

## HEAT CAPACITY OF LIQUID ALLOYS

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### Introduction

Of all the thermodynamic properties of liquid alloys heat capacity has been by far the most neglected quantity, and even for pure liquid metals accurate data are known only for a relatively small number of low melting elements. Since it has been recognized some time ago (1) that valuable information as to the atomic arrangements is contained in the heat capacities of liquid alloys, a review of the present state might be appropriate to stimulate interest.

### Liquid metals

The values of  $C_p$  for most liquid main group metals including Cu, Ag, Au and Zn, Cd, Hg near the melting point cluster around  $30 \text{ J K}^{-1} \text{ mol}^{-1}$ , i.e. close to  $3R$  for the vibrational contribution to the heat capacity of the solid plus the dilatation contribution  $C_d = C_p - C_v = \alpha^2 VT / \kappa_T$  where  $\alpha$  is the coefficient of thermal expansion and  $\kappa_T$  the isothermal compressibility (2). Any deviations are considered to be caused either by the anharmonicity of atomic vibrations or by electronic contributions. Especially for the high melting transition metals Margrave (3) has pointed out that deviations are mostly due to the electronic terms, and that the actual density of states at high temperatures should be taken into account and not the low temperature term  $C_{el} = \gamma T$ . Accurate data of some low melting metals show that  $C_p$  in the liquid state first decreases with increasing temperature, passes through a minimum, and then increases again. At very high temperatures (2000-5000 K)  $C_p$  of liquid transition metals may reach values of 8 to 10 R (4). Chapman (2) has developed a general theory for the heat capacity of monoatomic fluids, based on the radial distribution function. By applying the corresponding states principle he could show that  $C_v$  of the liquid metals investigated (Na, K, Hg, In, Sn, Pb) was a universal function of only two dimensionless parameters and decreased steadily with increasing temperature. The upturn in  $C_p$  is therefore caused by the dilatation term. With reasonable assumptions for the distance and energy parameters Chapman obtained a single curve for the reduced configurational heat capacity and concluded that the configurational heat capacities of these liquid metals obey a corresponding states law and that the decrease of  $C_v$  with temperature can be explained by the effect of temperature on the liquid structure. According to Kincaid and Byring (5) the decrease is caused by a gradual destruction of vibrational contributions as the liquid approaches increasingly a monoatomic gas. Close to the critical temperature  $C_v - C_{el}$  for Na, K, and Hg approaches  $2R$  which is explained by the gradual loss of excitations corresponding to the two shear modes (6). Hoch and Vernardakis (7) showed that the heat capacities of liquid Li, K, Na, Pb and Hg can be expressed as  $C_p = 3RF(\Theta_D/T) + gT + hT^{-2}$  where  $F(\Theta_D/T)$  is the Debye function,  $g$  the electronic heat capacity term, and  $h$  the anharmonic term which according to Faber (8) may be due to some crystallites or complexes in the liquid. The vibration of the atoms in the complexes would be quite anharmonic but with increasing temperature complexes and therefore anharmonicity of the liquid would disappear, and when the temperature is high enough

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a gas-like liquid would result. However, other thermophysical properties did not support the existence of clusters in these liquid metals (7).

Not all liquid metals obey Chapman's relationship (2) as was demonstrated for liquid Ga (9) and liquid Te (10). An application of the hard-sphere model to  $C_p$  of liquid Ga (9) also showed that it cannot be fully accounted for in terms of the simple hard-sphere approximations. In the case of liquid Te  $C_p$  decreases from  $49.32 \text{ J K}^{-1} \text{ mol}^{-1}$  at 740 K to  $33.47 \text{ J K}^{-1} \text{ mol}^{-1}$  at 1073 K. This behaviour was explained by an equilibrium between semiconducting and metallic regions in the liquid shifting towards the metallic state with increasing temperature using the effective medium percolation theory by Cohen and Jortner (11-13). The heat capacity of liquid Se on the other hand is  $35.95 \text{ J K}^{-1} \text{ mol}^{-1}$  at the melting point (494.33 K), passes through a shallow minimum at 780 K ( $33.28 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and increases to  $35.62 \text{ J K}^{-1} \text{ mol}^{-1}$  at 1000 K (14).

