygen is known with a high degree of accuracy. The heat of formation can be obtained from the unusually careful measurements of Roth and Wallasch[2] who burned numerous types of graphite to form CO_2, and from the heat of combustion of CO for which Berthelot and Thomsen found nearly identical values, their average value being, moreover, thoroughly corroborated by measurements of the free energy at different temperatures. On the other hand, the entropies of carbon monoxide and oxygen have been obtained from the very thorough investigation of Eucken, and that of graphite possesses an unusually high degree of accuracy. From the free-energy equation of Lewis and Randall[3] $\Delta F_{298} = -32560$, $\Delta H_{298} = -26140$; hence, $\Delta S_{298} = 6420/298 = 21.5$. Now assuming in accordance with the third law that we have been justified in taking the entropy of each of the substances as zero at the absolute zero of temperature, we may calculate ΔS from the values which we have obtained in the preceding sections, namely, for CO, 45.55; for C_G, 1.27; for $^1/_2O_2$, 24.10; whence, $\Delta S_{298} = 20.2$. The two values of ΔS differ by 1.3 entropy units, which corresponds to a combined error in $T \Delta S$, in ΔH and in ΔF of less than 400 calories. We may assert, therefore, that here we have agreement within narrow limits of experimental error, and in a case where Thomson's rule leads to an error in the free energy of over 6000 cal.

[1] THIS JOURNAL, **39**, 38 (1917).
[2] *Ber.*, **46**, 896 (1913); *Z. Elektrochem.*, **21, 1** (1915).
[3] THIS JOURNAL, **37,** 466 (1915).

$H_2 + \frac{1}{2}O_2 = H_2O(l)$.—In the next case that we shall consider, both ΔF and ΔH are probably known within 100 calories, but the entropies, especially that of hydrogen, are subject to minor uncertainties. From the equation given by Lewis and Randall,[1] $\Delta F_{298} = -56620$, $\Delta H_{298} = -68275$, whence $\Delta S_{298} = -39.12$. The individual entropies we have already obtained, namely, for $H_2O(l)$, 16.8; for H_2, 29.4; for $\frac{1}{2}O_2$, 24.1; whence $\Delta S = -36.7$. The two calculations of ΔS differ in this case by 2.4, corresponding to about 700 cal. This difference may be easily attributable in large measure to uncertainty in the experimental data for hydrogen, especially the heat of fusion. In this case the calculation of ΔF by Thomson's rule would be in error by over 11000 cal. If we assume the validity of the third law we may reverse our calculation and obtain for hydrogen per mol $S_{298} = 31.8$. If we are to accept the third law, this value is to be preferred to the one which we obtained by more direct methods.

$Hg + \frac{1}{2}Cl_2 = HgCl$.—We have obtained a rough value for the atomic entropy of gaseous chlorine, namely, $S_{298} = 27.8$. We shall now test the third law by assuming its correctness and calculating the entropy of chlorine through a number of different reactions, the first of which is the formation of mercurous chloride from its elements. Lewis and Rupert[2] determined the e. m. f. of the cell

$$Hg, HgCl, HCl \ (0.1 \ M), \ Cl_2$$

and found $E = 1.0896$. The process in the cell is merely the formation of calomel, hence, $\Delta F_{298} = -23074E = -25130$. Identical values for the heat of formation have been obtained by Nernst[3] and by Varet,[4] namely, $\Delta H_{298} = -31300$.[5] Although this value may still be in doubt by a few hundred calories it is undoubtedly more reliable than the majority of our thermochemical data. We thus find $\Delta S_{298} = -20.7$. We have found for HgCl, $S_{298} = 23.2$, and for Hg, $S_{298} = 17.8$. Hence, for $\frac{1}{2}Cl_2$, $S_{298} = 26.1$.

