The Dilation Contribution to the Heat Capacity of Copper and α-Brass

at Elevated Temperatures[1]

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For pure copper and an α-brass containing 9.7 atom % Zn, the compressibilities were measured from 77 to 800°K. and the heat contents of the brass, from 298 to 800°K. From these and other data found in the literature, the dilation term $C_p - C_v$ of the heat capacity was calculated. The Nernst–Lindemann approximate formula was found to express accurately the dependence of the dilation term on temperature for these two substances. However, data found in the literature for eight other substances indicate the Nernst–Lindemann approximation more usually gives too rapid an increase of the dilation term with temperature.

Introduction

Heat capacities of solids and liquids are always measured at constant pressure, C_p, while theoretical treatments apply to C_v, the heat capacity at constant volume. The difference, $C_p - C_v$, is called the dilation contribution. At the molal volume, V, and temperature, T, the dilation can be shown to equal

$$C_p - C_v = \alpha^2 V T / \varkappa_T \tag{1}$$

where α is the volume coefficient of thermal expansion and $\varkappa_T$ is the isothermal compressibility.

While the other terms are relatively well known, data on compressibilities are few except for the elements at room temperature and below. In the present work the compressibilities of copper and of an α-brass with 9.7 atom % zinc were measured from 77 to 800°K. with an ultrasonic pulse-echo technique. The method failed at higher zinc concentrations because of increased attenuation of the echoes.

Experimental Section

The copper specimen was machined to a cylinder 1.6 cm. in diameter and 1.27 cm. long from a cold-rolled OFHC grade ingot. Spectroscopic analysis showed impurities as Ag, 0.003, and Ni, 0.003 wt. %. The brass specimen in the form of a 1.9-cm. rod was kindly supplied by the Bridgeport Brass Co., from which a specimen 1.27 cm. long was machined. Their analysis showed Cu, 90.05, Zn, 9.93, Bi, 0.001, Fe, 0.005, Ni, 0.01, Pb, 0.003, and Sn, 0.00 wt. %.

The faces of the specimens were ground and polished parallel within 0.0005 cm. After annealing, the average grain sizes for the copper and brass were 0.015 and 0.025 mm., respectively. X-Ray diffraction showed sharp back-reflection lines and respective lattice constants of 3.6152 and 3.6355 Å., in good agreement with Pearson[2] for copper and 9.7 atom % zinc.

Ultrasonic Velocity Measurement. A Sperry ultrasonic attenuation comparator, Style 56A001, was used. Waves and their echoes were displayed on an oscilloscope from which the time of travel and the velocity could be measured. Longitudinal and transverse velocities were separately measured, using 10Mc X-cut and Y-cut quartz crystals. The adiabatic compressibility is

$$\varkappa_S = \frac{1}{\rho(V_1{}^2 - {}^4/_3 V_t{}^2)} \tag{2}$$

(where ρ is the density, V_1 is the longitudinal velocity, and V_t is the transverse velocity) from which the isothermal compressibility can be calculated.

$$\varkappa_T = \varkappa_S + \alpha^2 T V / C_p \tag{3}$$

The principal experimental difficulty was firmly

(1) Much of this material in this publication has been abstracted from the Ph.D. Thesis of Y. A. Chang, University of California, 1963.

(2) W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, Inc., New York, N. Y., 1958.

binding the quartz transducer to the specimen at elevated temperatures. At low temperatures Fisher nonaqueous stopcock grease served very well, but a number of bonding materials failed at elevated temperatures, including Sauereisen cement P-31, Biggs epoxy resin R-385, and a mixture of Na_2SiF_6 + $BaSO_4$ + Na_2SiO_4. Dr. Harold Chen of the Shell Development Co. kindly supplied the formula which proved to be the best of those tested. The bonding material was an epoxy resin formed by mixing Epon 1031 and nadic methyl anhydride, catalyzed by benzene-dimethylamine added at about 50°. This bond was excellent to 500°K., above which the echo intensity dropped sharply. However, it was usable to 800°K. The bond broke during cooling of the specimens leaving some black powder, probably carbon from decomposition of the resin.

