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## High Temperature Heat Contents of Three Alpha Brass Alloys

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High temperature heat contents of three alpha brass alloys containing 19.8, 29.1, and 34.2 atom % zinc were measured from 300° to 810° K., using a diphenyl ether drop calorimeter. The results show that  $C_p$  measurements of Kussmann and Wollenberger are much too high but do not contradict the small anomalies they found. Tables of heat capacities and heat contents were prepared which show anomalies of approximately the same size, agree with the present heat contents, and extrapolate to the low-temperature values.

DATA on heat contents above room temperature of alpha brass alloys are contradictory.  $C_p$  measurements of Kussmann and Wollenberger (6) show small, well-defined anomalies near 500° K. which they interpret as being due to disordering processes. However, their values are too high to join smoothly with Huffstutler's (2) low-temperature measurements, and integration of their  $C_p$  values gives heat contents higher than those determined by Ruer and Kremers (7). In each case, the discrepancy is large—approximately 8%. Measurements of an alpha brass containing 9.7 atomic % zinc by the present authors (1) agreed with Huffstutler and disagreed with Kussmann and Wollenberger. It was decided to extend the measurements to higher zinc alpha brasses.

### EXPERIMENTAL

Chemical analyses of the three alpha brass samples are shown in Table I. Metallographic examination showed the

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presence of a single well-annealed alpha phase.

Heat contents (300° to 800° K.) above room temperature were determined in a diphenyl ether drop calorimeter described elsewhere (3, 5). Samples consisting of single pieces weighing about 0.7 gram were wrapped in platinum foil so that the heat loss during the drop would be uniform and correctible. Heat given off during cooling in the calorimeter melted some of the diphenyl ether at its melting point, 300° K. The amount melted was determined by the expan-

Table I. Chemical Analyses of Alpha Brass Alloys, Wt. %

	Alloy No.		
	1	2	3
Cu	79.75	70.42	65.18
Sn	0.00	0.045	0.000
Pb	0.003	0.05	0.001
Fe	0.015	0.02	0.002
Ni	0.01	0.02	0.002
Bi	...	0.000	0.000
Zn	20.22	29.445	34.815

Table II. Experimental Results, Cal. per Gram-Atom

$x_{Zn} = 0.198$		$x_{Zn} = 0.291$		$x_{Zn} = 0.342$	
$T, ^\circ K.$	$H^\circ_T - H^\circ_{298.15}$	$T, ^\circ K.$	$H^\circ_T - H^\circ_{298.15}$	$T, ^\circ K.$	$H^\circ_T - H^\circ_{298.15}$
373.8	438	373.9	450	373.8	450
403.7	638	403.9	646	403.4	635
451.4	928	403.7	625	403.9	635
498.3	1226	451.4	942	451.0	929
565.0	1644	...	...	496.4	1175
611.4	1931	564.9	1647	498.0	1220
637.5	2117	564.8	1663	565.0	1658
699.4	2525	611.4	1964	611.0	1977
752.6	2874	637.9	2142	638.1	2137
806.0	3243	699.3	2540	699.6	2559
807.3	3222	752.1	2909	752.5	2903
756.0	2912	805.7	3248	806.5	3302
697.1	2529	808.3	3296	807.4	3322
656.3	2235	755.6	2898	755.7	2933
606.7	1886	697.6	2544	697.4	2517
552.0	1577	656.1	2220	655.3	2281
488.9	1166	606.8	1937	606.3	1931
446.7	897	552.2	1571	...	...
405.7	639	488.8	1160	488.8	1169
345.3	276	447.0	899	447.3	898
...	...	405.8	643	405.7	643
...	...	...	...	344.9	275

sion which was measured from mercury displaced into a capillary tube. Each gram of mercury displaced represents 18.91 calories (4). The performance of the calorimeter was checked frequently by dropping a solid platinum capsule (5).

The experimental results are given in Table II. The heat contents are approximately 3% higher than results reported by Ruer and Kremers (7) and are much lower than the integrated  $C_p$  values measured by Kussmann and Wollenberger (6).

#### DISCUSSION

Manifestly, the results of Kussmann and Wollenberger are too high. No doubt there was a systematic error in their differential calorimeter. However, there seems to be no reason to doubt the validity of the anomalies found by them. The latent heat of their anomalies amount only to approximately 30 calories per gram-atom for each composition. There are indications of such anomalies in the heat content data but the effect is not so large. It is likely that in a drop calorimeter the alloys dropped from a disordered state would not become fully ordered during cooling, so that the high temperature measured heat contents would be low by perhaps 10 calories per gram-atom. The effect in this case can hardly be greater than the

Table III. Thermal Properties of Alpha Brass Alloys

$T, ^\circ K.$	$x_{Zn} = 0.198$		$x_{Zn} = 0.291$		$x_{Zn} = 0.342$	
	$H_T - H^\circ_{298.1}$	$C_p^b$	$H_T - H^\circ_{298.1}$	$C_p^b$	$H_T - H^\circ_{298.1}$	$C_p^b$
298.15	0	5.80	0	5.80	0	5.81
400	602	6.01	603	6.04	603	6.04
450	908	6.21	909	6.18	910	6.26
483	...	...	...	...	1129	6.98
500	1224	6.48	1233	7.14	1246	6.74
513	1310	6.70	...	...	...	...
550	1553	6.43	1568	6.43	1570	6.43
600	1873	6.42	1890	6.48	1893	6.52
700	2526	6.64	2549	6.70	2559	6.80
800	3195	6.75	3225	6.82	3249	7.00

<sup>a</sup>Calories per gram-atom. <sup>b</sup>Calories per degree per gram-atom.

precision of the measurement, which amounts to  $\pm 15$  calories per gram-atom.

The following procedure was adopted in obtaining the smoothed values of Table III. Heat capacity *vs.* temperature curves were drawn with values lower than those of Kussmann and Wollenberger, but having anomalies of the same shape. Integrated heat contents derived from these curves agreed with heat contents obtained more directly with deviations never more than 10 calories per gram-atom.

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