### Liquid alloys

The heat capacity of liquid alloys will generally also decrease with increasing temperature but in most cases data are lacking and a constant temperature-independent value calculated from the Neumann-Kopp rule of additivity is assumed. One of the early direct measurements of  $C_p$  of a liquid alloy was that of Orr et al. (15) of an In-Sn alloy. They observed a marked decrease of  $C_p$  with increasing temperature which according to them could be interpreted as resulting from two possible causes: 1) a decrease in interactions of non-random associations between unlike atoms resulting in  $\Delta C_p$  positive; 2) changes in structure or in the vibrational and translational energy distributions such as those postulated for pure metals giving  $\Delta C_p = 0$  as was observed for the liquid In-Sn alloy (15). Therefore the quantity directly indicative of interactions or associations in a liquid alloy will be  $\Delta C_p$  and not  $C_p$ , and one would expect  $\Delta C_p$  either to be nearly zero or positive. This is indeed observed in most binary alloys. Only in a few systems with a positive enthalpy of mixing and a strongly positive excess entropy of mixing (Cd-Sn, Sn-Zn) Kleppa (16) found  $\Delta C_p$  negative, and a correlation between  $\Delta S^{M,XS}$  and  $\Delta C_p$ , and  $\Delta S^{M,XS}$  and the volume expansion on mixing ( $\Delta S_{vol} = \Delta V\alpha/\kappa_T$ ). Chen and Turnbull (17) found a positive  $\Delta C_p$  decreasing with temperature for a liquid Au-Si alloy near the eutectic composition. As an explanation they suggested three possible causes: 1) a change in the vibrational spectrum due to a change in the type of bonding during melting; 2) a decrease in non-random association between unlike atoms with increasing temperature; 3) changes in configurational entropy from the multiplicity of atomic positioning. They concluded that the change in structural configurational entropy with temperature makes a major contribution to  $\Delta C_p$ .

In 1967 Hultgren and Orr (1) remarked that the only direct  $C_p$  measurements for liquid alloys known to them were on one alloy each in the Bi-In and In-Sn system. Even today direct  $C_p$  measurements especially for an entire binary system are very scarce, and most information albeit sometimes of questionable reliability has to be drawn indirectly from  $\Delta H^M$  measurements.

A search of the literature has resulted in 78 binary alloy systems for which some information about  $\Delta C_p$  is known. These systems are listed in Table 1 together with  $\Delta C_p$ , the temperature range, and the enthalpy of mixing,  $\Delta H^M$ . Appended to Table 1 are the references to the systems listed in the table. Most of the systems are binaries between main group elements including elements of Group IB and IIB of the PSE. The reason is purely experimental: due to lower liquidus temperatures they are more easily accessible. Only seven systems have another transition element as component (Ce-Cu, Cu-Te, Cu-Ti, Ge-Pt, Pd-Si, Pd-Sn, Ni-Sn) of which two systems have two transition elements as components (Ce-Cu, Cu-Ti). Of the 79 systems 62 have a positive  $\Delta C_p$ , 13  $\Delta C_p = 0$ , and four a negative  $\Delta C_p$ . All but two (Bi-Ga, Ga-Hg) of the 62 systems with positive  $\Delta C_p$  have (at least over a limited concentration range) a negative enthalpy of mixing. For Bi-Ga  $\Delta C_p$  is very small and was obtained indirectly from the temperature dependence of  $\Delta H^M$ . In Ga-Hg  $C_p$  was measured directly and very precisely by a pulse modulation technique for the critical composition just above the liquid miscibility gap;  $\Delta C_p$  could not be calculated since the heat capacity of alloy plus container was measured but from the plot of  $C_p$  vs. temperature it is clear that  $\Delta C_p$  is positive at the critical temperature decreasing to zero about 5 K

