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THERMODYNAMIC PROPERTIES OF LIQUID METALS

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Summary

Although liquid metals are susceptible to statistical mechanical description, current theory does not provide quantitative values for either heats of fusion or heat capacities of liquid metals at high temperatures. Only recently has a generally applicable experimental technique--levitation calorimetry--become available. At the moment, the very crude estimation rules

$$\Delta S_{fus} \approx 2.2\text{-}2.3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$Cp(liq) \approx 7\text{-}8 \text{ cal deg}^{-1} \text{ gram-atom}^{-1}$$

are as good as the data and the theory. A table of consistent thermodynamic data for liquid metals has been assembled, including estimates for the many high-melting transition metals which have not yet been studied.

CASE FILE
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Thermodynamic Properties of Liquid Metals

In extreme environments, where refractory metals are to serve ultimate requirements, one hopes to take advantage of the large amount of energy required to melt and raise the condensed phases (solid and liquid) to the temperature where vaporization becomes appreciable and/or mechanical structures fail. Thus, it is necessary to evaluate carefully the various refractory metals to establish their properties and provide data for engineering design purposes in high temperature systems. These data are especially critical in estimating performance under extreme heat fluxes, as might be generated in a nuclear accident or in re-entry.

Although the basic need for high temperature thermodynamic data is obvious, one quickly finds that practically all of the currently available data cover solids (up to 1500-2000°K, in a few cases) or phases melting at ~1500°K or lower.[1,2,3] Very few measurements on liquids of any kind at temperatures above 2000°K have been published. Recently, the new technique of levitation calorimetry has been described and used for studies of metals melting up to ~ 3000°K. Results on several transition metals have been reported.[4,5,6]

It is the purpose of this report to summarize the current state of knowledge about the thermodynamic properties of liquid metals, including heats of fusion and heat capacities.

Experimental Techniques

There are several experimental techniques for determining the properties of liquid metals:

(1) Classical drop calorimetry of liquid metal samples contained in non-reactive capsules.

(2) Vapor pressure studies of the solid and liquid phases and determination of the heats of fusion from the difference in the slopes of ln P_s and ln P_l vs 1/T plots.

(3) Freezing point depression studies and utilization of phase diagram data.

(4) Electrochemical studies in which either solid or liquid metals are included in the cell reaction.

(5) Levitation calorimetry where molten drops fall into a calibrated calorimeter block in an inert atmosphere.

Except for the relatively low-melting metals, only the first two techniques have been widely applied. Only levitation calorimetry has provided direct heat of fusion and Cp data at $T \gtrsim 3000$°K.

Estimation and Semi-theoretical Approaches

One is tempted to hope that liquid metals would be a state of matter which statistical mechanics could describe satisfactorily and thus, that calculation of the ordinary thermodynamic properties would not only be formally possible but also reasonably close to the experimental facts. This is unfortunately not the case. Thus, one finds in modern references,[2,7,8,9] statements that

(1) the heat capacities of liquids amount to 7-8 cal deg^{-1} gram-atom^{-1};

(2) little is known of the temperature dependence of Cp for inorganic substances in the liquid state although a tendency for Cp to decrease with increasing temperature has been observed;

(3) at present it is still common to use constant Cp values for liquids but substantial errors may enter into calculations that are extrapolated to very high temperatures;

(4) the entropy of fusion is approximately constant and in the range 2.2-2.3 for many metals;

(5) periodic behavior within families of the periodic table is observed;

(6) entropies of fusion of disordered alloys may be calculated additively from the entropies of fusion of the component metals.

