TABLE V

IONIC ENTROPIES REFERRED TO $H^+ = 0$ AT HYPOTHETICAL ONE MOLAL CONCENTRATION AND 298°K.

	$S_{1\,M.\,298°}$		$S_{1\,M.\,298°}$		$S_{1\,M,\,298°}$
Li^+	1	Fe^{+++}	−67	I^-	27
F^-	− 5	Cu^{++}	−23	Ba^{++}	4
Na^+	15	Zn^{++}	−24	Tl^+	26.5
Mg^{++}	−19	Br^-	20.5	Tl^{+++}	−87
Cl^-	15.5	Rb^+	25	Pb^{++}	2
K^+	22	Ag^+	16	OH^-	−2
Ca^{++}	− 9	Cd^{++}	−14	CO_3^{--}	−14
Fe^{++}	−22	Sn^{++}	−12	SO_4^{--}	9

centration and 298°K. To these might be added many more estimated from the relation found between the entropy of solution and the ionic radii.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MEASUREMENT OF COEFFICIENTS OF EXPANSION AT LOW TEMPERATURES

SOME THERMODYNAMIC APPLICATIONS OF EXPANSION DATA

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This research was undertaken with the purpose of obtaining data on coefficients of thermal expansion of solids at low temperatures which are required for testing theories of the solid state. The mathematical development of such theories involves certain differential coefficients, for example, the various elastic moduli, the specific heat and the coefficient of expansion. The functional relations of these quantities are, therefore, important topics for experimental investigation. While most of the important coefficients have been studied at ordinary temperatures, the experimental difficulties have practically limited quantitative work at low temperatures to measurements of specific heats and of coefficients of expansion, and of a few other properties, such as electrical conductivity, whose relations to the main problem are still obscure.

We have three important principles that indicate the method of attack: the third law of thermodynamics,[2] the quantum theory of specific heats[3] and the approximate constancy of the ratio of the specific heat of a substance to its coefficient of expansion which was discovered by Grüneisen.[4]

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[1] National Research Fellow while a part of this work was done.

[2] Lewis and Gibson, THIS JOURNAL, **42**, 1542 (1920).

[3] (a) Einstein, *Ann. Physik*, [4] **22**, 180 (1907). (b) Debye, *ibid.*, [4] **39**, 789 (1912). (c) Born and Kármán, *Physik. Z.*, **13**, 297 (1913); **14**, 15 (1913).

[4] Grüneisen, *Ann. Physik*, [4] **26**, 211 (1908).

Representing volume by V, absolute temperature by T, pressure by P and entropy by S, classical thermodynamics gives the relation $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$. The third law then requires that the volume coefficient of expansion of a perfect crystal approach zero at low temperatures in order that its entropy may become zero independently of the pressure. The approximate validity of the Grüneisen relation and the known behavior of specific heats satisfactorily confirm the third law, but our data show that expansion measurements at still lower temperatures are required for adequate tests of theories of lattice mechanics, such as those of Grüneisen[4,5] and of Born.[6] Reference should also be made to the much less elaborate, but very suggestive theory of Ornstein and Zernicke.[7] The results of such theoretical discussions are necessarily of doubtful accuracy, but being in fair agreement with the facts as far as known, they may, if used with due caution, prove of considerable value. Thus it will be shown that such a semi-theoretical expression leads to satisfactory values for the entropies of solids.

Apparatus and Method

The expansion measurements were made by a modified Fizeau[8] method, in which the displacement of a system of interference bands gives length changes in terms of the half wave length of light used. A Fizeau apparatus can be made sensitive to 0.01 band, or about 2.7×10^{-7} cm. For the expansion over a 5° interval of a 1cm. sample having a coefficient of 10^{-5}, this corresponds to an error of about 0.5%. The accuracy of nearly all expansion work is, however, limited by other factors, such as temperature control and measurement, mechanical displacements, hysteresis effects and, in some cases, by corrections for the refractive index of air. In order to obtain true differential coefficients, not merely total expansions over long temperature intervals, the methods developed in low-temperature vacuum calorimetry have been applied to the problem, and the instantaneous coefficients of expansion of a number of substances have been found from about 90°K. to 310°K.

In the Fizeau method, plane-polished quartz or glass plates are held apart by a known length of the material to be investigated, the wedge-

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[5] (a) Grüneisen, *Ann. Physik*, [4] **33**, 65 (1910); **39**, 257 (1912); **55**, 371 (1918); **58**, 753 (1919); *Verh. deut. physik. Ges.*, **13**, 426, 491, 836 (1911). (b) Grüneisen and Goens, *Z. Physik*, **26**, 235, 250 (1924); **29**, 141 (1924).

[6] Born, "Dynamik der Kristallgitter," Teubner, Leipzig, **1915**; and a second edition, much amplified, Teubner, Leipzig, **1923**. See also numerous journal articles.