Table 1. Relative Heat Capacity and Enthalpy of Mixing of Liquid Alloys

System	$\Delta C_p(T; x_1)$ (J K <sup>-1</sup> mol <sup>-1</sup> )	T-range (K)	Ref.	$\Delta H^M(T; x_1)$ (J mol <sup>-1</sup> )	Ref.	Remarks
Ag-Al	22.5 <sup>*</sup> (1100; 0.7)	1073-1123	1)	-8700 <sup>*</sup> (1073; 0.7)	2)	$\Delta C_p$ indir., const.; $\Delta H^M$ pos. & neg., by two different groups.
Ag-Ga	3.84(900; 0.55)	773-1028	2)	-4810 <sup>*</sup> (1028; 0.75)	2)	$\Delta C_p$ indir., const.; $\Delta H^M$ pos & neg.
Ag-Ge	25.80(930; 0.74)	930-1200	3)	-795 <sup>*</sup> (1280; 0.90)	4)	$C_p$ direct, for one comp.; $\Delta C_p$ decr. with T; $\Delta C_p = -0.6$ (1000 K); $\Delta H^M$ pos. & neg.
Ag-In	1.17(1000; 0.3)	743-1280	5)	-4800 <sup>*</sup> (1280; 0.60)	5)	$\Delta C_p$ indir., const.
Ag-Sb	11.1 <sup>*</sup> (1100; 0.8)	950-1300	4)	-7950 <sup>*</sup> (950; 0.8)	4)	$\Delta C_p$ indir., const., $\Delta H^M$ pos. & neg.
Ag-Sn	pos.	-	4)	-3210 <sup>*</sup> (1280; 0.8)	4)	$\Delta C_p$ indir.; $\Delta H^M$ pos. & neg.
Ag-Te	0	1165-1378	6)	-20750 <sup>*</sup> (1165; 0.667)	6)	$\Delta H^M$ const.
Al-Bi	0	940-1077	7)	+4200 <sup>*</sup> (1077; 0.5)	7)	$\Delta H^M$ const., misc. gap, $\Delta H^M$ max. interpolated.
Al-Ca	50(973; 0.67) 21(1000; 0.92)	953-1038	8) 9)	-39230 <sup>*</sup> (1038; 0.67)	9)	$\Delta C_p \approx 20$ (1200; 0.80) indir. $\Delta C_p$ indir., const.; $\Delta H^M$ for Al(1) + Ca(s) + Al <sub>2</sub> Ca(s)
Al-Cu	4.28(1200; 0.5)	1073-1423	2)	-19150 <sup>*</sup> (1073; 0.45)	2)	$\Delta C_p$ indir., const.; $\Delta H^M$ by two different groups.
Al-Ga	0	952-1235	10)	+660 <sup>*</sup> (952; 0.50)	10)	$\Delta H^M$ const.
Al-Te	pos.	1000-1188	11)	-64000 <sup>*</sup> (1188; 0.40)	12)	$\Delta \bar{C}_p(\text{Te}) = 63 \pm 10$ , indir.
As-Cd	45.6 <sup>*</sup> (1000; 0.45)	983-1013	13)	-7020 <sup>*</sup> (983; 0.45)	13)	$\Delta C_p$ indir., pos. and neg.; $\Delta H^M$ pos. & neg.
As-Sn	pos.	870-1100	14)	-	-	$C_p$ by drop cal.; $C_p$ first decr., then incr. with T.
Au-Cd	pos.	773-873	15)	-17200 <sup>*</sup> (1000; 0.5)	16)	$\Delta \bar{C}_p(\text{Cd})$ indir., pos., 10.2(825; 0.30)
Au-Cs	10.26 <sup>*</sup> (1040; 0.5)	900-1180	17)	-41510 <sup>*</sup> (900; 0.5)	17)	$\Delta C_p$ indir., const.