Tabulation of Data

Currently available data from several sources[1-3] and from the original literature have been reviewed and the results are compiled in Table I. In the high-temperature region, the elements Ca(1116°K), Ge(1210°K), Ag(1234°K), Au(1336°K), Cu(1356°K), Be(1557°K), Si(1685°K), Ni(1726°K) and Fe(1809°K), have been done by conventional drop calorimetry while the elements Cu(1356°K), Co(1765°K), Fe(1809°K), Pd(1825°K), Ti(1940°K), Pt(2042°K), V(2193°K), and Mo(2893°K) have been studied by levitation calorimetry.[4-6] Several of the rare earth metals have also been studied at high temperatures and into the liquid range.[10]

Conclusions, Predictions and Questions

One quickly realizes that reliable data are missing for at least half of the high-melting metals (MP > 1500°K) and thus any attempt to develop a strong correlation is doomed at this time. The data are scattered, sparse and of questionable accuracy. At this stage, the very crude correlation of Tamman and earlier investigators,[11]

$$\Delta S_{fus} \approx 2.2\text{-}2.3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

is still as good as the data. Actually, deviations of 1-5 cal deg^{-1} mole^{-1} are found among the elements for which experimental data are available.

One can often calculate reasonable values for $\Delta H_{fus} = \Delta S_{fus} \times MP(°K)$ if ΔS_{fus} is in the range 2-3 cal deg^{-1} mole^{-1} but periodicity in ΔH_{fus} is simply a reflection of the periodic behavior of melting points. So few experimental values for Cp(liq) are known that no real correlation can be developed although it is clear that Cp can vary over the range 7-12 cal deg^{-1} mole^{-1} for liquids and this could reflect as a 40-60% uncertainty in thermodynamic properties of high temperature liquid metals.

Predicted values for ΔH_{fus}, ΔS_{fus} and Cp(liq) are given in Table I.

Finally, it is important to point out a question that is as yet unanswered concerning the properties of liquid metals at T > 3000°K--is the report of a decreasing trend in Cp with increasing temperature for low melting metals,[12] also applicable to liquid Pt, Nb, Mo, Ta, W, etc.? The possibility of the opposite trend is at least raised by reports of an exponential upturn in Cp as f(T) for solids as they are heated near their melting points, but the cause of this phenomenon--creation of an extended defect structure at high temperatures[13]--is perhaps only a solid-state effect and not applicable to liquids. The sketch illustrates the kind of question being asked and some of the possible answers.