[7] Ornstein and Zernicke, *Proc. Acad. Sci. Amsterdam*, **19**, 1289, 1295, 1304, 1312 (1917).

[8] (a) Fizeau, *Ann. chim. phys.*, [4] **2**, 143 (1864); **7**, 335 (1866). (b) For various modifications of the fundamental method, see Benoit, *Trav. Mem. Bur. Int.*, **1C**, 1 (1881); **6** (1888). (c) Pulfrich, *Z. Instrumentenk.*, **13**, 365, 401, 437 (1893); **18**, 261 (1898). (d) Valentiner and Wallot, *Ann. Physik*, [4] **46**, 837 (1915).

angle between the plates being adjusted for a difference of about 20 half wave lengths in the separations at opposite sides. When the plates are illuminated by parallel, monochromatic light and viewed from the direction of the source, straight, parallel and equally spaced interference bands appear at the reflecting surfaces. As the supports expand, the wedge angle remains constant and the bands move across the plate; when each band has reached the position formerly occupied by its neighbor, the separation of the plates has changed by half a wave length. An expansion measurement, therefore, consists of determining, for a definite temperature interval, the number of bands which pass a fiducial mark.

The interferometer plates, made by Wm. Gaertner and Company of Chicago, were cut from crystalline quartz, with the reflecting surfaces perpendicular to the optic axis, and plane-polished to 0.05 wave length. The upper plate was cylindrical, 3 cm. in diameter and 1 cm. thick. An angle of 20′′ between the faces served to throw light reflected from the upper surface out of the field. The lower plate has a base 3 cm. in diameter, and a central portion an additional 1.035 cm. thick. The upper reflecting surface, 2.2 cm. in diameter, was undercut to leave a step 0.5 cm. wide around the piece, 1.035 cm. below the reflecting surface. This shape provided for measurements of expansion relative to quartz, using an interference path of the order of 0.01 cm., as well as for absolute measurements using a long path. In the relative method, three samples about 1.045 cm. long, plane at one end and bluntly pointed at the other, were evenly spaced around the step, and plates and samples clamped together with light springs.. By polishing the points of the samples, the wedge angle between the plates was adjusted to give properly spaced bands. In the absolute method, the lower plate was inverted, and samples about 0.4 cm. long were clamped between the reflecting surfaces. In either case, reflection from the lower surface of the lower plate was prevented by blackening it with India ink, and a number of small spots of India ink were placed on the lower surface of the upper plate to serve as fiducial marks.

When set up, the interference apparatus was placed inside a copper block weighing 2.4 kg. A plate-glass window transmitted light, and shielded the apparatus from heat radiation. The block was then hung by strong silk threads in a steel container.[9] When in use, a Dewar tube was brought up over the container, and small amounts of liquid air were added at short intervals. The temperature of the container was controlled sufficiently well in this way to make liquid baths unnecessary, except above room temperature, in which case water was used. Heat lost to the container was balanced by electrical energy in a coil wound on the block, the input being regulated to maintain the temperature constant to 0.1°. The variable junction and 30 cm. of the leads of a copper-constantan thermocouple

[9] Gibson and Giauque, THIS JOURNAL, **45**, 98 (1923).

were placed inside the block, and the fixed junction in a Dewar tube of cracked ice. The electromotive force of the couple was read to the nearest microvolt on a White potentiometer. The thermocouple was calibrated against the standard couple of Eastman and Rodebush.[10]

A steel outlet tube 1 cm. in diameter and 1 meter long placed near the edge of the top of the container carried the wires and served as the vacuum lead. A glass line was sealed on with de Khotinsky cement, and the wires were brought out through the cement. A mercury aspirator backed by a Nelson oil pump maintained the pressure below 0.0001 mm. as read on a McLeod gage. The light path was through an axial tube 2.5 cm. in diameter and 14 cm. long. A plate with a hole for the light path was welded on at the top, and the vacuum joint made with a plate-glass window and a rubber gasket impregnated with stopcock grease.

The interference method requires a strong source of monochromatic light; a mercury arc in Pyrex glass was used. The green line can be readily isolated by means of a color filter, and gives excellent interference bands. Ultraviolet radiation was absorbed by the walls of the lamp. Light entered the apparatus vertically. The image of a small portion of the arc was thrown on an adjustable slit which was at one principal focus of a collimating lens of 23 cm. focal length, the reflecting surfaces of the plates being at the other. The edge of a reflecting prism was set parallel to the slit, 4 cm. below it and 0.1 cm. back, so that the cone of light just missed the prism going down, was made parallel by the lens, and on reflection from the plates at a small angle with its former path, struck the prism and was reflected horizontally into a telescope. The apparatus being arranged for auto-collimation, the images of the bands and of the marks on the upper plate were viewed with the telescope focused for infinity. A color filter was interposed between the eye and the telescope whenever desired. The telescope was fitted with a filar micrometer eyepiece whose traveling crosshairs were set parallel to the bands. As nearly as possible, the light path was enclosed in blackened tubing, thus reducing the general illumination of the field to a satisfactory value.