System	$\Delta C_p(T; x_i)$ ( $J K^{-1} mol^{-1}$ )	T-range (K)	Ref.	$\Delta H^M(T; x_i)$ ( $J mol^{-1}$ )	Ref.	Remarks
Au-Ga	11.71 <sup>*</sup> (925; >0.8)	823-1028	2)	-18200 <sup>*</sup> (830; 0.60)	18)	$\Delta C_p$ indir., const., second max 8.05 (925; 0.55)
Au-Ge	8.85 <sup>*</sup> (800; 0.33)	765-873	19)	-		$C_p$ dir., const., $\Delta C_p = 7.00$ (800; 0.5)
Au-Ge	4.0(630; 0.72)	630-990	20)	-5900 <sup>*</sup> (1223; 0.65)	2)	$C_p$ dir., for one comp.; $\Delta C_p$ decr. with T
Au-In	4.93 <sup>*</sup> (900; 0.55)	823-1028	2)	-18625 <sup>*</sup> (823; 0.60)	2)	$\Delta C_p$ indir., const.
Au-In	8.67 <sup>*</sup> (800; 0.60)	720-1300	21)	-17880 <sup>*</sup> (823; 0.55)	22)	$\Delta C_p$ indir., decr. with T; second max. (800; $\geq 0.8$ )
Au-Pb	7.90(850; 0.33)	817-873	19)	-		$C_p$ dir., const.; $\Delta C_p = 6.27$ (830; 0.5)
Au-Pb	6.07 <sup>*</sup> (800; 0.45)	800-920	87)	-		$C_p$ by DSC, sec. max. (800; >0.7) $\Delta C_p$ decr. with T.
Au-Pb	3.85 <sup>*</sup> (875; 0.55)	823-923	2)	-2000 <sup>*</sup> (823; 0.60)	2)	$\Delta C_p$ indir., const.; $\Delta H^M$ possibly neg & pos.(22)
Au-Sb	5.49(800; 0.33)	733-873	19)	-3200 <sup>*</sup> (923; 0.75)	2)	$C_p$ dir. const.
Au-Si	18.8(625; 0.80 <sub>5</sub> )	625-1350	23)	-		$C_p$ by drop cal. for one comp.; $\Delta C_p$ decr. with T to -5.6 (1350 K)
Au-Si	5.7 <sup>*</sup> (1000; 0.50)	1373-2000	24)	-7620 <sup>*</sup> (1373; 0.70)	24)	$\Delta C_p$ indir., const.; calorimetry at 1373 K; $\Delta C_p$ mass spectrometry 1550-2000 K.
Au-Sn	8.97(563; 0.814)	563-800	25)	-		$C_p$ by DSC, $\Delta C_p$ decr. with T to 7.82 (636K)
Au-Sn	8.75 <sup>*</sup> (700; 0.50)	700-1500	26)	-12620 <sup>*</sup> (707; 0.55)	26)	$\Delta C_p$ indir., second max. >9.16 (700; $\geq 0.80$ ) $\Delta C_p$ decr. with T to -2.87 (1500; $\geq 0.5$ )
Au-Sn	pos., then neg.	1100-1873	27)	-15400 <sup>*</sup> (1873; 0.5)	27)	$\Delta C_p$ first pos. (up to 1100 K) then neg. (up to 1873 K), by comp. with literat.
Au-Sn	6.12(780; 0.50)	691-873	19)	-		$C_p$ dir. const.
Au-Sn	5.5 <sup>*</sup> (700; 0.50)	700-900	28)	-		$C_p$ by DSC, second max. (700; $\geq 0.80$ ); $\Delta C_p$ decr. with T
Au-Sn	7.45 <sup>*</sup> (698; 0.50)	573-723	29)	-12320 <sup>*</sup> (723; 0.5)	29)	$\Delta C_p$ indir., const., second max (698; $\geq 0.8$ )
Au-Sn	5.5 <sup>*</sup> (1070; 0.35)	950-1250	30)	-11060 <sup>*</sup> (973; 0.5)	30)	$\Delta C_p$ indir. const.

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System	$\Delta C_p$ (T; $x_i$ ) (J K <sup>-1</sup> mol <sup>-1</sup> )	T-range (K)	Ref.	$\Delta H^M$ (T; $x_i$ ) (J mol <sup>-1</sup> )	Ref.	Remarks
Au-Te	0.55(800; 0.33)	737-873	19)		89)	$C_p$ dir., const.
	$\approx 0$	700-1000	88)	-500*(1000; 0.3)	88)	$\Delta H^M$ neg. & pos.
	2.10(737; 0.33)	737-1200	89)	-1070*(737; 0.45)	89)	$\Delta C_p$ indir., decr. with T; $\Delta H^M$ neg. & pos.
Au-Tl	0	823-923	2)	-1170*(823; 0.65)	2)	$\Delta H^M$ const.
Ba-Mg	4.5*(1000; 0.3)	-	31)	-8330*(1050; 0.30)	32)	$C_p$ by drop cal.
Bi-Ga	0.56*(700; $\sim 0.5$ )	545-873	33)	+2060*(545; 0.45)	33)	$\Delta C_p$ indir., const.
Bi-In	-0.5(600; 0.5)	383-750	34)	-1840*(900; 0.4)	16)	$C_p$ direct for one comp., const.; with $C_p$ for In(L) by Grönvold(90) $\Delta C_p = 0$ or slightly pos.
Bi-Pb	0	623-723	35)	-1100*(623; 0.52)	35)	$\Delta H^M$ const.
Bi-Se	pos.(1000; 0.4)	1000-1100	36)	-22450*(998; 0.40)	37)	$C_p$ by drop cal. for one comp., sharp decr. of $C_p$ within 20 K above liq.; $\Delta H^M$ const. or very slight f(T)
Bi-Te	pos.(?) (860. 0.4)	860-923	38)	-10000*(877; 0.46)	39)	$C_p$ by const. T-gradient cal. for one comp., sharp decr. of $C_p$ within 30 K above liq.
Ca-Mg	4.8*(1100; 0.5)	-	31)	-6280*(1150; 0.46)	40)	$C_p$ by drop cal.
Cd-In	neg.	623-723	41, 42)	+1486*(623; 0.48)	42)	$\Delta H^M$ a slight f(T), decr. with T (41, 42)
Cd-Pb	0	623-723	35)	+2648*(623; 0.50)	35)	$\Delta H^M$ const.
Cd-Sb	4.78*(693; 0.57)	693-903	43)			$C_p$ dir. by const. T-gradient cal.; $\Delta C_p$ decr. with T, $\Delta C_p \approx 0$ at $\sim 833$ K
	2.34*(783; 0.5)	693-773	44)	-2520*(693; 0.55)	44)	$\Delta C_p$ indir., const. with T; $\Delta H^M$ pos & neg.
Cd-Sn	-1.5(675; 0.5)	623-723	35)	+2028*(623; 0.60)	35)	$\Delta C_p$ indir., $\Delta C_p$ const.
Cd-Tl	neg.	623-723	42)	>+2369*(623; >0.60)	42)	$\Delta H^M$ a slight f(T), by two different groups.

