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A SURVEY OF METAL SOLUBILITIES IN LIQUID ZINC

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INTRODUCTION

A program ^{was} ~~has been~~ initiated ^{on this} ~~in the~~ Chemical Engineering Division toward the possible development of a fuel decontamination process by means of fractional precipitation from metallic zinc solution. In order to gather background material on alloy systems of interest, a literature survey of the binary phase diagrams of zinc in the zinc-rich regions (>50 a/o zinc) was undertaken, as well as the crystallography of the solid phases which are expected to precipitate from solution, the latter for purposes of identification. 79 references. (auth)

Sources

Use was made in varying degrees of four compilations of phase diagrams: M. Hansen, "Aufbau der Zweistofflegierungen," which covers the literature to 1935;⁽¹⁾ the Metals Handbook published in 1949;⁽²⁾ Smithells, "Metals Reference Book," published in 1949;⁽³⁾ Gmelin's "Handbuch der anorganischen Chemie," 8th edition, which covers the literature to the end of 1949.⁽⁴⁾ Hansen's compilation is outdated in many instances. The compilation by Smithells lists phase diagrams without commentary and does not appear to have the reliability required for this survey. The Metals Handbook lists only a relatively small number of systems. The information in Gmelin is widely scattered and only occasional reference to it was made.

Metallurgical Abstracts was used to cover the period between the publication of Hansen's book and 1956. Appropriate references are listed in Haughton's bibliography of metal alloys.⁽⁵⁾

Crystallographic data were obtained from the original literature, as well as from tabulations by Smithells⁽³⁾ and by Donnay and Nowacki.⁽⁶⁾

Choice of Reference Material

Whenever possible liquid solubility data were obtained from the original papers in order to preclude errors caused by taking points from graphs with incomplete grids. In a number of papers, however, no data were tabulated and the information had to be taken from figures. It will be indicated in this survey when this was done. If more than one set of data was found for a given system, a choice was made on the basis of what appeared to be the most careful investigation or on the basis of consistency

with other work. Often it was not possible, however, to make a positive decision about the most reliable work because no obvious reasons for any existing discrepancies were apparent. In those instances a choice was made by taking the most recent data.

Presentation of Data

The binary additions to zinc are listed in the alphabetical order of their chemical symbols. Section A lists the systems for which no liquidus data were found. Section B lists systems in which a liquid miscibility gap occurs. Section C lists simple eutectic systems. Section D lists the systems other than simple eutectics for which liquidus data were available. An index to all systems is given before Section A. Solubilities are plotted on a log (atom per cent of solute) versus $1/T$ (K) graph arranged in such a way that the phase diagram is simulated. The figures are gathered in Appendix II. Generally a smooth curve is drawn through the points. Where peritectic points in the phase diagram indicate definite discontinuities in slope, such discontinuities have also been introduced in the log N_s vs $1/T$ plots. It should be noted that between these discontinuities thermodynamic theory permits these curves to be straight lines provided that certain conditions are met.

Short horizontal lines have been drawn at the peritectic and eutectic points, and the 2-phase regions between have been designated by the phases in equilibrium with each other. Short arrows have been drawn at either end of the solubility curve in order to indicate by their upward or downward direction whether the point is a eutectic, a peritectic or a maximum (congruently melting intermetallic compound). If no arrow has been drawn the solubility curve extends further without an invariant equilibrium at the endpoint.

The accuracy of the curves is usually the same as that of the original work. Points copied from phase diagrams rather than from tabulated data have a lesser accuracy which is difficult to estimate.

Tables of solubilities are attached as Appendix III. Solubilities are listed as both atom per cent (a/o) and weight per cent (w/o) of solute. Included in Appendix III are data concerning the compositions of liquid phases in equilibrium with each other in systems in which a miscibility gap occurs, provided the tie-lines are known.

Phases have been designated in the discussion by the symbols employed in the most important reference used. Although consistency is not necessarily attained this way, it is felt that easier reference can be made to the original literature.

Crystal data, when available, are given with the discussion of each system. They are separately tabulated in Appendix IV for easier comparison.