The steel container, the collimating apparatus and the telescope were mounted separately on the side of a pier, thus giving ample opportunity for adjustment and insuring stability. No vibration from the building, or from the ebullition of the liquid air was discernible in the bands.

The green band system greatly predominates; hence the number of green bands transited as the temperature changed could be counted without use of a color filter. The band width in each system being proportional to the wave length, the appearance of the green bands, as modified by the others, changed sufficiently to permit describing each band as it passed a fiducial mark, and assigning it a serial number. Once the whole tempera-

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[10] Eastman and Rodebush, THIS JOURNAL, **40**, 489 (1918).

ture range had been covered, a band could be identified from its description, and further counting was avoided, except as a check.

The final measurements of band positions were made in monochromatic light, using Wratten filter No. 62 to transmit the green line, 5461 Å. The traveling cross-hairs of the micrometer were set on maximum darkness. Either five consecutive or six alternate bands were measured, setting alternately on the bands and the fiducial marks. The temperature was easily maintained constant to 0.1°, but in order to make certain that band drifts had ceased, the measurements were repeated at ten-minute intervals until satisfactory constancy was shown. The average reading of all the bands was taken for the position of the central band. From this, the position of the fiducial marks and the measured band width, the fraction of a green band to be added to the serial number was determined. The sum denoted by Δ bands$_g$, is the number of green bands displaced between the temperature at which band No. 0 was in the standard position, and the temperature of the measurements.

Measurements in the yellow were often taken, especially when the long interference path was used, as they afford an independent check of the band count. Wratten filter No. 22 was used to transmit the yellow lines 5770 Å. and 5791 Å. The superposition of the two band systems gave more or less blurred maxima whose separation corresponded to the average wave length. When the bands of one system fell exactly in the middle between those of the other, the field was practically uniform and measurements were impossible.

Δ bands$_g$ $\times$ 5461/5781.5 gives the number of yellow bands equivalent to Δ bands$_g$. On subtracting the measured fraction of a yellow band from this number, the fractional part of the result represents the calculated separation of green band No. 0 and the following yellow band. (In case a point at which the field became uniform is included in the interval, then 0.50 band must be added.) This quantity, called the displacement constant, must remain the same for all measurements of a series. Since an error of 1 band in the serial number makes an error of 0.055 band in the displacement constant, the sensitivity of the method (0.01–0.02 band) was ample to check the count.

About every fourth measurement was made at room temperature. The values of Δ bands$_g$ so found, when calculated to a single temperature, usually showed a steady drift, and fixed the corrections to be applied to intermediate data. For all the substances investigated, positive values of Δ bands$_g$ correspond to decreases in length. The length changes, Δl, were then found from the relation $\Delta l = -5.461/2\ \Delta \text{ bands} \times 10^{-5}$. An empirical equation was then found which represented Δl as a function of temperature with an accuracy of about 1%, and the residual Δl's were plotted against temperature. The experimental values of dl/dT were then found at round values of the temperature by adding corresponding values of the derivative of the equation and of the slope of the difference plot. In case the absolute method was used, the coefficient of expansion, α, is given by the relation $\alpha = (1/l_0)(\mathrm{d}l/\mathrm{d}T)$. In case the relative method was used, the expression becomes $\alpha = 1/l_0[(\mathrm{d}l/\mathrm{d}T) + 1.035\ \alpha\text{-quartz}_{11}]$. l_0 has been taken as the length at room temperature in preference to other possible choices, such as the instantaneous value, or that at absolute zero. The values of 1.035 α-quartz$_{11}$ were found by interpolation in Table XI.

Experimental Results

The following tables summarize the experimental results. For each substance one table gives the changes in length and the next the coefficients of expansion. For aluminum, copper, silver and rock salt, the length of changes are for the samples of given length, relative to 1.035 cm. of quartz parallel to the axis; for Pyrex glass and quartz, which were measured by the absolute method, the length changes are calculated for unit length of sample. In each case, all measurements near room temperature were used to fix the drift corrections and, therefore, appear as a single one.

Aluminum.—The measurements were made on samples turned from hand-rolled aluminum rod. The behavior was satisfactory. Corrections were readily made for the drift, which totaled 0.5% of the largest expansion. The band count was checked by the indirect method in nearly every case. The regularity of the points on the difference plot gave further evidence that no gross errors were made, and showed that the expansion of the samples was reproducible.

