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by

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SUMMARY

The heats of formation of α-solid solution copper-zinc alloys containing from 1 to 33.5 at.% Zn have been measured at 573°K using a liquid tin solution calorimeter. Excess entropies of formation have been calculated from the heats of formation and ~~the~~ excess free energies of formation obtained in earlier vapour pressure studies. The results show that the solutions are approximately ideal up to 10 at.% zinc and then show negative deviations from ideality that increase with the concentration of zinc. ~~in the alloy.~~

INTRODUCTION

In spite of the efforts of several workers[1,2,3] the entropies of formation of solid copper-zinc alloys are ill-defined. Experimentalists who have used the vapour pressure technique to determine partial free energies of solution of zinc $\left(G^m_{Zn}\right)$ and have then obtained partial entropies of formation $\left(S^m_{Zn}\right)$ by the use of the relationship

$$-\frac{\partial G^m_{Zn}}{\partial T} = S^m_{Zn}$$

have had difficulty in determining accurate temperature dependencies from the comparatively limited temperature ranges of ~ 150°K that are experimentally possible. The free energies of formation (G^m) ~~determined in these studies~~ are however reliable and there is good agreement between

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Hargreaves[1], Herbenar, Siebert and Duffendack[2], and Argent and Wakeman[3] about the values of the free energies of formation of these alloys at ~1000°K. Several workers[4,5,6] have made comparatively limited studies of the heats of formation (H^m) of the alloys but insufficient data were available before the present investigation for reliable estimates of the entropies of formation (S^m) to be made by combining the heats and free energies of formation using the relationship

$$\frac{H^m - G^m}{T} = S^m$$

EXPERIMENTAL

The alloys used in this investigation came from two sources. Specimens of 23 alloys used by Argent and Wakeman[3] were available and used after a further check of their compositions by X-ray fluorescence analysis. A further 20 new alloys were made from 99.999% copper and 99.999% zinc by melting the components in sealed clear silica tubes. The alloys were thoroughly mixed by shaking and quenched in water. This procedure ensured that long range segregation was slight. The ingots were then annealed in sealed silica capsules for one week at 850°C. X-ray fluorescence analysis indicated that in all cases the alloys were within 0.3 at.% of the intended compositions. A further check on the composition and homogeneity of the alloys was made by means of lattice parameter determinations on ten of the alloys; the lattice parameters agreed with the previously reported values to within ± 0.3% with respect to composition.

The liquid tin calorimeter and the experimental procedures used for the heat of formation determinations have been described elsewhere[7] and only a brief description will be given here. The calorimeter consists of a stirred bath of approximately

250 gms of liquid tin contained in a molybdenum crucible and the crucible is supported within a heavy copper jacket which is heated by a resistance heating element. Externally caused drifts or fluctuations in the jacket temperature are kept to less than 0.001° by means of a sensitive resistance thermometer temperature controller. The temperature difference between the jacket and the crucible is measured by means of a copper-constantan differential thermocouple and the jacket temperature is measured separately by a calibrated platinum-platinum + 10% rhodium couple. The calorimeter and a separately heated dispenser unit, which holds the specimens prior to dropping them into the bath, are contained in a chamber that was evacuated and then filled with argon to reduce zinc losses from the specimens.

When the calorimeter reached a steady state the specimen's temperature was recorded and it was dropped into the tin bath. Readings of the jacket and differential temperatures were then taken at frequent intervals. The total heat effect after the reaction was complete was evaluated from the change in the differential temperature, the measured heat capacity of the calorimeter and a correction for the heat transfer between the jacket and crucible. The heat capacity of the calorimeter was determined from the temperature drop accompanying the addition of a specimen of solid tin, using the known heat content data for tin.

Approximately spherical specimens of the pure metals and alloys ~ 5 mm. in diameter were used for all the determinations. The tin bath was maintained at 650(±2)°K, and the specimen temperatures from run to run did not vary by more than ±6° from 573°K.* The tin bath was replaced before the total concentration of solute metals reached 2 at.%.

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* This temperature is above the supposed disordering temperature for α brasses (9,10,11) but below the ordering temperature for β brass ; it was chosen to minimize zinc losses.

