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Thermodynamics of Alloys

(Calorimetry)

Final Technical Report

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U.S. Department of the Army
Contract No: DA-91-591-EUC-2029
Report Period : 1st December 1961 - 30th November 1962

The research reported in this document has been made possible through the support and sponsorship of the U.S. Department of the Army, through its European Research Office.

Synopsis:

The method of tin-solution calorimetry is being used for the study of the thermodynamic properties of rare earth alloys. Details of the design and construction of the calorimeter were given in a previous report, but some modifications have been made because of the large heat effects encountered in the present experiments. Preliminary studies have been made of the heats of solution, in liquid tin at ca. 630°K, of pure elements cerium and lanthanum. Values of $\Delta \bar{H}_{ce} = -69{,}500$ (mean deviation 900) cal/g.atom Ce and $\Delta \bar{H}_{La} = -68{,}200$ (mean deviation 750) cal/g.atom La, corresponding to infinite dilution values, have been obtained. The validity and significance of the results are discussed briefly and plans for future work outlined.

Introduction:

For some time past, the thermodynamic properties of alloys and their relation to phase structure and to the size, valency, electronegativity and etc. of the component atoms, have received considerable theoretical and experimental attention. Of particular interest, are recent studies of alloys involving transitional metals [1 - 5]. These have revealed the profound influence on the thermodynamic properties of contributions originating from the incomplete electron energy bands which exist below the valency levels in these materials. Comparatively few such systems have been thoroughly investigated, and in order to elucidate the significant alloying factors, thermodynamic studies of alloys of transitional and other metals from the first three long periods are being continued. With the increasing availability of rare earth materials, however, it is clearly of interest to extend such studies to these elements of the later period, with their similar transitional electronic structures. A programme of tin-solution calorimetric studies of rare earth alloys is therefore planned with the aim of contributing to the understanding of the alloy chemistry of these materials and to the general problem of the inter-relation of electronic structure and thermodynamics of alloy formation. The necessary preliminary investigations of the heats of solution of individual rare earth elements in liquid tin have been begun with the experiments with lanthanum and cerium described in the present report.

Experimental Apparatus:

A tin-solution calorimeter similar to that of Orr, Goldberg and Hultgren [6] has been constructed. Details of the present instrument were given in a previous report [7] and a brief account will suffice here.

The calorimeter proper consists of a molten-tin bath contained in a molybdenum crucible and stirred by a molybdenum impeller attached to a silica shaft. The crucible is totally enclosed in a heavy nickel-plated copper isothermal jacket, which is heated on all sides by non-inductively wound heaters. This assembly is surrounded by a series of nickel radiation shields. Power supplied to the heaters is stabilized by a voltage regulator and the temperature is controlled by means of a saturable reactor proportional controller activated by a platinum resistance element wound directly beneath the main heater. The temperatures of the crucible and the isothermal jacket are measured by individual copper-Constantan thermocouples and the temperature difference by means of a separate differential (copper-Constantan-copper) couple. Above the isothermal assembly is mounted a specimen dispenser unit enclosed within its own separate furnace and radiation shield assembly. This enables specimens to be preheated as desired before dropping into the calorimeter. Both units of the calorimeter are enclosed within a water-cooled vacuum envelope, evacuated to 10^{-5} mm. Hg during operation.

During the present report period a number of minor modifications have been made to the apparatus and some further experiments providing checks against established data were carried out. The replacement of all measurement and control circuit leads by screened cable has resulted in improved stability and the heat transfer coefficient has been reduced by replacing the molybdenum stirrer shaft by silica and by redesigning the crucible support to give only knife-edge contact.

A Pye galvonometer pre-amplifier and a Pye "Scalamp" galvanometer have been incorporated into the potentiometric circuit; accurate measurements to approximately 0.015 μ V are now possible. These together with the alteration of the means of couple positioning to ensure better thermal contact, have resulted in improved temperature sensing and measurement.