TABLE I

RELATIVE EXPANSIONS OF 1.0456 CM. OF ALUMINUM

T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$
315.3	23.6	269.2	96.8	115.9	314.6
314.5	24.9	239.3	143.6	114.5	315.6
310.7	30.9	226.5	162.9	98.1	331.8
297.0	52.7	196.5	208.0	89.3	339.5
276.4	85.5	158.9	261.1	86.5	341.6
273.9	89.4	124.7	304.3		

TABLE II

COEFFICIENTS OF EXPANSION OF ALUMINUM

T	$\alpha \times 10^5$	T	$\alpha \times 10^5$	T	$\alpha \times 10^5$
85	0.881	150	1.693	270	2.199
90	1.020	170	1.815	297	2.275
100	1.187	190	1.917	315	2.319
110	1.323	210	2.000		
130	1.539	240	2.107		

Copper.—The samples were turned from hard-rolled copper rod. The behavior was satisfactory, and no appreciable drift occurred. Green bands only were measured; the band count was verified by repetition. An accident prevented measurements from being made at the lowest temperatures.

TABLE III

RELATIVE EXPANSIONS OF 1.0450 CM. OF COPPER

T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$
312.0	10.7	285.0	36.9	198.9	121.5
310.9	12.0	261.4	60.0	170.8	149.6
304.0	18.5	237.8	82.9	139.4	179.9
295.0	27.0	223.5	96.9	108.6	206.8

TABLE IV

COEFFICIENTS OF EXPANSION OF COPPER

T	$\alpha \times 10^5$	T	$\alpha \times 10^5$	T	$\alpha \times 10^5$
120	1.203	200	1.513	280	1.648
140	1.290	220	1.538	295	1.679
160	1.384	240	1.564	310	1.699
180	1.459	260	1.606		

Silver.—The samples were turned from a silver rod that had been cast in graphite and hammered. The measurements at room temperature showed complete absence of drift. This was fortunate, as accidents twice caused displacements of several bands. Green bands only were measured, the band count being verified by repetition.

TABLE V

RELATIVE EXPANSIONS OF 1.0425 CM. OF SILVER

T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$
310.3	18.5	260.3	78.7	189.0	155.4
306.3	23.5	250.0	91.3	179.7	180.1
295.0	36.9	241.9	101.3	134.9	237.2
280.1	54.6	228.9	117.6	101.2	279.3
277.2	57.8	228.3	118.3	92.4	289.8
274.3	61.4	212.1	138.7	86.8	296.2
267.8	69.5	211.6	139.3		
265.4	72.1	192.7	163.5		

TABLE VI

COEFFICIENTS OF EXPANSION OF SILVER

T	$\alpha \times 10^5$	T	$\alpha \times 10^5$	T	$\alpha \times 10^5$
90	1.406	180	1.732	270	1.864
110	1.501	210	1.785	298	1.896
130	1.606	240	1.823	310	1.908
150	1.666				

Sodium Chloride.—Samples cut from a specimen of rock salt proved to have sufficient mechanical strength. Corrections were made in the usual way for the drift, which amounted to 1% of the largest expansion. The band count was checked by the indirect method in almost all cases. The experimental conditions were unusually favorable and there is every reason to believe that very high accuracy was attained.

TABLE VII

RELATIVE EXPANSIONS OF 1.0667 CM. OF ROCK SALT

T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$
310.3	25.1	218.0	337.2	127.7	616.1
304.6	44.6	209.5	365.6	126.7	618.7
295.0	78.1	207.9	370.5	103.9	678.0
277.8	137.4	192.0	421.1	103.5	678.6
262.4	189.5	187.7	436.1	94.4	697.5
252.4	223.7	169.6	490.6	85.8	720.1
240.2	264.6	155.2	536.2	85.4	719.6
239.8	265.6	145.5	565.0		
234.0	284.2	138.4	585.5		

TABLE VIII

COEFFICIENTS OF EXPANSION OF ROCK SALT

T	$\alpha \times 10^5$	T	$\alpha \times 10^5$	T	$\alpha \times 10^5$
85	2.278	180	3.478	280	3.916
100	2.537	200	3.543	300	3.986
120	2.843	220	3.641	310	4.016
140	3.103	240	3.742		
160	3.294	260	3.834		

Pyrex Glass.—Measurements of the expansion of Pyrex glass, although of no great theoretical interest, were important to us because we wished to use it in a hydrogen thermometer. Further, because of its low coefficient, it was well adapted for use in testing out the absolute method. The sample was a ring cut from 2.3 cm. tubing, and finished to give three-point support at each end. Both green and yellow bands were measured, and satisfactory checks obtained. The data, however, showed the marked lack of reproducibility long known to be characteristic of glasses. The measurements given in Table IX were chosen from about 35 to give the smooth curve which best represented all the data, and probably largely averaged out the lag in expansion. Unless the expansions of other lots differ from these by more than 5%, which is unlikely, they are amply accurate for the purpose for which they were required.