RESULTS

Several determinations of the heats of solution of pure copper and zinc were made during the course of the investigation. The results, evaluated at the solution temperature, 650°K, were found to be linearly dependent on the total concentration of solute metals in the tin. The relative partial molar enthalpies of copper and zinc in infinitely dilute solution in liquid tin at 650°K, obtained by extrapolation to zero concentration, are tabulated in Table I. The standard reference states are solid copper and solid zinc respectively. The tabulated uncertainties are 95% confidence limits based on the standard deviations of the measured values from the straight lines drawn through the data.

The heats of formation of the alloys at 573°K were evaluated from the reactions

$$Cu_{(s,Ti)} = Cu\ (\text{in Sn})_{(\ell,Tf)} \quad \ldots \Delta H_1 \qquad (1)$$

$$Zn_{(s,Ti)} = Zn\ (\text{in Sn})_{(\ell,Tf)} \quad \ldots \Delta H_2 \qquad (2)$$

$$Cu_{1-x}\,Zn_{x(s,Ti)} = (1-x)\ Cu\ (\text{in Sn})_{(\ell,Tf)} + xZn\ (\text{in Sn})_{(\ell,Tf)} \quad \ldots \Delta H_3 \qquad (3)$$

(where Ti = initial specimen temperature, Tf = final solution temperature, ℓ = liquid, s = solid).

Combination of reactions 1, 2, 3 gives

$$(1-x)Cu_{(s,Ti)} + xZn_{(s,Ti)} = Cu_{(1-x)}Zn_{x(s,Ti)} \quad \ldots \qquad (4)$$

and the heat of formation at Ti, ΔH_{Ti} is given by

$$\Delta H_{Ti} = (1-x)\,\Delta H_1 + x\Delta H_2 - \Delta H_3 \quad \ldots \qquad (5)$$

The final solution temperature does not enter the calculations provided that it is the same for reactions 1, 2, 3 and thus no assumptions need to be made about

changes in heat content for the alloys between Ti and Tf.

Values of ΔH_1 and ΔH_2 corresponding to the average solute concentration for each alloy run were obtained from the linear heats of solution plots found for the pure metals.

The results for the alloys are given in figure 1 as a function of the atomic fraction of zinc x_{Zn}, together with data by Körber and Oelsen[4] at 293°K, Weibke[5] at 363°K and Kleppa[6] at 298°K.

DISCUSSION

The scatter in the heats of formation for the first 10 at.% zinc is ±50 cal. mole^{-1} and this scatter increases to ±100 cal. mole^{-1} at higher zinc concentrations. The zinc losses that were possible from the specimens during the times for which they were held in the dispenser unit were unlikely to account for more than a small fraction of the observed scatter.

The shape of the heat of formation curve is interesting in that there appears to be a rapid increase in the exothermic heat of formation at concentrations greater than 32 at.% zinc.

To evaluate the entropies of formation from the observed heats of formation, data are required on the free energies of formation at the same temperature. Unfortunately the free energies of formation at 573°K are not known and extrapolation from the data that is available at 1000°K would be liable to considerable error. It therefore seems best to evaluate the entropies at 1000°K taking advantage of the fact that the specific heats of copper-zinc alloys do not deviate greatly from the Kopp-Neumann rule. The maximum reported value of ΔC_p[8], the deviation from an additivity value is 0.16 cal.mole^{-1}. This suggests that the error in assuming $H^m_{573} = H^m_{1000}$ will probably not be greater than ±100 cal.mole^{-1}.