$Pb + Cl_2 = PbCl_2$.—Lewis and Brighton[6] found for the cell

$$Pb, PbCl_2, KCl \ (0.1 \ M), \ HgCl, \ Hg; \ E_{298} = 0.5391.$$
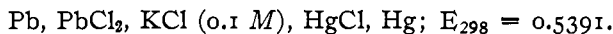
Unfortunately the potassium chloride solution on the calomel side was not saturated with lead chloride and, therefore, on account of the appreciable solubility of the latter we must make a correction, which we calculated to be 2 millivolts, in order to obtain the value of E for the cell

[1] THIS JOURNAL, **36**, 1981 (1914).

[2] *Ibid.*, **33**, 299 (1911).

[3] *Z. physik. Chem.*, **2**, 23 (1888).

[4] *Ann. chim. phys.*, [7] **8**, 102 (1896).

[5] Thermochemical data have been usually obtained not at 298° but at about 291° A. However, unless otherwise stated, we may regard the difference as negligible.

[6] THIS JOURNAL, **39**, 1906 (1917).

in which the sole process is the formation of mercury and lead chloride from lead and mercurous chloride. For this process, therefore, $E = 0.537$ and $\Delta F_{298} = -24780$. Combining this with the previous value for the formation of calomel we find for the formation of lead chloride, $\Delta F_{298} = -75040$. For ΔH Berthelot found -83900, while Thomsen obtained a lower value and Koref and Braune obtained one appreciably higher. Cohen[1] and Brönsted[2] have discussed the calculation of this quantity from electromotive-force measurements, and Lewis and Brighton have made a new determination which should be accurate provided that the heat of formation of calomel is correct, namely, $\Delta H = -84000$. Adopting this value, which is almost identical with that of Berthelot, we find $\Delta S_{298} = -30.1$. We have found for $PbCl_2$, $S_{298} = 33.2$, and for Pb, $S_{298} = 15.4$, from which we find for $1/_2Cl_2$, $S_{298} = 24.0$.

$Ag + 1/_2Cl_2 = AgCl$.—The difference in potential between silver, silver chloride and mercury, calomel is 0.0459.[3] From this we find the free-energy change in the reaction between silver and mercurous chloride, and adding the above value for the free energy of formation of the latter, we find for the free energy of formation of silver chloride $\Delta F_{298} = -26200$. For ΔH Thomsen obtained -29400 and Berthelot -29000. From the measurements of Brönsted with electrolytic silver chloride a somewhat higher value is obtained, but until the thermodynamic identity of the two forms of silver chloride is demonstrated we must be satisfied with the mean of the values of Thomsen and Berthelot, $\Delta H_{298} = -29200$. Hence, $\Delta S_{298} = -10.1$. We have found for $AgCl$, $S_{298} = 23.4$, and for Ag, $S_{298} = 10.2$, whence for $1/_2Cl_2$, $S_{298} = 23.3$.

$Tl + 1/_2Cl_2 = TlCl$.—From the measurements of Lewis and von Ende[4] the difference in potential between thallium, thallous chloride and mercury, mercurous chloride is 0.8235, whence, proceeding as before, we find for the formation of thallous chloride, $\Delta F_{298} = -44110$. Unfortunately the heat of formation has been determined only by Thomsen, and his value, $\Delta H_{298} = -48580$, may be in considerable error. Using this value, $\Delta S_{298} = -15.0$. We have found for thallous chloride $S_{298} = 28.6$, and for thallium $S_{298} = 14.6$, whence for $1/_2Cl_2$, $S_{298} = 29.0$.

$Na + 1/_2Cl_2 = NaCl$.—From the normal electrode potentials of sodium[5] and chlorine[6] we find for the reaction

$$Na + 1/_2Cl_2 = Na^+ (M) + Cl^- (M); \quad \Delta F_{298} = -94090.$$
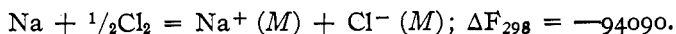
[1] Z. Elektrochem.. 17, 143 (1911).

[2] Z. physik. Chem., 37, 328 (1911).

[3] This is with white precipitated silver chloride. This measurement recently made by Dr. Linhart has not yet been published.

[4] THIS JOURNAL, 32, 732 (1910).

[5] Lewis and Kraus, Ibid., 32, 1459 (1910).