TABLE IX

TOTAL EXPANSIONS PER CM. AND AVERAGE COEFFICIENTS OF EXPANSION OF PYREX GLASS G 702—EJ

T	$-\Delta l \times 10^5/l^5$	Mean T	$\frac{1}{l_0}\frac{\Delta l \times 10^5}{\Delta T}$
315.9	− 6.6	307	0.37
298.0	0.0	273	.34
248.9	16.9	233	.32
218.3	26.6	202	.29
185.1	36.4	158	.24
130.4	49.4	121	.17
111.8	52.5	99	.11
86.7	55.3		

Quartz, Parallel to the Optic Axis; the Expansion of the Reference.—Absolute measurements of the expansion of quartz were necessary for the calculation of the data relative to quartz. A plate 0.4 cm. thick was cut from a crystal and plane-polished. This and the lower interferometer plate were examined by Dr. Hulin of the Geology Department of the University of California, who reported that both were cut perpendicular to the axis within a possible error of 1°, which was within the limits of permissible deviation. Three cylinders 0.3 cm. in diameter were cut from the plate. One end of each sample was polished to an ellipsoidal surface, and the other was left plane. The final lengths averaged 0.3965 cm. A maximum difference of 0.1 band was found between two series; the difference curve was drawn to average them.

TABLE X

EXPANSIONS OF QUARTZ, PARALLEL TO THE OPTIC AXIS, PER CM.

T	$-\frac{\Delta l}{l_0} \times 10^5$	T	$-\frac{\Delta l}{l_0} \times 10^5$	T	$-\frac{\Delta l}{l_0} \times 10^5$
317.9	1.1	229.7	63.7	123.3	117.1
309.2	8.0	225.3	65.9	122.7	117.3
303.8	12.3	202.1	79.3	114.9	119.6
295.0	18.7	193.7	84.6	108.5	122.1
272.3	35.6	174.2	93.9	95.3	126.4
271.6	35.7	157.4	103.0	85.7	128.7
267.4	38.6	137.8	110.5	85.2	128.7
252.4	49.2	136.4	111.1		
240.0	56.7	136.4	111.8		

TABLE XI

THE COEFFICIENT OF EXPANSION OF QUARTZ PARALLEL TO THE OPTIC AXIS AND dl/dT FOR THE REFERENCE

T	$\alpha \times 10^5$	$1.035\alpha \times 10^5$	T	$\alpha \times 10^5$	$1.035\alpha \times 10^5$
85	0.240	0.248	210	0.574	0.594
90	.267	.276	220	.595	.616
100	.305	.316	230	.616	.638
110	.338	.350	240	.637	.659
120	.369	.382	250	.658	.681
130	.396	.410	260	.679	.703
140	.420	.435	270	.700	.725
150	.444	.459	280	.722	.747
160	.466	.483	290	.743	.769
170	.489	.506	300	.764	.791
180	.511	.528	310	.785	.812
190	.531	.550	320	.806	.834
200	.553	.572			

Discussion

Errors.—The experimental checks secured make it reasonably certain that the whole number of bands was in every case correct. The original direct count was always verified by repetition and, except in the measurements on copper and silver, by the indirect method also. Errors due to permanent displacements of any character were reduced to the order of 0.02 band by the drift correction. The regularity of the points on the difference plots indicated that individual measurements at low temperatures could be reproduced with an accuracy of 0.1 to 0.2 band. Temperature equilibrium was definitely established in every experiment, the drift amounting to only a few hundredths of a band per hour. True lag in the expansion is a possible explanation of some of the discrepancies; in the case of Pyrex glass it was evidently the controlling factor. Probably the real explanation of the usual errors lies in the finite size of the slit, in conjunction with small displacements of the optical system. The difference plot indicated that the probable errors in the measurements on the 0.3965cm. sample of quartz were about 0.03 band, making the equivalent error in the expansion of the reference about 0.08 band. The probable error of an individual relative measurement, including the error in the reference, is estimated as 0.25 band, or 0.5×10^{-5} cm. The use of sensitive difference plots in the final calculations of the coefficients of expansion greatly reduced the effect of these accidental errors. The temperature scale is the only important source of systematic error of which we are aware. On the basis of unfinished work with a hydrogen thermometer, the errors of the scale are judged to be of the order of 0.2°; and of the size of the degree, never more than 1%. This may cause a maximum error of 1% in the coefficients of expansion without, however, greatly affecting the length changes.

Previous Work

Metals.—Recent experimental papers by Souder[11] and by Hidnert[12] have included discussions of previous data for aluminum and copper which need not be repeated here. These papers are particularly important in that the authors systematically attack the problem of the relations of composition and heat treatment to expansion. Our work is in good general agreement with that of other observers, especially at room temperature. Although the low-temperature data of Ayers[13] and of Shearer[14] on aluminum and of Dorsey[15] on copper scatter somewhat, they can be represented fairly well by the graph of our own data. Discrepancies are also found in the case of silver. Our results are 1 to 2% lower than those of Dorsey over most of the range; the room-temperature data summarized in the Landolt-Börnstein "Tabellen" also show considerable variations. It is,

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[11] Souder and Hidnert, *Sci. Pap. Bur. Stand.*, **17,** 497 (No. 426) (1922); **17,** 611 (No. 433) (1922).