Figure 2 shows the value of $G^{xs} = G^m - RT\,(x_{Zn}\ln x_{Zn} + x_{Cu}\ln x_{Cu})$ calculated from the data of Argent and Wakeman[3],

the values of H^m from the present investigation and the derived values of S^{xs}. The standard deviation for G^m_{Zn} was $\pm$ 110 cal mole^{-1} and the 95% confidence limits * for G^{xs} are $\pm$ 25 cal mole^{-1} at 30 at.% zinc. Thus the expected errors in S^{xs} are $\sim \pm$ 0.1 cal deg.$^{-1}$mole^{-1} at 30 at.% zinc and $\pm$ 0.05 cal deg.$^{-1}$ mole^{-1} at 10 at.% zinc. Table II presents the most probable values of $H^m_{573^\circ}$, $G^{xs}_{1,000^\circ}$ and $S^{xs}_{1,000^\circ}$ tabulated at 5 at.% intervals. It will be noticed that the alloys have nearly ideal entropies up to ~10 at.% zinc but show increasingly negative deviations from ideality up to the $\alpha/\alpha+\beta$ phase boundary. Due to reasons that will be explained later the values at concentrations greater than 32 at.% zinc are suspect.

Evidence for short range ordering in the brasses at low temperatures is comparatively strong. Several workers[9,10,11] have observed humps in the specific heat versus temperature curves for brasses containing more than ~8 at.% zinc. The shape of this hump was of the type normally associated with an order-disorder transformation. However the heat involved was not greater than 40 cal. mole^{-1}; that is about 1/10th of the heat of disordering β^1 brass. Childs and Le Claire[12] observed an internal friction peak at 573°-623°K for alloys containing more than 8 at.% zinc which they associated with short range order in the alloys. Koster and Schule[13] measured the electrical resistance and Hall effect for the alloys and again suggested that their observations could be interpreted on the basis of short range ordering in the alloys occurring between 523°K and 433°K.

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* G^{xs} was calculated using

$$G^{xs} = (1 - x_{Zn}) \int_0^{x_{Zn}} \frac{G^m_{Zn} - RT\ln x_{Zn}}{(1 - x_{Zn})^2} \, dx_{Zn}$$

and the error was calculated on the assumption that the variances of the strips used in the graphical integration could be summed to give the overall variance.

The excess entropies obtained in the present work may be understood if short range order persists to comparatively high temperatures in α brasses containing more than 10 at.% zinc, and if this degree of order increases rapidly as the $\alpha / \alpha + \beta$ phase boundary is approached.* The values of H^m for the α phase alloys are $\sim$400 cal mole^{-1} more negative at the phase boundary than would be expected from a. a smooth extrapolation of the values obtained at lower concentrations, or b. an integration of the values of H^m_{Zn} determined at 1,000°K (3). This enthalpy difference is of the magnitude to be expected if a. the α phase that comes into equilibrium with the ordered β' brass is ordered on a long range basis with an enthalpy of ordering similar to that found for ½ CuZn or ¼ Cu_3Au (14) and b. alloys containing less than $\sim$ 30 at.% zinc only show short range order. Some support for this view is found in Thomas's observations of superdislocations in α brasses containing high concentrations of zinc (15). However this evidence is not conclusive as Cohen and Fine(16) have suggested that superdislocations may be observed in structures showing a high degree of short range order. The doubt about the structural state of the α brasses containing high concentrations of zinc makes the assumption $H^m_{573°} \simeq H^m_{1000°}$ suspect, and in deriving values of $S^{xs}_{1000°}$ a substantial enthalpy of disordering may need to be considered for alloys containing $>$30 at.% zinc.

n/ The extent of short range order in liquid alloys should be much less than in the solid state and measurements by Everett, Jacobs and Kitchener(17) and by Downie(18) show that the entropies become more nearly ideal on melting and that the negative deviations are at most one-half the magnitude of those found for solid alloys. The alternative interpretation

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* Unfortunately the accuracy of the present work is not sufficient to decide whether the fluctuations in the partial entropy of zinc observed by Argent and Wakeman(3) are real. Moreover, recently Filby and Pratt have investigated other phase alloys based on Group Ib solvents and Group IIb solutes and found fluctuations in the partial entropy of cadmium in gold+cadmium alloys (20) but not in silver + cadmium alloys (21).

that the negative excess entropies arise from changes in the vibrational spectrum on alloying is not supported by the available data on high temperature heat contents[19] or low temperature specific heats[8]. These data suggest that deviations from the Kopp-Neumann rule are small.

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FIGURE CAPTIONS

1. Heats of formation of the α-brasses.

   ○ This work 573°K, △ Weibke 363°K, ▽ Kleppa and King 298°K

   □ Korber and Oelsen 293°K.