System	$\Delta C_p(T; x_i)$ (J K <sup>-1</sup> mol <sup>-1</sup> )	T-range (K)	Ref.	$\Delta H^M(T; x_i)$ (J mol <sup>-1</sup> )	Ref.	Remarks
Ce-Cu	5.0*(1900; 0.33)	1650-2200	45)			C <sub>p</sub> by levitation cal., const.
Cs-K	pos. (?)		46)	+117*(384; 0.4)	16)	$\Delta C_p$ changing with T, min. between 700-900 K.
Cs-Na	pos. (?)		46)	+1000*(384; 0.4)	16)	see Cs-K
	~ 0	380-440	100)	+1096*(383; 0.4)	100)	
Cs-Sb	28.0(1000; 0.75)	1000-1130	47)	-95000*(1000; 0.75)	47)	C <sub>p</sub> by drop cal. from $x_{Cs} = 0.75-1.00$ , linear, const.
Cu-Ga	6.30(1050; 0.55)	988-1107	2)	-12650*(1107; 0.70)	2)	$\Delta C_p$ indir., const.
Cu-In	11.31*(1125; 0.75)	903-1348	48)	-6766*(955; 0.75)	48)	$\Delta C_p$ indir., const.; $\Delta H^M$ pos. & neg.
Cu-Sb	8.9*(1070; 0.75)	960-1190	49)	-6920*(1003; 0.75)	49)	$\Delta C_p$ indir., second max 7.0 (1070 ± 0.5) > 1190 K; $\Delta C_p \approx 0$ ; $\Delta H^M$ pos. & neg.
Cu-Sn	3.76(1250; 0.80)	1123-1423	2)	-5925*(1113; 0.80)	2)	$\Delta C_p$ indir., const., $\Delta H^M$ by two differ. groups; $\Delta H^M$ neg. but tends to be pos. for Sn-rich comp.
	9.2*(1073; 0.75)	-	50)	-		C <sub>p</sub> by adiabatic cal.
Cu-Te	16.54(870; 0.44)	727-1005	91)	-15300(727; 0.44)	91)	$\Delta C_p$ indir., const., standard state Te(l), Cu(s)
Cu-Tl	42.6(700; 0.60)	700-1600	51)	-3731*(1372; 0.50)	52)	$\Delta C_p$ calc., $\Delta C_p = 41.0$ (1600 K)
Ga-Hg	pos. (475; 0.503)	475-483	53)	+1800*(478; 0.55)	54)	C <sub>p</sub> dir. by pulse modulation technique for one comp., $\Delta C_p$ pos. for ~ 5 K above T <sub>c</sub>
Ga-In	0	423-742	55)	+1110*(423; 0.50)	55)	$\Delta H^M$ const.
Ga-Mg	3(972; 0.286)	-	56)	-11500*(972; 0.45)	56)	C <sub>p</sub> by cal. for one comp.
Ga-Te	60*(1120; 0.4)	liqu-1173	101)	-38800*(1200; 0.39)	58) 11) 101)	$\Delta H^M$ const. (1123-1200 K) C <sub>p</sub> direct by adiabatic cal. for 5 comp. $x_{Ga} = 0.30, 0.60, 0.67, C_p$ decr. slightly with T; $x_{Ga} = 0.40, 0.50$ , first incr. with T, then decr.