[12] Hidnert, *ibid.*, **17,** 91 (No. 410) (1922).

[13] Ayers, *Phys. Rev.*, **20,** 38 (1904).

[14] Shearer, *ibid.*, **20,** 52 (1904).

[15] Dorsey, *ibid.*, **25,** 88 (1907).

perhaps, useless to expect better agreement among the results for metals, as specific-heat measurements also show variations; accurate values for the coefficient of expansion of particular samples, over a wide range of temperatures, are nevertheless significant.

Rock Salt.—Very few rock-salt data are available for comparison. Fizeau[16] found $\alpha = 4.040 \times 10^{-4}$ at 40°, in agreement with the present work. A recent paper by Henglein[17] gives values based on specific-gravity measurements at the temperatures of ice, carbon dioxide and liquid air which agree with our own within the errors of her method.

Quartz.—There are many excellent data in the literature for the expansion of quartz above the ice point, but it is difficult to choose a fair method of comparing them with our own for the reason that the temperature ranges do not overlap sufficiently. Nearly all observers have expressed their results by means of equations of the type $\alpha = a + bt$, where t is the Centigrade temperature. If $\mathrm{d}\alpha/\mathrm{d}T$ is really a function of temperature, the values found for a and b will depend on the range covered by the measurements; $\mathrm{d}\alpha/\mathrm{d}t$ evidently decreases slightly with increasing temperature, resulting in larger values of a and smaller values of b than the data at higher temperatures. The differences found do not cast doubt on the assumption that the expansion of all samples is identical. For purposes of comparison, we have collected in Table XII the values $(\mathrm{d}\alpha/\mathrm{d}T)_{273.1}$, $\alpha_{273.1}$ and $\alpha_{298.1}$, as given by the linear equations, and have added values estimated from Dorsey's table, Scheel's values from the equation α =

TABLE XII

COMPARISON OF THE DATA FOR THE EXPANSION OF QUARTZ PARALLEL TO THE AXIS AT 273.1° AND 298.1°

Author	$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{273.1} \times 10^5$	$\alpha \times 10^5_{273.1}$	$\alpha \times 10^5_{298.1}$
Fizeau[a]	0.001770	0.710	0.754
Benoit[b]	.001602	.716	.756
Reimerdes[c]	.001638	.6925	.7334
Bein[d]	.001616	.71525	.7557
Scheel (1°)[e]	.001630	.7144	.7551
Scheel (2°)[f]	.001877	.7085	.7541
Dorsey[g]	(.0022)	.7542	(.80)
Buffington and Latimer	.002111	.7069	.7597

[a] Fizeau, *Compt. rend.*, **62,** 1101, 1133 (1866); *Pogg. Ann.*, **128,** 564 (1866).
[b] See Ref. 8b.
[c] Reimerdes, *Inaugural Dissertation*, Jena, 1898.
[d] Bein, *Verh. deut. physik. Ges.*, **14,** 1997 (1912).
[e] Scheel (1°), *Ann. Physik,* [4] **9,** 837 (1902).
[f] Scheel (2°), *Ber. physik. Ges.*, **5,** 3 (1907).
[g] Dorsey, *Phys. Rev.*, **27,** 1 (1908).

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[16] Fizeau, *Compt. rend.*, **64,** 314 (1867).

[17] Henglein, *Z. physik. Chem.*, **115,** 91 (1925).

$(0.7085 + 0.001877t - 0.00000216t^2) \times 10^{-5}$, and our own, calculated from the equation that holds from $T = 170°$ to $310°$, $\alpha = (0.1304 + 0.002111T) \times 15^{-5}$. Dorsey's values at low temperatures are higher than our own. This may have been due to an error in cutting his samples, as the coefficient perpendicular to the axis is large. Scheel gives 107.4×10^{-5} for $\Delta l/l_0$ between —190° and 16°, as against 106.2×15^{-5} calculated from our data.

Applications

The Third Law of Thermodynamics.—The present statement of the third law requires that the coefficient of expansion of a perfect crystalline solid approach zero at absolute zero. In the absence of expansion data at very low temperatures, some method of extrapolation must be devised in order to check the prediction. An indirect method due to Grüneisen has proved the most satisfactory.

The ratio of the specific heat of a substance to its volume coefficient of expansion gives the relation of energy input to volume change. The discovery by Grüneisen, already referred to, that this ratio is nearly independent of temperature, marked a great advance in our knowledge of the solid state, and at the same time strengthened the position of the third law.