Discussion

Experimental Methods

Conventional methods of X-ray diffraction, metallographic examination and thermal analysis were used for most systems. A few investigations were made, however, in which solubility data were obtained by sampling the melt after equilibration at the desired temperature and settling of the precipitate. Edmunds and Truesdale and co-workers investigated the solubilities of copper, iron and manganese in zinc^(7,8), Chiotti and co-workers, the solubility of uranium in zinc.⁽⁶²⁾ Currently a number of other systems are being examined in the Chemical Engineering Division by Knighton⁽⁶³⁾ by means of a similar method. As of the writing of this survey some data are available for barium, cerium, molybdenum, palladium, rhodium, ruthenium, and uranium. It must be emphasized that Knighton filtered the samples, which were taken within a half hour after the desired temperature was reached, whereas other workers sampled without the benefit of a filter and not until several hours had passed. Whereas the filtering technique is preferable in most cases, the filter is assumed to retain particles only of 12 microns or larger, and as a result very fine precipitates might on occasion have leaked into the sample, causing the solubilities found to be too high. Comparative data obtained by thermal analysis are available for the elements cerium, copper, manganese, and palladium (see, e.g., Figure 15). The solubilities determined by sampling are lower than those obtained by thermal analysis. In the case of cerium it is felt that the absolute reliability of the older data is low, particularly below 1 at/o cerium. For other cases, however, Edmunds attributes this to possible supercooling effects in thermal analysis experiments,⁽⁷⁾ claiming the highest possible accuracy for the sampling method. It would appear, however, that in most cases the occurrence of supercooling of 5 to 10 C would be recognizable in the time-temperature curves. Of course, either method may have problems as yet unrecognized. Another possible explanation for the differences may be the effect of particle size on the solubility. Usually a certain time was allowed for the precipitate to settle before sampling, thus giving the particles an opportunity to grow, whereas the arrests in thermal analysis curves are determined at incipient precipitation, when the particle size is presumably still very small. A calculation based on reasonable estimates of the interfacial tensions (free energies) and particle sizes may lead to an estimate of the effect and make a comparison with experiment possible. Experimentally one may take a series of samples at different times using filters of different pore-size and determine the solute content of the samples.

Recently, Willey compared the settling and filtration methods for the determination of the aluminum-rich liquidus in the aluminum-manganese system and found excellent agreement.⁽⁶⁶⁾ The apparatus developed by him has a facility to determine simple heating and cooling curves, in addition to a liquid metal filtration arrangement. No comparative results of sampling and of thermal analysis have been published as yet.

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The second point of interest is a method developed by Lihl to obtain alloys otherwise difficult to prepare.⁽⁹⁾ The components are dissolved in mercury in the desired proportions and the mercury is subsequently distilled off. The alloys thus obtained are normally free of mercury. It is estimated that phases characteristic of a temperature of 200-250 C are obtained. Lihl considers the phases present in these alloys to be in equilibrium and explains differences with alloy phases obtained from the melt by the freezing in of equilibrium conditions prevalent at higher temperatures. Until further proof for this is available phase relations obtained by conventional methods should be given preference.

Some Theoretical Considerations

The following generalizations may be made from the solubility curves.

1. The behaviors of the groups (Li, Na, K); (Mg, Ca, Ba); (Ti, Zr); (Sb, Bi); (Ni, Pd, Pt) indicate that the solubility in zinc increases with increasing atomic number within a vertical column of the Periodic Table. In the group (Cu, Ag, Au), silver occupies an intermediate position in that the solubility of silver at high dilution is almost identical with that of copper, but at high concentrations with that of gold.
2. The results with the groups (Ca, Ti, Cr, Mn, Fe) and (Sr, Zr, Mo, Ru) indicate minimum solubilities occur in the fifth and sixth groups.
3. Within the groups (Fe, Co, Ni) and (Ru, Rh, Pd) the solubilities increase in the order given.

The behavior of the alkali metals is undoubtedly due to the effect of size. The radii of these metals are large and are not likely to fit in the liquid structure of zinc.

The relative behavior of the elements in group VIII may be an electronic effect. Solubilities in the fifth and sixth groups are likely to be associated with the high heats of vaporization of these elements.