The similarity of density of the rare earths and liquid tin has necessitated modification of the stirrer to ensure immersion and rapid solution of the solid specimens; the stirring rate has been increased to 100 r.p.m. Also, because of the desirability of working with much smaller specimens an additional dispenser unit has been constructed. The existing dispenser requires a fairly critical size of specimen to ensure satisfactory operation. An auxiliary unit, suitable for a wider range of samples, has therefore been mounted on the top of the vacuum envelope; (see figure 1). The auxiliary dispenser consists of a circular disc, containing a series of circumferentially distributed holes into which specimens may be placed. By rotating the disc, the specimens are dropped one at a time into one column of the main dispenser, whence they are easily transferred to the calorimeter. The tin samples used for calibration purposes are housed in the other storage column of the main dispenser.

Experimental Procedures:

In preparation for a series of runs, approximately 240 g. of 99.999% pure tin are melted under vacuum into the molybdenum crucible. The oxide film which forms during the melting is removed mechanically. The specimens of tin for calibration are cut from bar stock and filed to shape. The rare earth materials are supplied by Johnson Matthey and Co. Ltd, and contain less than 0.04% impurities. Specimens of cerium and lanthanum are cut from ingot material and all surfaces filed clean. Between weighing and loading into the auxiliary dispenser, the specimens are stored in capsules, under carbon tetrachloride, to prevent oxidation. From the examination of specimens, there is no indication of significant contamination during the subsequent storage in the dispenser.

Prior to making a run, readings of jacket temperature and the temperature difference between crucible and jacket are taken for a period of thirty minutes to ensure that the calorimeter has reached an equilibrium state in which temperatures are constant to within ± 0.001°C. The specimen temperature is measured while in the main dispenser, immediately before it is dropped into the tin bath, after which the differential and jacket temperatures are measured at frequent intervals until well after the solution process is complete. The energy equivalent of the calorimeter is determined at intervals during a series of runs by measuring the temperature drop accompanying the heating and melting of solid tin specimens and using known heat content data for tin [8].

In the initial experimental drops with cerium, normal size specimens (0.5 - 0.8 g.) resulted in extremely large exothermic heat effects and hence undesirably large disturbance of the calorimeter equilibrium. To reduce this, and so minimize heat transfer corrections, modified techniques were adopted. A series of runs were made using the "balanced heat" technique. Smaller samples (ca. 0.2 g.) of cerium were sealed in pure tin capsules and the heats of solution of the resulting duplex specimens were measured; the heat effects associated with the tin capsule were then allowed for from standard data. As a further check, another series of measurements were made with much smaller specimens (ca. 0.1 g.) of cerium alone. The last technique proved most satisfactory and has been used in all subsequent measurements on cerium and lanthanum.

Treatment of Experimental Data:

The true heat effects resulting from the solution of any specimen in the tin bath are evaluated in the usual manner, i.e. from a knowledge of the heat capacity of the calorimeter (crucible and contents) and the temperature change, corrected for any exchange with the isothermal jacket, during the reaction period.

We may write for the calorimeter

$$C_c \cdot \frac{dT_c}{dt} = \frac{dQ}{dt} - K(T_c - T_j) \qquad (1)$$

where C_c = heat capacity of calorimeter

Q = heat effect due to solution

T_c = calorimeter temperature

T_j = jacket temperature

t = time

K = coefficient of heat transfer between calorimeter and jacket; Newton law behaviour being assumed.

Similarly for the jacket, assuming no exchange except with the calorimeter

$$C_j \cdot \frac{dT_j}{dt} = K\,(T_c - T_j) \qquad (2)$$

where C_j = heat capacity of jacket.