Of the substances investigated, aluminum, copper, silver and sodium chloride are isotropic crystalline solids whose specific heats fall on the Debye[3b,18] curve. Table XIII indicates the calculation of $C_p/3\alpha$ for these substances at various temperatures. The values of C_p were read from graphs prepared by Lewis and Gibson, and by Lewis, Gibson and Latimer[19] in their calculation of entropies; references to the original data are given in their papers. The trend of the $C_p/3\alpha$ values gives a very satisfactory confirmation of the third law, as in each case α increases slightly more rapidly with the temperature than does C_p. The limiting values of $C_p/3\alpha$ at absolute zero might be guessed from these results, but it is unnecessary for our purpose. The necessity of limiting the third law to

TABLE XIII

CALCULATIONS OF $C_p/3\alpha$

	T	C_p	$\alpha \times 10^5$	$\frac{C_p \times 10^{-4}}{3\alpha}$		T	C_p	$\alpha \times 10^5$	$\frac{C_p \times 10^{-4}}{3\alpha}$
Al	100	3.10	1.185	8.72	Ag	100	4.85	1.450	11.26
	160	4.62	1.758	8.76		160	5.63	1.694	11.08
	220	5.31	2.042	8.67		220	5.91	1.800	10.94
	280	5.70	2.223	8.55		280	6.02	1.876	10.70
Cu	100	3.90	(1.10)	(11.8)	½NaCl	100	4.29	2.537	5.64
	160	5.13	1.385	12.34		160	5.24	3.294	5.30
	220	5.55	1.540	12.01		220	5.59	3.641	5.12
	280	5.78	1.650	11.68		280	5.77	3.916	4.91

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[18] Lewis and Gibson, THIS JOURNAL, **39,** 2554 (1917).

[19] Lewis, Gibson and Latimer, *ibid.*, **44,** 1008 (1922).

crystalline solids is well illustrated by expansion data; quartz glass and supercooled silicon have negative coefficients of expansion at low temperatures, and we suspect that Pyrex glass has also.

Interatomic Constraints and Entropy.—It appears quite probable, on *a priori* grounds, that V and $C_p/3\alpha$ might be used to introduce into the entropy equation for solids[20] terms that depend on the constraints between atoms. To do this we shall make use of an expression for the frequency of vibration of the atoms of a solid considered as resonators. According to Grüneisen,[21]

$$\nu = M^{-\frac{1}{2}} \cdot V^{\frac{1}{3}} \cdot \left(\frac{C_v}{3\alpha}\right)_{T=0} \times \text{constant} \qquad (1)$$

where M is the atomic weight and V the volume per gram atom. Combining with Planck's equation for the entropy of a system of resonators,

$$S_v = NR\, ln\, \frac{kT}{h\nu} + \text{constant} \qquad (2)$$

where S_v is the entropy of one mole at constant volume, N is the number of degrees of freedom, three in our case, k is the gas constant per molecule and R per mole, and h is Planck's constant, we obtain

$$S_v = 3RlnT + 3/2\ RlnM + RlnV - 3/2\ Rln\ (C_v/3\alpha)_{T=0} + \text{constant} \qquad (3)$$

It is interesting to note that for a perfect monatomic gas, Equation 3 reduces to the well-known Sackur equation[22]

$$S = 3/2\ RlnT + 3/2\ RlnM + RlnV + \text{constant} \qquad (4)$$

Equation 1 was derived by Grüneisen for an "ideal" monatomic solid whose specific heat has reached the equipartition value; probably no real substance fulfils the conditions imposed. Equation 3, therefore, merely qualitatively indicates the form of the relations to be expected. In order to get a simpler basis for comparison of different substances, it is convenient to make arbitrarily a few minor changes in Equation 3. S_p is substituted for S_v, as it is of far greater practical importance, and differs from the latter by only about 0.2 unit in ordinary cases. $(C_p/3\alpha)_{T=160}$ is substituted for $(C_v/3\alpha)_{T=0}$ in order to avoid uncertain extrapolations. As the calculations are made for $T = 298.1$, $3/2RlnT$ is included in the constant term. Equation 3 is then replaced by

$$S_{p,\,298} = 3/2RlnM + RlnV - 3/2Rln\ (C_p/3\alpha)_{T=160} + 26.5 \qquad (5)$$

where the additive constant has been evaluated from the data on aluminum, copper and silver as indicated in Table XIV. The values of $S_{p,\,298}$ are taken from the table of Lewis, Gibson and Latimer.[19] The table includes calculations of the constant based on Grüneisen's values of $C_v/3\alpha$ for magnesium, iridium and lead. The agreement is satisfactory, as these $C_v/3\alpha$ values are very rough.[23]

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[20] Latimer, THIS JOURNAL, **43**, 818 (1921).