If one compares the phase diagrams of magnesium and zinc one finds certain characteristics which are undoubtedly associated with the position of zinc as a subgroup and amphoteric element. The large number of strong valence compounds which magnesium forms are not found for zinc. Instead, the numbers of electron compounds and coordination compounds appear to be increased, as well as the number of simple eutectic systems. One also finds more incongruently melting phases and, in general, more complicated solid-state phase relations. As a result, it may be surmised that solutions in liquid zinc deviate less from ideality than solutions in liquid magnesium.

Crystallography

A point of crystallographic interest is to be found among structures of the compositions MeZn_5 .

CaZn_5 belongs to the space group $D_{6h}^1 - C6/mmm$, (35,37) and BaZn_5 to $D_{2h}^{17} - Amam$.⁽¹²⁾ In addition, ThZn_9 is said to correspond crystallographically to the formula $(\text{Th}_{0.6} \text{Zn}_{0.4})\text{Zn}_5$ and also to belong to the space group $D_{6h}^1 - C6/mmm$.^(15,16) The table below lists the pertinent crystallographic data for these compounds.

<u>Formula of Space Group</u>		<u>Atoms per Unit Cell</u>	<u>a(Å)</u>	<u>b(Å)</u>	<u>c(Å)</u>	<u>c/a</u>
CaZn_5	D_{6h}^1	6	5.371		4.242	0.789
BaZn_5	D_{2h}^{17}	24	5.37	10.85	8.50	
$(\text{Th}_{0.6} \text{Zn}_{0.4})\text{Zn}_5$	D_{6h}^1	6	5.248		4.451	0.848

The D_{6h}^1 structure (type $D2x$) is found among a rather large group of compounds of composition MeX_5 , where Me may be thorium, calcium, strontium, barium or the rare earths, and X may be elements of the eighth group of the periodic table, as well as copper, silver, gold or zinc according to current data.⁽⁷²⁾

An apparent characteristic of this group is that the ratio of the Goldschmidt atomic radii of the elements varies between the rather narrow limits of 1.37 and 1.62, with the following distribution:

<u>Ratio of Radii</u>	<u>Number of Compounds</u>
1.37	1
1.42	2
1.44	3
1.46	5
1.49	1
1.50	1
1.56	3
1.60	2
1.62	1

and an average ratio of between 1.47 and 1.48. An examination of the ratio of the radii of magnesium, strontium, barium and thorium (or a weighted average of $0.6 \times r_{\text{Th}} + 0.4 \times r_{\text{Zn}}$) with zinc will show that MgZn_5 and ThZn_9

do not appear to fit in this group, that BaZn_5 is a borderline case, and that SrZn_5 , if it exists, most likely belongs to this group. The table below lists the Goldschmidt radii (Ref. 3, page 166).

Element	Goldschmidt Radius	$r_{\text{Me}}/r_{\text{Zn}}$
Mg	1.60	1.17
Ca	2.00	1.46
Sr	2.15	1.57
Ba	2.24	1.63 ₅
Th	1.80	1.31
($\text{Th}_{0.6}\text{Zn}_{0.4}$)	1.63	1.19
Zn	1.37	-

The ratio $r_{\text{Mg}}/r_{\text{Zn}}$ is far outside the range of 1.37 - 1.62. MgZn_5 has indeed been shown not to exist, the composition of the phase in question being $\text{Mg}_2\text{Zn}_{11}$.^(51,52)

SrZn_5 is well within the range and there are no reasons why this compound would not exist and be isomorphous with CaZn_5 . BaZn_5 is just outside the range. The rhombic structure with a unit cell volume of $495 \text{ \AA}^3$ is 4.06 times 122, the unit cell of CaZn_5 , and contains four times as many atoms, so that apparently only a slight distortion in the basal plane is sufficient to fit the barium atoms in the CaZn_5 type structure.