2. Enthalpies, excess free energies and excess entropies of formation of the brasses.

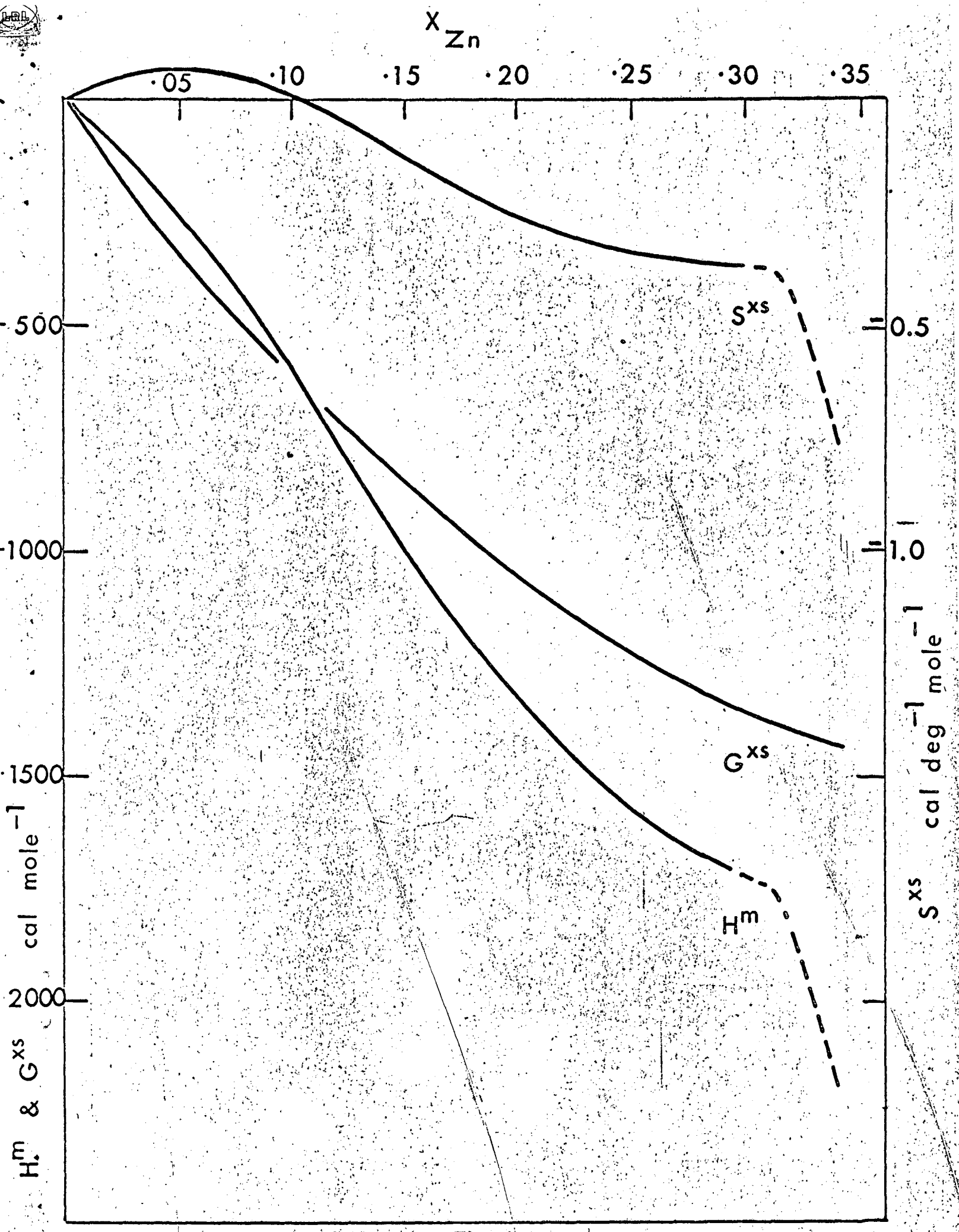
X_{Zn}
·05
·10
·15
·20
·25
·30
·35
-500
-1000
-1500
-2000
0.5
1.0
S^{xs}
G^{xs}
H^m
H^m & G^{xs} cal mole^{-1}
S^{xs} cal deg^{-1} mole^{-1}

Fig. 1.