The experimental arrangement is shown in Figure 1. Elevated temperatures were attained by means of a glass heating tape wrapped around the Pyrex tube; low temperatures, by immersing it in liquid nitrogen.

Results and Discussion

Ultrasonic Velocity and Compressibility. The measured longitudinal and transverse velocities are shown in Figure 2. The scatter of data is less than the stated accuracy (±1%) of the Sperry instrument. This corresponds to a somewhat larger (±3%) scatter in the compressibilities calculated from them. Calculations were made using thermal expansion data from the literature.[3-5]

It can be seen in Table I that compressibilities increase with temperature and with zinc content. Measurements with higher zinc alloys also showed qualitatively that compressibility increased with zinc content.

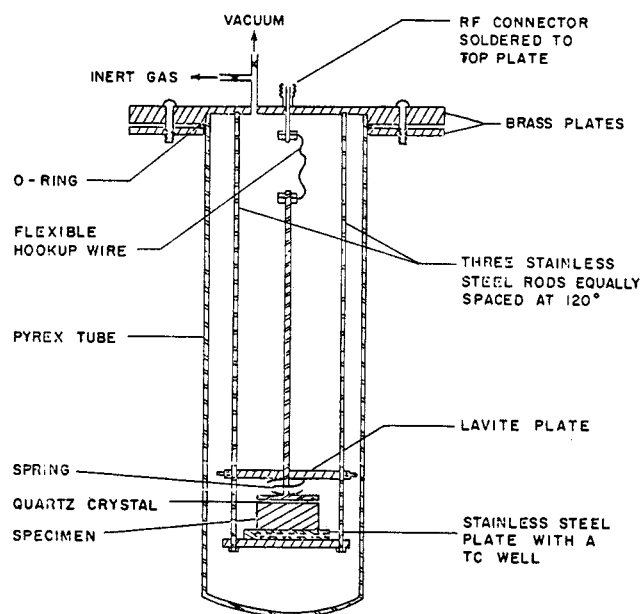*Heat Content.* Because the high-temperature heat capacities of brass measured by Kussmann and Wollen-
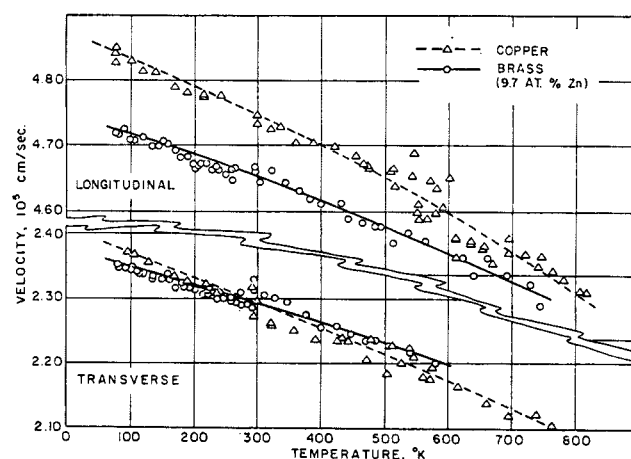

Figure 1. Apparatus.

Figure 2. Sonic velocities.

berger[6] disagreed with low-temperature values of Huffstutler[7] by about 0.45 cal./g.-atom deg. at room temperature, it was decided to repeat the work and extend it to higher temperatures by heat content measurements in a diphenyl ether drop calorimeter described

Table I: Measured Compressibilities

| | Compressibility, cm.²/dyne × 10¹² | | | |
| | χs | | χτ | |
T, °K.	Copper	Brass, $x_{Zn} = 0.097$	Copper	Brass, $x_{Zn} = 0.097$
77	6.96	7.53	7.00	7.56
100	6.99	7.55	7.03	7.59
200	7.09	7.65	7.21	7.79
298.15	7.20	7.77	7.42	8.00
400	7.32	7.89	7.63	8.23
500	7.48	8.04	7.88	8.48
600	7.67	8.20	8.18	8.76
700	7.87	8.37	8.50	9.07
800	8.10	8.86		

(3) (a) F. C. Nix and D. MacNair, *Phys. Rev.*, **60**, 597 (1941); **61**, 74 (1942); (b) P. Hidnert, National Bureau of Standards Scientific Paper 410, Vol. 17, U. S. Government Printing Office, Washington, D. C., 1922, p. 91.