Finally, the radius ratio of $(\text{Th}_{0.6}\text{Zn}_{0.4})\text{Zn}_5$ is outside the range again, by a rather large margin. This casts a serious doubt on the correctness of the CaZn_5 -type structure. The axial ratio is considerably larger than that of CaZn_5 and also of LaZn_5 ($c/a = 0.778$) and appears to be out of line. In addition, the formula $(\text{Th}_{0.6}\text{Zn}_{0.4})\text{Zn}_5$, in which four of every ten thorium atoms are randomly substituted by zinc atoms, suggests the existence of a range of homogeneity around the composition ThZn_9 for which no evidence has been found thus far. On the basis of the Goldschmidt radii one could expect isomorphy between ThZn_9 , LaZn_9 and CeZn_9 , the radius ratio in these compounds varying between 1.31 and 1.36. The Goldschmidt radius of uranium is given in Ref. 3, page 166, as 1.38 Å, whereas Hume-Rothery gives 1.54₅ Å (Ref. 73), the latter being 1.03 times half the interatomic distance in γ -uranium. The radius ratio of uranium and zinc then becomes 1.01 or 1.12, in either case much smaller than $r_{\text{La}}/r_{\text{Zn}}$ or $r_{\text{Ce}}/r_{\text{Zn}}$. This might suggest that UZn_9 and CeZn_9 or LaZn_9 would not be expected to be isomorphous.

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INDEX OF ALLOY SYSTEMS

<u>Symbol^a</u>	<u>Section^b</u>	<u>Table^c</u>	<u>Figure^d</u>
Ac	A	-	-
Ag	D	3	11
Al	C	4	1
Am	A	-	-
As	D	5	13
Au	D	6	11
Ba	D	7	3
Be	A	-	-
Bi	B	1	-
Bk	A	-	-
Ca	D	8	3
Cd	C	-	1
Ce	D	9	4
Cf	A	-	-
Cm	A	-	-
Co	D	10	8
Cr	D	11	6
Cs	A	-	-
Cu	D	12	11,15
Dy	A	-	-
Er	A	-	-
Eu	A	-	-
Fe	D	13	9
Fr	A	-	-
Ga	C	-	1
Gd	A	-	-
Ge	C	14	1
Hf	A	-	-
Hg	C	-	1
Ho	A	-	-
In	C	-	1
Ir	A	-	-
K	B	-	-
La	D	15	4
Li	D	16	2
Lu	A	-	-
Mg	D	17	3
Mn	D	18	7,15
Mo	D	19	6
Na	B	20	2
Nb	A	-	-
Nd	A	-	-
Ni	D	21	8
Np	A	-	-
Os	A	-	-

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INDEX OF ALLOY SYSTEMS (Continued)

Symbol ^a	Section ^b	Table ^c	Figure ^d
P	A	-	-
Pa	A	-	-
Pb	B	2	-
Pd	D	22	10
Pm	A	-	-
Po	A	-	-
Pr	A	-	-
Pt	D	23	10
Pu	A	-	-
Ra	A	-	-
Rb	A	-	-
Re	A	-	-
Rh	D	24	10
Ru	D	25	10
S	A	-	-
Sb	D	26	13
Sc	A	-	-
Se	A	-	-
Si	D	27	12
Sm	A	-	-
Sn	C	-	1
Sr	A	-	-
Ta	A	-	-
Tb	A	-	-
Tc	A	-	-
Te	A	-	-
Th	A	-	-
Ti	D	28	5
Tl	B	-	-
Tm	A	-	-
U	D	29	14
V	A	-	-
W	A	-	-
Y	A	-	-
Yb	A	-	-
Zr	D	30	5

^a No consideration has been given to elements not listed.

^b A: Systems for which no significant liquidus data were found.

B: Systems with a liquid miscibility gap.

C: Simple eutectic systems.

D: Systems other than eutectics for which liquidus data are available.

^c Appendix III.

^d Appendix II.

||

A. SYSTEMS FOR WHICH SCATTERED OR NO LIQUIDUS DATA ARE AVAILABLE

No consideration was given to combinations of zinc with the following elements: A, At, B, Br, C, Cl, F, H, He, I, Kr, N, Ne, O, Rn, Xe. No liquidus information was found on systems of zinc with the following elements: Ac, Be, Cs, Fr, Hf, Ir, Pa, Po, Ra, rare earths except Ce and La, Rb, Re, Sc, Ta, Tc, transuranic elements, Y. Systems with only scattered information are alloys with P, Os, S, Se, Sr, Te, Th, W. These are discussed below.