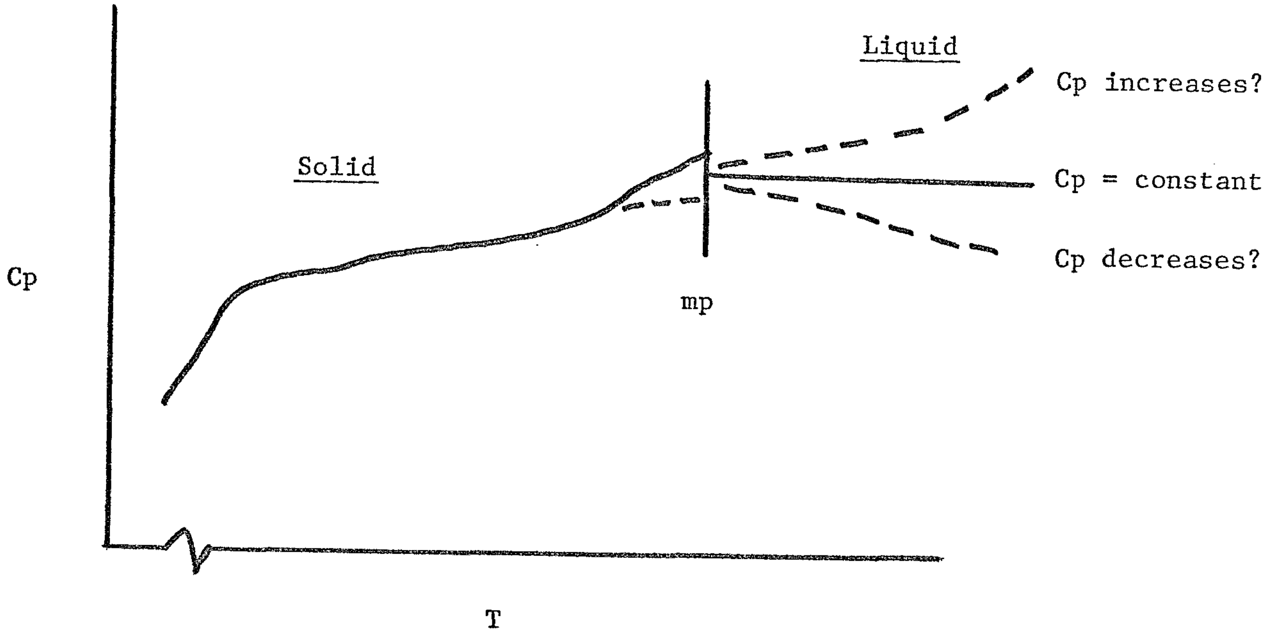

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Table 1

Thermodynamic Properties of Liquid Metals

Element	MP(°K)	ΔH_{fus} Kcal mole^{-1}	ΔS_{fus} cal deg^{-1} mole^{-1}	Remarks*
Ag	1234	2.65 ± 0.1	2.15	KEA; Cp = 8.00 (H)
Al	933	2.58 ± 0.03	2.76	H; Cp = 7.59 (H)
Au	1336	3.05 ± 0.1	2.29	KEA; Cp = 7.0 (H)
B	2303	(5.0 ± 1.0)	(2.3)	Est; Cp = (7.83) (H)
Ba	983	1.83 ± 0.1	1.86	KEA
Be	1557	3.5 ± 0.2	2.25	KEA; Cp = 7.04 (H)
Bi	544	2.6 ± 0.05	4.78	KEA; Cp = 7.30 (H)
C(graph)	(4073)	(25 ± 2)	(6 ± 1)	KEA; Cp = (6.2) (H)
C(dia)	(4073)	(28 ± 2)	(6.8 ± 0.5)	KEA
Ca	1116	2.0 ± 0.1	1.79	KEA; Cp = 7.000 (H)
Cd	594	1.53 ± 0.04	2.58	KEA; Cp = 7.10 (H)
Ce	1071	1.305 ± 0.05	1.218 ± 0.05	H; Cp = 9.01 (H)
Co	1765	3.76 ± 0.04	2.13	LC; Cp = 11.25 ± 0.50
Cr	2130	(4.047)	(1.9)	H; Cp = (9.4) (H)
Cs	303	0.50 ± 0.01	1.65	KEA; Cp = 7.62 (H)
Cu	1356	3.110 ± 0.075	2.29	LC; Cp = 7.9 ± 0.4
Dy	1682	2.643 ± 0.2	1.57 ± 0.12	H; Cp = 11.93 (H)
Er	1795	4.757	2.65	H; Cp = 9.25 (H)
Eu	1090	2.202 ± 0.05	2.02 ± 0.05	H; Cp = 9.11 (H)
Fe	1809	3.24 ± 0.06	1.79	LC; Cp = 10.35 ± 0.27
Ga	303	1.336 ± 0.01	4.41	KEA; Cp = 6.65 (H)
Gd	1585	2.403 ± 0.1	1.52 ± 0.06	H; Cp = 8.88 (H)
Ge	1210	8.8 ± 0.3	7.27	KEA; Cp = 6.60 (H)
Hf	2493	(5.7 ± 0.5)	(2.3)	Est; Cp = (8.0) (H)
Hg	234	0.55 ± 0.005	2.35	KEA; Cp = 6.806 (H)
Ho	1743	(2.911)	(1.67)	H; Cp = (10.50) (H)
In	429	0.78 ± 0.02	1.82	KEA; Cp = 7.05 (H)
Ir	2727	(6.300)	(2.3)	H; Cp = (9.35)(H)
K	337	0.571 ± 0.005	1.69	KEA; Cp = 7.68 (H)
La	1193	1.481 ± 0.05	1.24 ± 0.04	H; Cp = 8.20 (H)

Table 1 (cont'd)