(4) P. D. Merica and L. W. Schad, *Bull. Bur. Std.*, **14**, 571 (1919).

(5) H. W. Altman, T. Rubin, and H. L. Johnston, Report TR-264-28, Cryogenic Laboratory, Ohio State University, ASTIA Document AD-31268, 1954.

(6) A. Kussmann and H. Wollenberger, *Z. Metallk.*, **50**, 94 (1959).

(7) M. C. Huffstutler, Ph.D. Thesis, University of California, Berkeley, Calif., 1961.

elsewhere.[8,9] Results are shown in Table II. Derived C_p values are shown in Table III. They extrapolate to $C_p = 5.84$ at 298.15°K., agreeing with Huffstutler's determination. For copper, C_p values were taken from the literature.[10]

Table II: Experimental Heat Contents of α-Brass (cal./g.-atom deg.)

T, °K.	$H_T - H_{298}$	T, °K.	$H_T - H_{298}$	T, °K.	$H_T - H_{298}$
373.8	441	637.9	2079	656.5	2237
404.0	636	699.5	2481	606.5	1872
451.9	915	752.1	2704	551.9	1551
497.0	1203	806.3	3189	488.8	1156
564.9	1626	808.0	3130	447.2	897
611.2	1900	756.2	2847	405.8	636
611.6	1922	697.1	2441	345.2	282

Table III: Heat Capacities (cal./g.-atom deg.) and Dilation Term

T, °K.	Copper C_p	$C_p - C_v$	$10^5 A$	α-Brass C_p	$C_p - C_v$	$10^5 A$
77	2.98	0.02	2.21	3.05	0.01	1.58
100	3.84	0.02	1.68	3.95	0.03	1.68
200	5.41	0.10	1.68	5.42	0.10	1.68
298.15	5.84	0.17	1.68	5.84	0.17	1.68
400	6.04	0.24	1.68	6.06	0.25	1.68
500	6.19	0.32	1.68	6.21	0.32	1.68
600	6.34	0.40	1.64	6.33	0.40	1.68
700	6.48	0.48	1.64	6.42	0.49	1.72
800	6.62	0.57	1.63			

Dilation Contribution. Values of the dilation contribution (Table III) were calculated from eq. 1, using measured values of the compressibility (Table I) and other quantities from the literature.[2-5]

The resulting dilation terms were used to test the validity of the Nernst–Lindemann semiempirical equation. This equation, derived with the aid of certain considerations of Gruneisen, has been frequently used to estimate the dependence on T of $C_p - C_v$ at elevated temperatures, though it has been inadequately tested above room temperature. According to the Nernst–Lindemann equation

$$C_p - C_v = AC_p^2 T \qquad (4)$$

where A $(= \alpha^2 V/C_p^2 \varkappa_T)$ is assumed constant with temperature. As can be seen in Table III, A is satisfactorily constant except at 77°K. for both copper and α-brass.

The applicability of the Nernst–Lindemann equation

was tested for five additional metals and three non-metallic substances for which sufficient data were found in the literature (see Table IV). For each of these a constant, A, was chosen which fitted the data exactly at 300°K. For a rather high temperature in each case, the experimental $C_p - C_v$ was compared with the calculated value as shown in Table IV. Evidently, the equation tends to overestimate the dilational con-