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System	$\Delta C_p$ ( $T; x_i$ ) ( $J K^{-1} mol^{-1}$ )	T-range (K)	Ref.	$\Delta H^M$ ( $T; x_i$ ) ( $J mol^{-1}$ )	Ref.	Remarks
Ge-Pt	6.3(1300; 0.60)	1273-1352	59)	-52000*(1273; 0.42)	59)	$\Delta C_p$ indir., const.
Ge-Te	19.3(1080; 0.50)	1030-1150	60)	-14800(1028; 0.46)	60)	$\Delta C_p$ indir.
	13.4(990; 0.50)	990-1300	57)	-	57)	$C_p$ by drop cal. for one comp. $\Delta C_p$ decr. with T to 4.1 (1300 K)
	pos.	663-743	61)	-	61)	$C_p$ by DSC for one comp. ( $x_{Te} = 0.15$ ); between 663 and 743 K $C_p$ drops drastic.
Hg-Na	12.85*(633; ~0.70)	-	62)	-17450*(648; 0.60)	16)	$\Delta C_p$ indir., derived
	10.0*(628; ~0.80)	liqu.-673	92)	-	92)	$\Delta C_p$ indir., derived, $\Delta C_p(\min) = -2.5$ ( $x_{Hg} \approx 0.3$ )
Hg-Tl	pos.	288-533	63)	-816*(383; 0.60)	63)	$\Delta C_p$ indir.; $\Delta H^M$ tends to be pos. for Tl-rich comp., $\Delta \bar{C}_p(Tl)$ pos., decr. with T (64)
In-Na	6.44*(750; 0.65)	liqu.-773	93)	-9177*(723; 0.55)	93)	$\Delta C_p$ and $\Delta H^M$ indir. by emf.
In-Sb	2.5(923; 0.50)	-	65)	-3500*(923; 0.55)	65)	$\Delta C_p$ indir.
	4.3*(971; 0.70)	971-1158	66)	-3210*(957; 0.60)	66)	$\Delta C_p$ indir., max. +3.6 (1158; 0.60)
	pos.	-	67)	-	67)	$C_p$ by drop cal. for one comp. ( $x_{In} = 0.5$ ), $C_p$ max. at ~850 K (~50 K above m.p.)
In-Sn	0	394-758	68)	-197*(700; 0.50)	16)	$C_p$ dir. for one comp. ( $x_{In} = 0.528$ ), decr. with T
In-Te	37.2*(1050; 0.40)	737-1340	69)	-36500*(987; 0.45)	69)	$\Delta C_p$ indir., $\Delta C_p = 0$ ( $T < 1000$ K), $\Delta C_p = 37.2(987-1123)$ , $\Delta C_p = 18.20(1123-1340$ K)
	54.5*(1023; 0.40)	948-1123	70)	-34000*(998; 0.40)	71)	$C_p$ direct by adiabatic cal., $\Delta C_p$ first slightly incr. then decr. with T.
K-Na	1.59(305; 0.33)	305-320	72)	+737*(384; 0.60)	16)	$C_p$ direct for one comp. $\Delta C_p$ decr. with T, $\Delta C_p = 1.22(320$ K); see also Cs-K (46)
Li-Mg	8.4*(800; 0.50)	800-900	73)	-3300*(940; 0.50)	94)	$C_p$ by DSC, $\Delta C_p$ const.
Li-Pb	pos. (?)	800-900	74)	-29530*(1000; ~0.75)	75)	indir., $\Delta \bar{C}_p(Li)$ pos.
Mg-Pb	5.0*(1100; ~0.65)	943-1233	76)	-9600*(943; 0.64)	76)	$\Delta C_p$ indir., const.