Zn-Nb

Corrosion data indicate a relatively high solubility of niobium in liquid zinc.⁽⁶⁴⁾

Zn-P

The compounds Zn_3P_2 and ZnP_2 are known. Zn_3P_2 belongs to the space group D_{4h}^{15} with cell dimensions of $a = 8.097 \text{ \AA}$, $c = 8.316 \text{ \AA}$, $c/a = 1.418$, and 40 atoms per unit cell.⁽⁶⁸⁾

Zn-Os

Osmium and zinc form alloys. The solubility of osmium in zinc appears to be highly temperature dependent. There are no indications of intermetallic compound formation (Ref. 1, page 971).

Zn-S

ZnS melts at about 1600-1700 C (Ref. 1, page 1039). Its crystal structure is cubic ($T_d^2 - F_4^- 3m$) with $a_0 = 5.42 \text{ \AA}$ and 8 atoms per unit cell (Ref. 3, page 205) (zincblende, low temperature).

Zn-Se

Zinc and selenium are immiscible in the liquid state; as a layer of solid ZnSe is formed at the interface (Ref. 1, page 1069). The compound is isomorphous with zinc blende ($T_d^2 - F_4^- 3m$) and has $a_0 = 5.661 \text{ \AA}$.⁽⁶⁹⁾

Zn-Sr

The compound SrZn_{13} is face-centered cubic, space group $O_h^6 - Fm3c$, with $a_0 = 12.215 \pm 0.005 \text{ \AA}$ and 112 atoms per unit cell.⁽¹⁰⁾ Crystal data lists $a_0 = 12.24 \text{ \AA}$.⁽⁶⁾

From a comparison of the Zn-Ba and Zn-Ca systems one may obtain an estimate of the solubility of strontium in zinc as follows: There is no eutectic between SrZn_{13} and Zn, unless a eutectic is located very close to 100 a/o Zn and 419 C. From the nearly median position of strontium between calcium and barium in melting point, Goldschmidt radius and lattice parameter of the MeZn_{13} compound (size factors), but the somewhat

lower boiling point compared to that of calcium and barium (bonding factor), one might estimate the heat of formation of SrZn_{13} to be a little above the average between that of BaZn_{13} and CaZn_{13} . Hence, the solubility curve for strontium is likely to be somewhat steeper than the average of the curves for calcium and barium. Thus, one may assume the liquidus curve to pass through a point at about 5.5 a/o strontium and 825 C ($1/T = 9.1 \times 10^{-4}$).

Zn-Te

The liquidus between ZnTe (m.p. 1239 C) and 100 a/o zinc could not be determined with any accuracy as a result of the volatility of zinc. Modern techniques may be applied here to give more definite results. There may be a eutectic at 419 C close to the zinc axis (Ref. 1, page 1085). ZnTe is isomorphous with ZnS (zinc blende) and has $a_0 = 6.089 \text{ \AA}$.⁽⁷⁰⁾

Zn-Th

The compound ThZn_9 is isomorphous with many compounds of the AB_5 type. It has the space group $D_{6h}^{16} - p6/mmm$ with $a = 5.248 \text{ \AA}$, $c = 4.451 \text{ \AA}$, $c/a = 0.8481$ and 6 atoms per unit cell.^(6,15,16) Nowotny⁽¹⁵⁾ writes the formula of the compound as $(\text{Th}_{0.6} \text{Zn}_{0.4})\text{Zn}_5$, indicating that some of the thorium atoms are replaced by zinc atoms in the lattice structure.

Th_2Zn has also been reported.⁽¹⁶⁾

Zn-V

Corrosion data indicate a relatively high solubility of vanadium in liquid zinc.⁽⁶⁴⁾

Zn-W

It has been reported that tungsten does not dissolve in zinc at 1350 C.⁽¹³⁾ In view of the results obtained by Knighton for molybdenum⁽⁶³⁾ this report needs confirmation. Corrosion data indicate, however, that tungsten may be less soluble in liquid zinc than molybdenum.⁽⁶⁴⁾

B. SYSTEMS WITH A LIQUID MISCIBILITY GAP

Zn-Bi

The most recent determination of the convolute has been made by Kleppa by means of activity measurements.⁽¹⁷⁾ His data for the critical point and the branch facing the zinc axis do not agree with previous work (Ref. 1, page 348).