Element	MP(°K)	ΔH_{fus} Kcal $mole^{-1}$	ΔS_{fus} cal deg^{-1} $mole^{-1}$	Remarks*
Li	453	0.70 ± 0.03	1.54	KEA; Cp = 7.26 (H)
Lu	1936	(4.457)	(2.3)	H; Cp = (11.45) (H)
Mg	923	2.1 ± 0.1	2.28	KEA; Cp = 7.8 (H)
Mn	1517	(3.5 ± 0.5)	(2.3)	Est; Cp = (11.0) (H)
Mo	2893	8.32 ± 0.07	2.88	LC; Cp = 8.2 ± 0.5
Na	371	0.63 ± 0.02	1.70	KEA; Cp = 7.61 (H)
Nb	2748	(6.3 ± 1.0)	(2.3)	Est; Cp = (8.00) (H)
Nd	1289	1.707 ± 0.1	1.32 ± 0.08	H; Cp = 11.66 (H)
Ni	1726	4.1 ± 0.08	2.38	KEA; Cp = 10.30 (H)
Os	3045	(7.0 ± 1.0)	(2.3)	Est; Cp = (8.6) (H)
Pb	600	1.15 ± 0.03	1.92	KEA; Cp = 7.32 (H)
Pd	1825	4.01 ± 0.05	2.19	LC; Cp = 9.1 ± 0.5
Po	519	(1.2 ± 0.5)	(2.3)	Est.
Pr	1204	1.646 ± 0.100	1.36 ± 0.06	H; Cp = 10.27 (H)
Pt	2042	5.30 ± 0.15	2.61	LC; Cp = 8.7 ± 0.5
Ra	973	(2.2 ± 0.5)	(2.3)	Est.
Rb	312	0.525 ± 0.01	1.68	KEA; Cp = (7.5) (H)
Re	3453	(7.9 ± 1.0)	(2.3)	H; Cp = (10.8) (H)
Rh	2233	(5.1 ± 0.5)	(2.3)	Est; Cp = (10.0) (H)
Ru	2583	(5.9 ± 0.5)	(2.3)	Est; Cp =(10.0) (H)
Sc	1812	3.369	1.86	H; Cp = (10.57) (H)
Se	493	1.5 ± 0.3	3.04	KEA
Si	1685	12.1 ± 0.4	7.19	KEA; Cp = 6.10 (H)
Sm	1345	2.13 ± 0.1	1.58	KEA; Cp = (12.0) (H)
Sn	505	1.69 ± 0.03	3.55	KEA; Cp = 7.10 (H)
Sr	1043	(2.4 ± 0.5)	(2.3)	Est; Cp = (7.4) (H)
Ta	3250	(7.6 ± 1.0)	(2.3)	Est; Cp = (8.00) (H)
Tb	1630	2.580 ± 0.10	1.59 ± 0.06	H; Cp = 11.11 (H)
Tc	2413	(5.5 ± 0.5)	(2.3)	Est.
Te	723	4.18 ± 0.3	5.78	KEA; Cp = 9.00 (H)
Th	2028	(3.853)	(1.9)	H; Cp = (11.00) (H)
Ti	1940	3.78 ± 0.06	1.95	LC; Cp = 11.9 ± 0.7
Tl	576	1.03 ± 0.03	1.79	KEA; Cp = 7.2 (H)

Table 1 (cont'd)

Element	MP(°K)	ΔH_{fus} Kcal mole^{-1}	ΔS_{fus} cal deg^{-1} mole^{-1}	Remarks*
Tm	1818	4.025 ± 0.05	2.22 ± 0.05	H; Cp = 9.89 (H)
U	1405	2.036	1.45	H; Cp = 11.45 (H)
V	2193	4.05 ± 0.15	1.85	LC; Cp = 12.0 ± 0.4
W	3680	(8.4 ± 2.0)	(2.3)	Est; Cp = (8.5) (H)
Y	1793	2.75 ± 0.1	1.53	KEA; Cp = 10.30 (H)
Yb	1097	1.830 ± 0.008	1.67	ref. 10b; Cp = 8.79 (10b)
Zn	692	1.74 ± 0.03	2.49	KEA; Cp = 7.5 (H)
Zr	2125	(4.038)	(1.90)	H; Cp = (8.0) (H)

*In this table,

"KEA" refers to the book by Kubachewski, Evans and Alcock (Ref. 2);

"LC" means Levitation Calorimetry;

"Est." means estimated;

"H" refers to the book by Hultgren, Orr, Anderson and Kelley (Ref. 3) and subsequent revised data compiled by Hultgren, _et_. _al_.

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