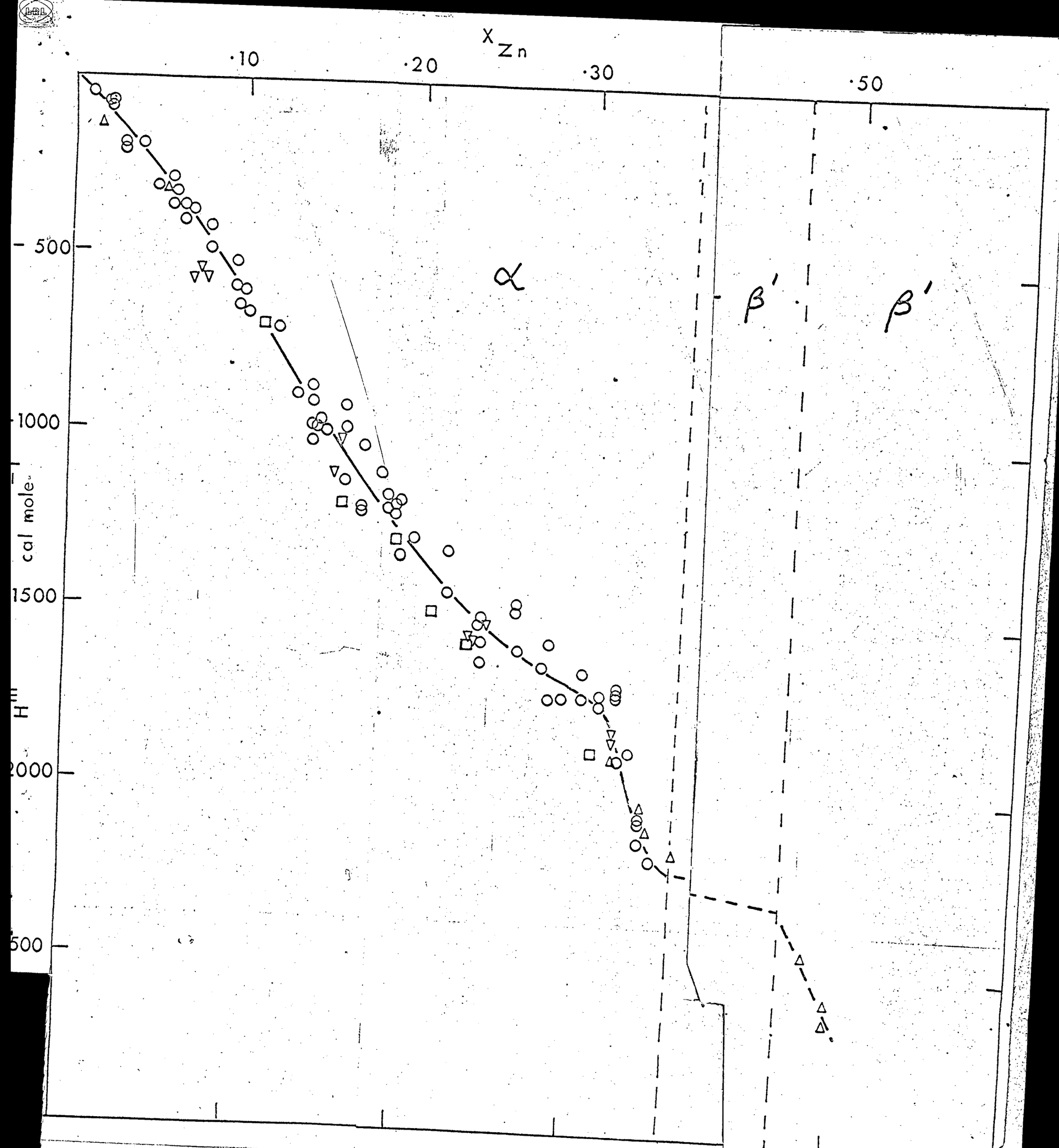

Fig. 2.