Table I of Appendix III lists the data obtained by Kleppa. The critical point was determined to be at 605 C and at 85 a/o zinc. Ref. 1 gives a monotectic point at 416 C and 99.34 a/o zinc. At this temperature the bismuth-rich layer contains about 37 a/o zinc. There is a eutectic at 254.5 C and 8.1 a/o zinc.⁽¹⁾

Zn-K

The miscibility gap is very extensive and appears to include the composition KZn_{13} . This compound dissociates at about 590 C, so that between 590 and 419.4 a two-phase region, KZn_{13} + liquid, exists and two liquid phases above 590 C (Ref. 1, page 842).

KZn_{13} belongs to the space group O_h^6 - Fm3c with $a_0 = 12.360 \text{ \AA}$ and 112 atoms per unit cell.^(11,18)

Zn-Na

The phase diagram is similar to that of the Zn-K system. At 557 C the compound NaZn_{13} decomposes and two liquid phases are formed (Ref. 1, page 934). Liquidus data below 557 C were taken from Mathewson and are shown in Figure 2. The data are listed in Table XX.

NaZn_{13} is isomorphous with KZn_{13} , space group O_h^6 - Fm3c, $a_0 = 12.2836 \pm 0.0003 \text{ \AA}$, 112 atoms per unit cell.^(11,18)

Zn-Pb

The data obtained by Waring and co-workers are tabulated in Table II.⁽²⁰⁾ The critical point is at about 790 C and the critical composition is about 76 a/o zinc. There is a monotectic point at 417.8 C and 99.98 a/o zinc, and a eutectic at 318.2 C and 1.6 a/o zinc.

Zn-Tl

The miscibility gap extends from a monotectic point at 99.2 a/o zinc to a thallium-rich solution with about 15 a/o zinc at 416 C. There is a eutectic at 291 C, 10.3 a/o zinc (Ref. 1, page 1087).

C. SIMPLE EUTECTIC SYSTEMS

Zn-Al

The eutectic occurs at 88.7 a/o zinc (95.0 w/o) and 382 C.(21,22) A suspected peritectic reaction at 443 C could not be confirmed. Aluminum solubility data between 50 and 88.7 a/o zinc are tabulated in Table IV, Appendix III. The liquidus curve is plotted in Figure 1. Solet and St. Clair reported a liquidus curve slightly displaced to higher temperatures, but the complete reference was not available and had, therefore, to be disregarded.(23)

Zn-Cd

The eutectic occurs at 265 C and 26.7 a/o Zn (Ref. 1, page 462). The liquidus curve is plotted in Figure 1.

Zn-Ga

The system has a eutectic at 25 C and about 5.3 a/o zinc.(24) The liquidus curve is plotted in Figure 1.

Zn-Ge

The eutectic occurs at 398 C and 94.6 a/o zinc. The liquidus curve is plotted in Figure 1. Solubility data between 50 and 94.6 a/o zinc are tabulated in Table XIV.(25)

Zn-Hg

This system has a eutectic at -42.5 C and 1.6 a/o zinc. Actually, however, the system belongs to a class by itself for the purpose of this survey, since two peritectic transformations take place: at 42.9 C, 10 a/o zinc and at 20 C, and about 6 a/o zinc. The peritectics may involve compounds of the compositions Hg_3Zn_8 and HgZn_2 , but at lower temperatures the zinc contents decrease below the stoichiometric amounts. The order of precipitation from a zinc-rich solution is as follows: From a liquid containing 100 to 10 a/o zinc, zinc precipitates. Between 10 and 6 a/o zinc, " Hg_3Zn_8 " precipitates and between 6 and 1.6 a/o zinc, " HgZn_2 " crystallizes (Ref. 1, page 819). The liquidus curve is plotted in Figure 1.

The composition of Hg_3Zn_8 is hexagonal with $a = 2.7132 \text{ \AA}$, $c = 5.4801 \text{ \AA}$, and $c/a = 2.0198$.(6)

Zn-In

The system has a eutectic at about 143 C and probably at about 2.0 a/o Zn. There is some disagreement about the eutectic composition, having been given as 8, 4, 2.8 and 2.0 a/o Zn.(26-30) The liquidus curve is plotted in Figure 1.