[6] Lewis and Rupert, Loc. cit.

For the difference in free energy between solid sodium chloride and an aqueous solution at molal ion concentration[1] we have

$$Na^+ (M) + Cl^- (M) = NaCl(s); \Delta F_{298} = 1850.$$
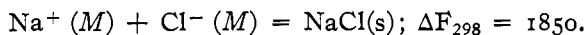
Adding these equations we have for the formation of the solid salt, $\Delta F_{298} =$ —92240. For ΔH Thomsen finds —97700 and Berthelot —97900, average —97800. Hence $\Delta S_{298} = $ —18.7. We have found for NaCl, $S_{298} = 17.4$, and for Na, $S_{298} = 12.2$, whence for $^1/_2Cl_2$, $S_{298} = 23.9$.

Comparison of the Several Values for the Entropy of Chlorine.—We have thus obtained for the atomic entropy of gaseous chlorine six different values, namely, from specific heats, 27.8; from HgCl, 26.1, from PbCl₂, 24.0; from AgCl, 23.3; from TlCl, 29.0; from NaCl, 23.9; the mean being 25.7. The average deviation from the mean amounts to nearly two entropy units or 600 calories. It is our belief that these differences are not outside the limits which might reasonably be assigned to experimental error in the data employed, especially the heats of reaction. We hope that measurements now in progress in this laboratory will give more precise information regarding these important quantities.

The Entropy of Potassium.—We have seen that the specific heat of potassium is so high and so abnormal that without accurate measurements at very low temperatures its entropy cannot be determined by the direct method, but by assuming the third law we may calculate it by means of two separate reactions. From the electrode potentials of potassium,[2] chlorine, and bromine,[3] and from the free energies of solution obtained by Rodebush, we find

$$K + ^1/_2Cl_2 = KCl(s); \Delta F_{298} = \text{—97930}$$
$$K + Br(l) = KBr(s); \Delta F_{298} = \text{—90900}.$$
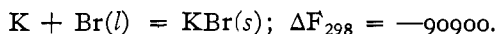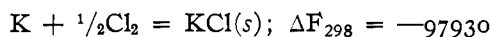
For the first of these reactions Thomsen and Berthelot both obtain $\Delta H =$ —105700, for the second Thomsen gives —95300, and Berthelot —95600, average —95450. Hence, for the two reactions, $\Delta S_{298} = $ —26.1 and $\Delta S_{298} = $ —15.3, respectively. We have found for KCl, $S_{298} = 19.7$ and for $^1/_2Cl_2$, $S_{298} = 25.7$. Also for KBr, $S_{298} = 22.4$ and for Br(l), $S_{298} = $ —18.5. Hence, for the two reactions we find for potassium $S_{298} = 20.1$ and $S_{298} = 19.2$, respectively. The agreement is entirely satisfactory. We may provisionally assume the average 19.7 as the entropy of potassium.

S (*rhombic*) = S (*monoclinic*).—We have seen from the specific heat data that the entropy of monoclinic sulfur is a trifle higher than that of rhombic. Assuming the third law, we may calculate the exact difference. From the free-energy equation of Lewis and Randall[4] $\Delta F_{298} = 17$, and

[1] From an investigation by W. H. Rodebush, to be published shortly.
[2] Lewis and Keyes. THIS JOURNAL, **34**, 119 (1912).
[3] Lewis and Storch, *Ibid.*, **39**, 2544 (1917).
[4] THIS JOURNAL, **36**, 2468 (1914).

$\Delta H_{298} = 82$, hence $\Delta S_{298} = 0.22$. Adding this to the entropy of rhombic sulfur we find for monoclinic sulfur $S_{298} = 7.8$.