From (1) and (2), writing $T_c - T_j = T_d$ we have

$$\frac{dT_d}{dt} = \frac{dQ}{C_c\,dt} - K\left(\frac{1}{C_c} + \frac{1}{C_j}\right) T_d \qquad (3)$$

But in a pre-reaction period, where $dH = 0$, and the equilibrium differential temperature = Td_o

$$\frac{dT_{do}}{dt} = -K\left(\frac{1}{C_c} + \frac{1}{C_j}\right) T_{d_o} \qquad (4)$$

So that from (3) and (4), writing $T_d - T_{d_o} = \Delta T_d$

$$\frac{d\,\Delta T_d}{dt} = \frac{dQ}{C_c \cdot dt} - K\left(\frac{1}{C_c} + \frac{1}{C_j}\right) \Delta T_d \qquad (5)$$

Integrating this over the reaction period gives

$$\frac{Q}{C_c} = \Delta T_d + K\left(\frac{1}{C_c} + \frac{1}{C_j}\right)\int_0^t \Delta T_d \cdot dT \qquad (6)$$

The coefficient of heat transfer $K\left(\frac{1}{C_c}+\frac{1}{C_j}\right)$ for any experimental run is evaluated from the post-reaction behaviour of the calorimeter, i.e. where $dH = 0$, since equation (5) then gives

$$d. \ln \Delta T_d = -K\left(\frac{1}{C_c}+\frac{1}{C_j}\right) dt \qquad (7)$$

so that the heat transfer coefficient is conveniently obtained from a plot of log ΔT_d versus time. The value of $\int_0^t \Delta T_d . dt$ corresponds to the area under the curve of ΔT_d versus time over the reaction period and is evaluated by the summation of squares.

Results and Discussion:

An example of a typical experiment with a small pure cerium specimen is shown in figure 2a, which illustrates the variation of ΔT_d and T_j during the run. The data plotted here refer to the solution in liquid tin, at 634°K, of a 0.00054 g.atom cerium sample, dropped from the dispenser at an initial temperature of 317°K. The initial drop of ΔT_d, due to the absorption of heat by the cold specimen, followed by rapid exothermic solution and finally a return to equilibrium are clearly evident. The plot of log ΔT_d versus time after drop, $(t - t_o)$, used for the evaluation of K is shown in figure 2b. The start of the linear region, at approximately 8 minutes, indicates the end of the solution process. The validity of the heat transfer correction based on the modified expression for Newton's law is shown by the excellent linearity of the log plot and the resultant constancy of the corrected temperature rise ΔT_c^* when evaluated at any time in the post-reaction period; ΔT_c^* is constant within ±

0.07 μV (± 0.001°C), which represents less than 0.1% of the total value of 65.6 μV.

The results obtained with a series of small pure cerium specimens are given in table 1. The observed heat effects represent a combination of specimen heating and solution components and specific heat data for cerium has therefore been employed to evaluate the more significant isothermal heat of solution values. Cerium exists in the f.c.c. form from -10°C to 730°C and the Cp data for this allotropic form, obtained by Spedding, Mc.Keown and Daane [9], have been used to calculate the change in heat capacity of the samples between dispenser and bath temperatures $[\int_{T_i}^{T_f} Cp_{ce} . dT]$. Deduction of these quantities from the experimental values thus yields partial heats of solution of cerium in tin at 634°K, referred to f.c.c. cerium as the standard state. Values are assembled in table 2; the corresponding alloy compositions are calculated as the mean value of the bath composition before and after the corresponding experiment. In table 3 are given the results of experiments using the "balanced heat technique" i.e. duplex tin plus cerium samples. The agreement between the results obtained by the different techniques is most satisfactory and confirms the reality of the extremely large exothermic heats of solution. Similar values were also obtained in the initial experiments with large cerium samples, but these have not been included because of the large correction factor involved in these values, as a result of excessive solution periods and temperature changes.