Zn-Sn

The eutectic occurs at 15.2 a/o zinc and 199 C (Ref. 1, page 1080). The liquidus curve is plotted in Figure 1.

D. SYSTEMS FOR WHICH LIQUIDUS DATA ARE AVAILABLE, WITH THE EXCEPTION OF SIMPLE EUTECTIC SYSTEMS

Zn-Ag

The system has five solid phases at room temperature: α -solid solution of zinc in silver (0-35 a/o zinc), ξ (48-53 a/o zinc) transforming into β at higher temperatures, γ (60-62.5 a/o zinc), ϵ (71-84 a/o zinc) and η -solid solution of silver in zinc (Ref. 1, page 69). The liquidus has four peritectics.⁽³¹⁾

The silver solubility curve is drawn in Figure 11. The data were obtained from a curve in Ref. 31 and are listed in Table III. The γ phase, "Ag₅Zn₈," belongs to the space group $T_d^3 - I\bar{4}3m$, with $a_0 = 9.3407 \pm 0.003 \text{ \AA}$ (at 61 a/o Zn) and 52 atoms per unit cell.^(6,32)

Zn-As

There are two solid phases at room temperature aside from the two terminal phases: ZnAs₂ between 25 and 33.5 a/o zinc, and Zn₃As₂ at 60 a/o zinc. Zn₃As₂ undergoes an allotropic transformation at 672 C.⁽⁷¹⁾ The liquidus has two maxima, at 771 C and 33.3 a/o zinc, and at 1015 C and 60 a/o zinc. There is a eutectic at 20 a/o zinc and 723 C and one at 39 a/o zinc and 760 C. There appears to be no eutectic or peritectic at more than 1 C from the melting point of pure zinc. The exact point of intersection of the liquidus with the 672 C horizontal (Zn₃As₂ transition) is not known, but an extrapolation of Figure 12 to 672 C ($1/T = 10.59 \times 10^{-4}$) yields 96.35 a/o zinc.

The solubility data are plotted in Figure 13 from data tabulated in Table V. The compound Zn₃As₂ appears to be the only product of primary crystallization for liquid compositions of more than 60 a/o zinc.

Zn₃As₂ is tetragonal ($D_{4h}^{15} - P4/nmc$) with $a = 8.31_6 \text{ \AA}$, $c = 11.76 \text{ \AA}$, $c/a = 1.41_8$ and 40 atoms per unit cell.

Zn-Au

Seven solid phases appear at room temperature:⁽³³⁾ α -solid solution of zinc in gold from 0-9 a/o zinc; an α_2 -phase (Au₃Zn) between 20 and 30 a/o zinc; a β -phase (AuZn) between 38 and 57 a/o zinc; a γ -phase (AuZn₂ or a solid solution of gold in AuZn₃) between 65 and 69 a/o zinc; a γ_2 -phase (AuZn₃) between 72 and 79 a/o zinc;

an ϵ phase at about 88 a/o zinc; and an η -solid solution of gold in zinc. α_2 transforms into α at higher temperatures and disappears above 425 C; γ_2 transforms into γ_1 , and this into γ as the temperature is increased, γ being stable only above 150 C.

The liquidus shows maxima at 725 C (AuZn) and at 644 C (AuZn₂), and two peritectics:

There are two eutectics, at 626 C and 62.5 a/o zinc and at 642 C and 34.5 a/o zinc. The primary crystallization product from melts containing between 66 and 91.5 a/o zinc is the γ -phase (AuZn₂) which decomposes eutectoidally into $\beta + \gamma_1$ at 150 C (compositions between 62 and 75 a/o zinc) or into $\gamma_1 + \epsilon$ (compositions between 75 and 83 a/o zinc at 416 C); γ_1 in turn will form γ_2 or $\gamma_2 + \epsilon$ at lower temperatures. Between 91.5 and 97 a/o zinc ϵ precipitates and from 97 to 100 a/o zinc the η -phase solidifies.

The phases which may be present in an unannealed specimen with 66 a/o zinc or more are: η , ϵ , γ_2 , γ_1 and a trace of β .