System	$\Delta C_p(T; x_i)$ (J K <sup>-1</sup> mol <sup>-1</sup> )	T-range (K)	Ref.	$\Delta H^M(T; x_i)$ (J mol <sup>-1</sup> )	Ref. Remarks
Mg-Sn	10.4*(1150; ~0.65)	1073-1213	76)	-14800*(1073; 0.64)	76) $\Delta C_p$ indir., const.
Mg-Sr	4.0*(1000; ~0.70)	-	31)	-5520*(1080; 0.65)	32) $C_p$ by drop cal., $\Delta C_p$ const.
Na-Pb	12.5*(698; 0.76)	698-803	102)	-17900*(698; 0.60)	102) $\Delta C_p$ and $\Delta H^M$ indir. by emf; second max $\Delta C_p$ appears by extrapolation at $x_{Na} = 0.57$ at 648 K; $\Delta C_p$ decr. with T
Na-Sn	4.64*(810; 0.25)	liq. -856	93)	-20737(773; 0.54)	93) $\Delta C_p$ and $\Delta H^M$ indir. by emf; second max $\Delta C_p = 4.24$ ( $x_{Na} = 0.44$ ); $\Delta C_p$ neg ( $x_{Na} < 0.041$ )
Na-Tl	21.0*(873; ~0.5)	liq. -873	95)	-20080(873; 0.55)	95) $\Delta C_p$ and $\Delta H^M$ indir. by emf; second max $\Delta C_p = 12.5$ ( $x_{Na} \sim 0.75$ ); $\Delta C_p$ incr. with T (?)
Ni-Sn	4.2*(673; ~0.50)	593-893	77)	-11700*(753; 0.50)	78) $\Delta C_p$ indir., const.
Pb-Sn	27*(1623; 0.75)	1623-1723	79)	-19500*(1773; 0.60)	16) $\Delta C_p$ indir., $\Delta C_p = 27.0$ (1723; 0.60)
Pd-Si	0	623-723	80)	+1390*(623; 0.50)	80) $\Delta H^M$ const.
Pd-Sn	60(?)*(1600; 0.63)	1380-1838	81)	-87000*(1380; 0.63)	81) $\Delta C_p$ indir., const.; $\Delta H^M$ by two groups; $\Delta H^M = -56000$ (1838; 0.63) (82)
Pd-Sn	pos. (?)	700-800	83)	-74900*(1723; 0.665) 98)	indir., $\Delta C_p^\infty$ (Pd) pos.
S-Tl	~0	631-753	84)	-79400*(753; 0.33)	84) $\Delta H^M$ const.
Sb-Se	pos. (900; 0.40)	900-1100	36)	-29400*(935; 0.40)	37) $C_p$ by drop cal. for one comp., sharp decr. of $C_p$ within ~25 K above liq.; $\Delta H^M$ very slight f(T)
Sb-Sn	0.5*(930; ~0.50)	783-1108	85)	-1390*(905; 0.50)	16) $\Delta C_p$ indir., const.
Sb-Zn	14.00*(828; ~0.45)	828-918	86)	-3310*(823; 0.45)	86) $\Delta C_p$ indir., decr. with T, $\Delta C_p \sim 0$ at 1010 K; $\Delta H^M$ neg. and pos.



## HEAT CAPACITY OF LIQUID ALLOYS

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System	$\Delta C_p$ (T; $x_i$ ) (J K <sup>-1</sup> mol <sup>-1</sup> )	T-range (K)	Ref.	$\Delta H^M$ (T; $x_i$ ) (J mol <sup>-1</sup> )	Ref. Remarks
Se-Tl	$\sim 0$	631-753	84)	-93300*(753; 0.33)	84) $\Delta H^M$ const.
	23.2*(700; 0.40)	655-738	96)	-32600(675; 0.333)	96) $\Delta C_p$ indir. by cal.
	10.92(672; 0.333)	672-825	97)	-	$C_p$ by drop cal. for two comp.; at $x_{Se} = 0.333$ $\Delta C_p$ decreases with T to 3.05 at 835 K
Sn-Zn	$\sim 0$	923	65)	+3350*(923; 0.4)	65) $\Delta C_p$ indir.
	-3*(750; 0.50)	703-798	35)	+3412*(703; 0.44)	35) $\Delta C_p$ indir., const.
Te-Tl	4.5*(830; 0.33)	740-1123	99)	-28100*(917; 0.33)	99) $\Delta C_p$ indir., incr. slightly with T, $\Delta C_p = 6.7$ (1070; 0.33), $\Delta C_p$ should decr. at still higher T

Footnote : Numbers marked with an asterisk(\*) are extreme values (maxima or minima) of  $\Delta C_p$  or  $\Delta H^M$  in the system.  
In parentheses are temperature in K and mole fraction  $x_i$ . The mole fraction is that of the element listed first in alphabetical order.

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above  $T_c$ . Of the 12 systems with  $\Delta C_p = 0$   $\Delta H^M$  is positive for six, weakly negative for three, and strongly negative for three. Of the four systems with a - relatively small - negative  $\Delta C_p$  three have a positive  $\Delta H^M$  and one (Bi-In) a negative. However, when  $\Delta C_p$  for the latter system is calculated using the adiabatically determined  $C_p$  for indium,  $\Delta C_p$  is either zero or slightly positive.