Typical ΔT_d and correction plots for experiments with lanthanum are illustrated by those for a 0.00041 g.atom specimen (T_i = 317°K, T_f = 632°K) given in figure 3; the results of a series of experiments with small pure lanthanum samples are assembled in table 4. Again, the heat values given here combine heating and solution terms. In the case of lanthanum it is not possible at present to obtain completely unambiguous values for the isothermal heat of solution at the bath temperature. While under equilibrium conditions, lanthanum is close packed hexagonal in structure from − 271 to 310°C, at which temperature it becomes face centred cubic, the sluggishness of the f.c.c. to c.p.h. transformation usually results in the existence of a mixture of the two phases at room temperature. The available specific heat data [10] take no account of the transformation and are attributed to the f.c.c. form at all temperatures from 1137°K down to room temperature; it is likely, however, that the measurements strictly refer to a (c.p.h./f.c.c.) phase mixture. Nevertheless, in the absence of alternative values, these data have been used to evaluate $\int_{T_i}^{T_f} C_{P_{La}} \cdot dT$ and these quantities combined with the present experimental data to obtain partial heats of solution in tin at 632°K, tentatively attributed to f.c.c. lanthanum as the standard state; these are listed in table 5. Errors associated with the uncertain specimen state are unlikely to be large. Since typical heats of allotropic transformation in the rare earths are of the order of 750 cal./g.atom, they probably do not exceed 2 - 300 cal./g.atom.

Because of the known high affinity of cerium and lanthanum

TABLE 1.

Run No.	T_i °K	T_f °K	ΔT_d μV	ΔT_c^{*} μV	Q cals/g.atom Ce	$\int_{T_i}^{T_f} C_{Pce} \cdot dT$ cals/g.atom Ce
11.03	317	634	38.9	56.3	69,991	2232
11.04	317	634	48.0	65.6	67,179	2232
11.06	318	634	59.7	81.0	66,839	2226
11.07	317	634	53.9	76.0	67,253	2232
11.08	318	634	44.2	63.3	67,685	2226
11.10	318	634	52.7	74.7	65,599	2226
11.11	317	634	58.5	79.0	66,202	2232

TABLE 2.

Composition, atom % Ce	$\Delta \bar{H}_{ce}$ cal./g.atom Ce.
0.0328	- 72,223
0.0575	- 69,411
0.0874	- 69,065
0.1196	- 69,485
0.1530	- 69,911
0.1675	- 67,925
0.1978	- 68,434

TABLE 3.

Run No.	T_i °K	T_f °K	Q cals/g.atom Ce
9.02	321	631	65,285
9.04	321	631	64,808
9.05	320	631	66,806
9.07	321	631	67,162

TABLE 4.

Run No.	T_i °K	T_f °K	ΔT_d μV	ΔT_c^* μV	Q cals/g.atom La	$\int_{Ti}^{T_f} Cp_{La} dT$ cals/g.atom La
12.01	315	631	29.4	40.34	64,017	2189
12.04	317	633	30.1	40.66	65,809	2190
12.06	316	632	41.4	62.44	67,394	2189
13.03	316	632	28.7	38.62	65,277	2189
13.04	317	633	46.0	64.88	66,989	2190
13.06	316	633	41.3	55.74	66,049	2197
13.07	317	632	32.0	42.61	66,230	2183
13.08	317	632	30.6	40.43	66,555	2183

TABLE 5.

Composition, atom % La	$\Delta \bar{H}_{La}$ cal./g.atom La
0.0099	- 66,206
0.0469	- 67,999
0.0709	- 69,583
0.0273	- 67,466
0.0519	- 69,179
0.0801	- 68,246
0.1034	- 68,413
0.1229	- 68,738

for oxygen, the possibility of oxidation side-reactions was considered. Calculations show, however, that the observed effects are too small to be consistent with the complete reaction of the cerium with either free oxygen or oxide or with oxygen in solution. Also, the amount of oxygen necessary for complete oxidation of all cerium sample is at least two orders of magnitude greater than the probable solubility of oxygen in tin. Partial oxidation is extremely unlikely in view of the constancy of the values observed. Macro- and micro-examination of the tin-rare earth baths after completing the experiments showed no evidence of oxidation.