Table IV: Dilatation Heat Capacities

Substance	Temp., °K.	Data source	$C_p - C_v$, cal./g.-atom deg. Exptl.	Calcd.	Dev., %
Cu	800		0.57	0.59	+ 3.5
Brass, 9.7 atom % Zn	750		0.53	0.52	− 1.9
Zn	650	a–d	0.72	0.86	+19.4
In	400	a, e, f	0.75	0.79	+ 5.3
Al	800	a, b, g, h	0.90	1.15	+27.8
Pb	600	a, e, g	0.87	1.22	+40.2
Sn	500	a, e, i	0.53	0.62	+17.0
KCl	1000	j–o	1.34	1.44	+ 7.5
NaCl	700	l, o–r	0.92	1.03	+12.0
MgO	1400	l, o, s, t	0.49	0.59	+20.4

^{a} See ref. 2. ^{b} See ref. 10. ^{c} G. A. Alers and J. R. Neighbours, *J. Phys. Chem. Solids*, **7**, 58 (1958). ^{d} E. Gruneisen and E. Goens, *Z. Physik*, **29**, 141 (1924); E. A. Owen and E. L. Yates, *Phil. Mag.*, **17**, 113 (1934). ^{e} A. I. Kaznoff, Ph.D. Thesis, University of California, Berkeley, Calif., 1961. ^{f} J. Graham, A. Moore, and G. V. Raynor, *J. Inst. Metals*, **84**, 86 (1955). ^{g} See ref. 4. ^{h} P. M. Sutton, *Phys. Rev.*, **91**, 816 (1953). ^{i} H. D. Erfling, *Ann. Physik*, **34**, 136 (1939); B. G. Childs and S. Weintroub, *Proc. Phys. Soc.* (London), **B63**, 267 (1950). ^{j} M. H. Norwood and C. V. Briscoe, *Phys. Rev.*, **112**, 45 (1958). ^{k} F. D. Enck, *ibid.*, **119**, 1873 (1960). ^{l} K. K. Kelley and E. G. King, U. S. Bureau of Mines Bulletin No. 592, U. S. Government Printing Office, Washington, D. C., 1961. ^{m} F. D. Enck, D. G. Engle, and K. I. Marks, *J. Appl. Phys.*, **33**, 2070 (1962). ^{n} K. E. Salimaki, *Ann. Acad. Sci. Fennicae*, *Ser. A VII*, **56**, 40 (1960). ^{o} C. O. Hodgman, "Handbook of Chemistry and Physics," 36th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1956. ^{p} W. C. Overton, Jr., and R. T. Swin, *Phys. Rev.*, **84**, 758 (1951). ^{q} A. Eucken and W. Dannohl, *Z. Elektrochem.*, **40**, 814 (1934). ^{r} L. Hunter and S. Siegel, *Phys. Rev.*, **61**, 84 (1942). ^{s} C. Susse, *J. Rech. Centre Natl. Rech. Sci. Lab. Bellevue* (Paris), **54**, 23 (1961). ^{t} M. Durand, *Physics*, **7**, 297 (1936).

(8) R. Hultgren, P. Newcombe, R. L. Orr, and L. Warner, National Physical Laboratory Symposium No. 9, Paper 1H, HMSO, London, 1959.

(9) W. Kendall, R. L. Orr, and R. Hultgren, *J. Chem. Eng. Data*, **7**, 516 (1962).

(10) R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963.

tribution; copper and brass are the most favorable of all the substances. However, in spite of the considerable overestimate, the magnitude of the error seldom exceeds 0.2 cal./deg. g.-atom and is usually of the order of 0.1.

The experimental values of the heat capacity of copper and brass were satisfactorily accounted for at all temperatures as the sum of a lattice vibrational (Debye) term, C_D, the dilation term, and an electronic contribution term, C_{el}.

$$C_p = C_D + (C_p - C_v) + C_{el} \qquad (5)$$

In these calculations C_D was taken from an assumed Debye temperature for copper and brass of 315 and 308°K., respectively. Electronic heat capacities were assumed to be $1.64 \times 10^{-4} T$ for copper[10] and $1.78 \times 10^{-4} T$ for brass.[11]

(11) J. Rayne, *Phys. Rev.*, **108**, 22 (1957).