[21] Grüneisen, *Ann. Physik*, [4] **39**, 293 (1912).

[22] Sackur, *Ann. Physik*, [4] **36**, 598 (1911); **40**, 67 (1913).

[23] Ref. 21, p. 294.

TABLE XIV

EVALUATION OF THE CONSTANT OF EQUATION 5

	M	V	$\frac{C_p \times 10^{-4}}{3\alpha}$	$S_{p,\,298}$	Constant
Al	26.97	10.00	8.76	6.82	26.34
Cu	63.57	7.10	12.34	8.18	26.84
Ag	107.88	10.27	11.08	10.25	26.28
Mg	24.32	14.00	8.1	8.3	27.2
Ir	193.1	8.61	32.1	8.7	26.5
Pb	207.2	18.27	8.0	15.53	27.5

Possibilities for the extension of the scope of Equation 5 at once suggest themselves; certain limitations are, however, obvious. The specific heat must have approximately reached the equipartition value; non-crystalline substances must be excluded as they deviate widely from the Grüneisen relation. Binary compounds crystallizing in the regular system appear to offer the best chance. The data are very fragmentary; sodium chloride appears to be the only substance fulfilling the conditions for which all the data are available. By assuming that $C_p/3\alpha$ for potassium chloride and lead sulfide changes in about the same way as for the substances given in Table XIII, it is possible to make an approximate calculation for these also.

It is necessary to replace M in Equation 5 by some other mass function. Latimer[20] has shown that in solid compounds whose specific heats have reached the equipartition value, the mass contribution of each element is $3/2 R \ln M$ per gram atom. The required function is, therefore, the geometric mean of the atomic weights, as V and C_p are taken per gram atom. For binary compounds Equation 5 becomes

$$S_{p,\,298} = 3/2 R \ln \sqrt{M \cdot M'} + R \ln V - \frac{3}{2} R \ln \left(\frac{C_p}{3\alpha}\right)_{T=160} + 26.5 \qquad (6)$$

where $S_{p,\,298}$ is evidently the entropy per gram atom.

The results of the calculations are summarized in Table XV. The check obtained for sodium chloride is regarded as particularly significant. Unfortunately, there are insufficient data to permit similar calculations for substances crystallizing in other systems.

TABLE XV

ENTROPIES OF SALTS ACCORDING TO EQUATION 6

	$\left(\frac{C_p \times 10^{-4}}{3\alpha}\right)_{T=160}$	$S_{p,\,298}$	
		Calcd.	Obs.
NaCl	5.30	9.22	8.72 9.25
KCl	6.0	9.8	9.85
PbS	10.7	10.4	11.4

Acknowledgment is due to the Bureau of Standards for a copy of their extensive manuscript bibliography on thermal expansion.

Summary

The instantaneous coefficients of expansion of aluminum, copper, silver, rock salt, quartz parallel to the optic axis, and Pyrex glass have been determined by an interference method for temperatures between 90° and 315°K.

The coefficients of expansion of the crystalline solids approach zero at low temperatures, in agreement with the prediction of the third law of thermodynamics. The coefficients of expansion change slightly more rapidly with temperature than do the specific heats.

Guided by a semi-theoretical expression due to Grüneisen, terms depending on the constraints between atoms are introduced into the equation for the entropy of solids. The entropies of six monatomic solid metals are satisfactorily represented by the equation $S_{p,\,298} = 3/2RlnM + RlnV - 3/2Rln\ (C_p/3\alpha)_{T\,=\,160} + 26.5$. A simple extension to binary compounds proves successful.

It is pointed out that data at still lower temperatures are required before adequate tests of theories of lattice mechanics can be made.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF BROWN AND STANFORD UNIVERSITIES]

SOLUTIONS OF THE ELECTRONEGATIVE ELEMENTS IN LIQUID AMMONIA. I. THE ACTION OF SELENIUM, TELLURIUM, ARSENIC AND A SOLUTION OF SULFUR IN LIQUID AMMONIA UPON CYANIDES

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Introduction

Chlorine dissolves readily in water in accordance with the equation, $Cl_2 + HOH \rightleftharpoons HCl + ClOH$. A solution of chlorine in water contains, therefore, in addition to free chlorine, hydrochloric and hypochlorous acids, which contain, in terms of the valence theory respectively, univalent negative and univalent positive chlorine. It is known that liquid ammonia reacts with the halogens in the same manner that water does, although more energetically. Chlorine and bromine, for instance, readily react with liquid ammonia, even at —40°, to form ammonium chloride or bromide and nitrogen gas in the same manner that fluorine reacts with water to give hydrofluoric acid and ozonized oxygen.[2] Iodine is very

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[1] National Research Fellow.

[2] There is evidence for the formation during these reactions of the very unstable chloro- and bromo-amines, the hypochlorous and hypobromous acids of the ammonia system (Franklin, unpublished work).