It is considered therefore that the values reported here correctly represent the partial heats of solution of cerium and of lanthanum in liquid tin at ca. 634°K. The constancy of the value obtained in each series indicates that the compositions of the resultant alloys all lie within the range of Henrian behaviour for the solutes, i.e. the observed heats of solution correspond to infinite dilution values. The extremely large exothermic values are indicative of strong interaction between the individual solutes and the solvent tin. This is consistent with the known existence of very stable compounds in the solid state in both the Ce-Sn and Ce-La systems and can be attributed in general terms to the large difference in electronegativity between the components. A tendency to electron transfer, associated with the existence of vacant 4f levels in the rare earth elements would seem likely to be a fundamental contributory factor.

In order to investigate further the significance of the degree of electron occupation of 4f levels in determining alloying behaviour, the work is being continued with similar studies with other rare earth elements. Consideration will also be given to the variation of behaviour with allotropic form. Following the appropriate studies of the heats of solution in tin of pure rare earths, the investigations should shortly be extended to the proposed study of the thermodynamics of formation of rare earth alloys.

References:

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10. R. Hultgren, "Selected Values for the Thermodynamic Properties of Metals and Alloys" (University of California, 1959).

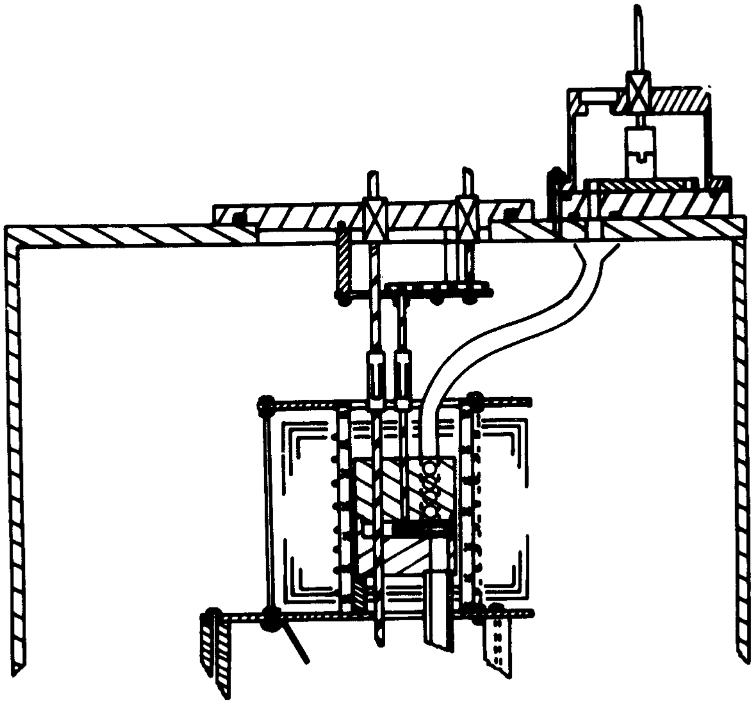

Figure 1. Main and auxiliary specimen dispenser.

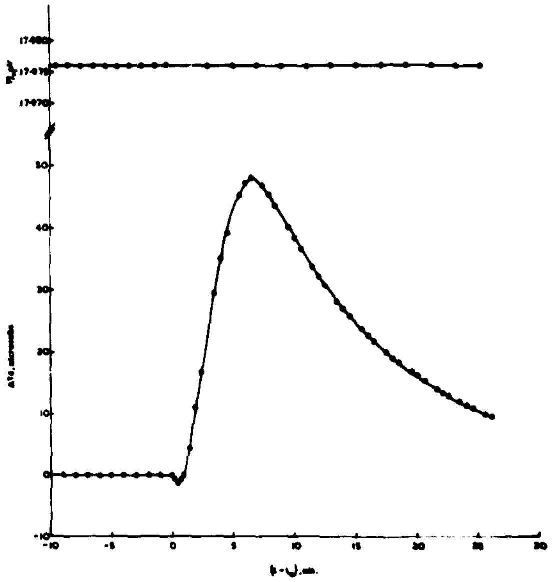

Figure 2a. Data for solution of cerium in liquid tin at 634°K.