For all systems where  $C_p$  has been measured directly (Ag-Ge, Au-Ge, Au-In, Au-Si, Au-Sn, Cd-Sb, Ge-Te, In-Te), and therefore presumably with higher precision,  $\Delta C_p$  decreases with increasing temperature and seems to approach  $\Delta C_p = 0$ . Exceptions seem to be the adiabatically determined constant  $\Delta C_p$  values for Au-Ga, Au-In, Au-Sb, Au-Sn, Au-Te and Cu-Sn by one group of authors (Itagaki and co-workers) but they found a constant  $\Delta C_p$  for Au-In and Au-Sn where DSC measurements (Janitsch, Komarek, Mikler) have definitely established that  $\Delta C_p$  decreases with increasing temperature. In the In-Te system  $\Delta C_p$  for  $\text{In}_2\text{Te}_3(\text{L})$  seems to first increase slightly then to decrease with increasing temperature. In the Au-Sn system  $\Delta C_p$  seems to become negative at very high temperature (Hayer et al.) but this observation again is based on indirect measurements. In the In-Te system measurements of  $\Delta H^M$  (Said, Castanet) have indicated that  $\Delta C_p = 0$  for  $T < 1000$  K, and  $\Delta C_p$  positive for  $T > 1000$  K decreasing with temperature but again the evidence is indirect. Although the data in general are still too sketchy and in many cases too unreliable some generalizations can be made. As pointed out previously (18) chemical short range order (association of unlike atoms) can be expected to occur in about 300 out of 435 liquid binary systems of main group (plus IB and IIB) elements, therefore some deviations from metallic bonding will be the rule and not the exception. A comparison shows that all systems with positive  $\Delta C_p$  belong to the 300 systems with chemical short range order (CSRO), and it is safe to assume that more of these systems will show a positive  $\Delta C_p$  although in cases with strong CSRO  $\Delta C_p$  - at least over a limited temperature range - can also be zero (e.g. Ag-Te, partly Ga-Te). The magnitude of  $\Delta C_p^*$  (maximum value) for systems with CSRO can cover a wide range from  $54 \text{ J K}^{-1} \text{ mol}^{-1}$  for In-Te to about  $4 \text{ J K}^{-1} \text{ mol}^{-1}$  for Au-Ge but for most system  $\Delta C_p^*$  close to the liquidus temperature seems to fall into the range from  $5$  to  $10 \text{ J K}^{-1} \text{ mol}^{-1}$ . The temperature range over which  $\Delta C_p$  decreases to zero also varies between  $150$  to  $200$  K (Ag-Ge, Cd-Sb) and about  $500$  K (Au-Si, Au-Sn). There are indications that  $\Delta C_p$  might even become slightly negative at higher temperatures (Ag-Ge, Au-Si, Au-Sn) but more experimental confirmation is needed. There is apparently no relationship between the magnitudes of (negative)  $\Delta H^M$  and  $\Delta C_p^*$  small:  $\Delta H^M$  - values can be associated both with large  $\Delta C_p^*$  (e.g. Ag-Ge) and small  $\Delta C_p^*$  (e.g. Cd-Sb) as can be large  $\Delta H^M$  - values (small  $\Delta C_p^*$  in Au-In and Au-Sn, large  $\Delta C_p^*$  in In-Te). When  $\Delta H^M$  is positive  $\Delta C_p$  is either zero or possibly slightly negative but evidence for this is scarce and indirect. Just above a miscibility gap  $\Delta C_p$  is also positive (Ga-Hg) but it decreases much faster with increasing temperature towards zero (or negative values?) than in systems with CSRO. Density fluctuations (clusters) between like atoms are much less stable than interactions between unlike atoms as a comparison of the system Ga-Hg and Cd-Sb shows.

#### Conclusion

The relative heat capacity of a liquid alloy, the (positive) deviation from Neumann-Kopp rule is therefore in many instances an important indicator of CSRO as has been previously realized for associations in liquid organic binary systems (19). The physical interpretation of CSRO and consequently of  $\Delta C_p$  is another matter. The volume change on mixing due to the size difference of the pure component atoms will possibly be a contributing factor but it cannot explain the entire deviation or else it would have a larger effect on  $\Delta C_p$  of systems with a positive  $\Delta H^M$ . Presently the most plausible interpretation of CSRO are interactions or non-random associations between unlike atoms decreasing with increasing temperature as pointed out previously (15, 17). This leaves unanswered the questions of life time of the associations and of the type of interaction (covalent or ionic) but it can be explained by a temperature dependent chemical equilibrium between actual or hypothetical species. Such a reaction can be for example the dissociation of associated unlike atoms (associates), the randomization of ionic groupings, a temperature dependent charge-transfer (especially in transition metal alloys) or an equilibrium between differently charged ions. Thermodynamic quantities, especially  $\Delta C_p$ , will not be able to settle these questions but they are very sensitive indicators of CSRO.

As far as  $\Delta C_p$  is concerned much more experimental work of higher precision and reliability is required - a still largely untouched field for interested experimental thermodynamicists and thermochemists.

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