$6C_G + 3H_2 = C_6H_6(l)$.—If we may employ the third law it furnishes an extraordinarily powerful method for determining the free energy of a large number of compounds which cannot readily be investigated by other methods. It is only necessary to know the specific heat of the compound at various temperatures, its heat of formation, and the entropies of its elements. We may illustrate the method by calculating the free energy of formation of benzene. From the very careful investigations conducted by Roth[1] and by Richards[2] we find for the formation of benzene from its elements $\Delta H_{298} = 11700$. We have found for benzene $S_{298} = 44.5$, for six gram atoms of graphite $S_{298} = 7.6$, and for three mols of H_2, $S_{298} = 95.4$. Hence, $\Delta S_{298} = -58.5$; $298 \Delta S = -17400$ and $\Delta F_{298} = 11700 + 17400 = 29100$.

Conclusion.

We have obtained in nine cases direct tests of the third law of thermodynamics. The average discrepancy in these nine cases has proved to be 1.6 entropy units or less than 500 cal. We believe that these discrepancies lie within the limits of experimental error which might reasonably be assigned in the individual cases, and furthermore that the discrepancies are less in those cases where the experimental accuracy seems the greater.

It has long been the desire of chemists to calculate free-energy changes from thermal data, but we now see that in the majority of the cases which we have considered, the values both of ΔF and of $T\Delta S$ have been more accurate than those of ΔH.

While we hope that in the near future more accurate data concerning heats of reaction may be available, in the meantime we may assert that the third law rests upon a more adequate experimental basis than either the first or second laws of thermodynamics possessed at the time of their universal adoption. We believe, therefore, that it would be an excess of conservatism to refuse the acceptance of this powerful weapon of calculation in energetics until additional data are made available.

Therefore, we have not hesitated to embody the values of entropy obtained by means of the third law in our final collection (Table VIII) of the atomic entropies of the elements. In this table we have brought together the values obtained in the several sections of this paper, and, except in the case of those data which depend upon Dewar's average specific heats alone, we have made in each case a rough estimate of the probable accuracy. These estimates are expressed by letters placed after the entropy values. Thus a, b and c indicate that the value is hardly likely to

[1] Roth and v. Auwers, *Ann.*, **407**, 152 (1914).
[2] Richards and Barry, THIS JOURNAL, **37**, 993 (1915).

be in error by more than one-third of an entropy unit, one unit, or two units, respectively.

We shall not discuss the table further at this time, except to point out that the atomic entropies show with respect to atomic weight, or atomic number, the same sort of periodicity that occurs in other important atomic properties. In certain rough calculations this fact may be utilized in the estimation of the entropies of elements for which experimental data are not yet available.

TABLE VIII. Atomic Entropies.

Hydrogen (g)	15.9 b		Bromine (l)	18.5 c
Helium (g)	29.2 b		Zirconium	9.5
Lithium	7.6		Molybdenum	7.5
Beryllium	7.3		Ruthenium	6.9
Diamond	0.6 a		Rhodium	7.6
Graphite	1.3 a		Palladium	8.9
Nitrogen (g)	22.8 b		Silver	10.2 a
Oxygen (g)	24.1 b		Cadmium	11.6
Sodium	12.2 a		Tin	11.5
Magnesium	8.3 a		Iodine	15.7 b
Aluminum	6.9 a		Lanthanum	13.7
Silicon (met.)	4.7 a		Cerium	13.8
Sulfur (rhomb.)	7.6 b		Tungsten	8.4
Sulfur (monocl.)	7.8 b		Osmium	7.8
Chlorine (g)	25.7 c		Iridium	8.7
Argon (g)	36.4 b		Platinum	10.0
Potassium	19.7 c		Gold	11.0
Calcium	11.0 a		Mercury (l)	17.8 b
Titanium	6.6		Thallium	14.6 a
Chromium	5.8		Lead	15.4 a
Manganese	7.3		Thorium	13.6
Iron	6.6		Uranium	11.1
Nickel	7.2			
Cobalt	7.2			
Copper	8.0 a			
Zinc	9.8 a			

BERKELEY, CAL.

CHEMICAL REACTIONS IN THE CORONA. I. OZONE FORMATION.

BY F. O. ANDEREGG.

Introduction.

Among the problems which are attracting attention at the present time the question of the nature of the forces which hold the atoms together in the molecule is of great importance. The most probable suggestion is that these forces are due to the electrons and positive nuclei of the differ-