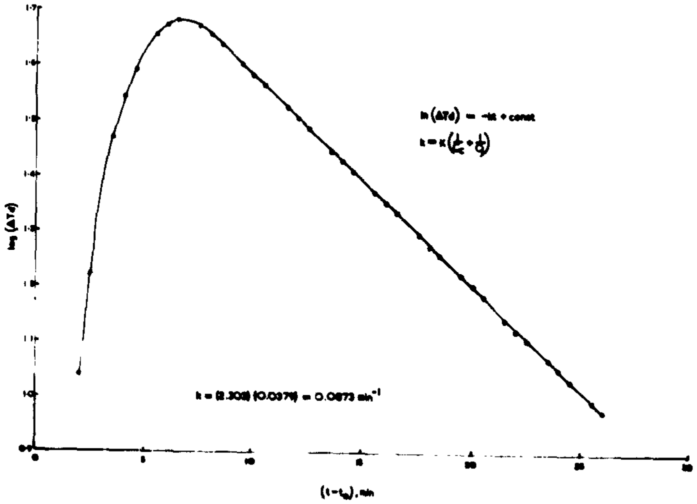

Figure 2b. Determination of the correction constant, k.

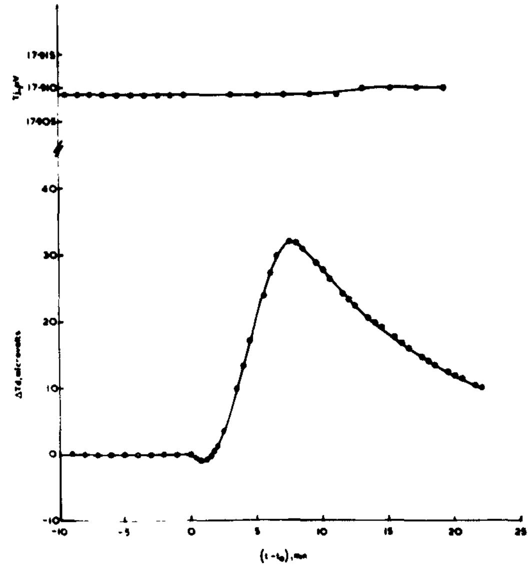

Figure 3a. Data for solution of lanthanum in liquid tin at 632°K.

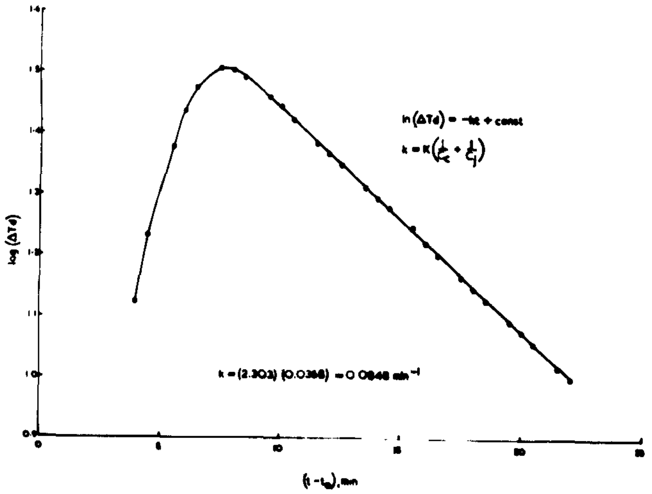

Figure 3b. Determination of the correction constant, k.

U.S. Department of the Army Contract No. DA-91-591-EUC-2029

(University of Birmingham Contract Code No. 10935)

Annex to Final Report (Contract Period 1.12.61 - 30.11.62)

(a) Principal Investigator

Dr. J.N. Pratt

(b) Full-time Salaried Personnel Employed

Graduate Research Worker: Mr. A.W.H. Morris

Junior Technical Assistant: Miss L. Aston

(c) Allocation of Funds

Salaries, insurance, fees etc. for personnel employed	£900 - 0 - 0
Equipment, consumable materials etc.	£800 - 0 - 0
General Overheads	£150 - 0 - 0
Total ...	£1850 - 0 - 0