The liquidus between 67 and 100 a/o zinc is plotted in Figure 11. The data are taken from Ref. 33 and listed in Table VI.

The γ -phase is cubic ($T_d^3 - 1\bar{4}3m$). γ_1 (at 75 a/o zinc) is cubic, probably with 32 atoms per unit cell;⁽³⁴⁾ γ_2 (at 77 a/o zinc) is cubic with 90 atoms per unit cell;⁽³⁴⁾ ϵ and η are close-packed hexagonal with axial ratios of 1.55-1.60 and 1.80-1.90, respectively (Ref. 2, page 1174).

Zn-Ba

Knighton has determined the solubility of barium in zinc between 800 and 600 C by a sampling method.⁽⁶³⁾ His data are listed in Table VII and are plotted in Figure 3. An extrapolation of these data shows the solubility at 900 C to be in essential agreement with the one literature value found, namely 5.3 a/o barium at about 900 C.⁽¹⁰⁾ This point is included in Figure 3.

There does not appear to be a zinc-rich eutectic.⁽¹⁰⁾

There exists a compound BaZn₁₃ which is face-centered cubic, probably belonging to the space group $O_h^6 - Fm3c$ and having $a_0 = 12.33 \pm 0.005 \text{ \AA}$ and 112 atoms per unit cell.⁽¹¹⁾ BaZn₅ is orthorhombic, space group $D_{2h}^{17} - Amam$, $a = 5.37 \text{ \AA}$, $b = 10.85 \text{ \AA}$, $c = 8.50 \text{ \AA}$ and 24 atoms per unit cell.⁽¹²⁾ It is noteworthy that BaZn₅ apparently does not belong to the space group $D_{6h}^1 - P6/mmm$ as do CaZn₅, LaZn₅ and possibly ThZn₉. This point has been elaborated upon in the discussion.

Zn-Ca

The phase relations on the calcium-rich side are not clear.^(1,35) Between 60 and 100 a/o zinc there are four solid phases with very limited ranges of homogeneity: Ca_2Zn_3 , CaZn_5 , CaZn_{13} and Zn.⁽³⁶⁾ The formulas CaZn_5 and CaZn_{13} have been established by X-ray diffraction.^(11,35,37)

The liquidus in this range shows maxima at 688 C (Ca_2Zn_3) and 717 C (CaZn_{13}), and a peritectic at 675 C and about 80 a/o zinc involving CaZn_5 .⁽³⁶⁾ There is a eutectic between CaZn_5 and Ca_2Zn_3 and one between Ca_2Zn_3 and Ca, the exact locations of which are not certain. No eutectic has been found between CaZn_{13} and Zn.⁽³⁶⁾

The liquidus between 90 and 100 a/o Zn has been plotted in Figure 3 from Donski's data⁽³⁶⁾ (Table VIII). Because of his assignment of CaZn_{10} to the first maximum it appears likely that his data are somewhat in error, even though Pâris agrees with Donski in this range.⁽³⁸⁾

CaZn_5 has D_{6h} symmetry, possibly D_{6h}^1 - $P6/mmm$ with $a = 5.405 \text{ \AA}$, $c = 4.183 \text{ \AA}$, $c/a = 0.774$ and 6 atoms per unit cell.⁽³⁷⁾ Nowotny finds $a = 5.371 \text{ \AA}$, $c = 4.242 \text{ \AA}$, $c/a = 0.789$.⁽³⁵⁾

CaZn_{13} belongs to the space group O_h^6 - $Fm3c$ with $a_0 = 12.33 \pm 0.005 \text{ \AA}$, and 112 atoms per unit cell.⁽¹¹⁾

Zn-Ce

Two solid phases, $\delta(\text{CeZn}_9)$ and $\epsilon(\text{CeZn}_{11})$, besides a terminal solid solution, η , of cerium in zinc have been found between 90 and 100 a/o zinc.⁽⁶⁶⁾ Compounds CeZn_5 and CeZn also have been identified.⁽⁶⁰⁾

The liquidus curve has a maximum at 972 C at the composition CeZn_9 and two peritectics

The liquidus between 90 and 99.9 a/o zinc is plotted in Figure 4 from points obtained from a diagram in Ref. 60. The region below 2.8 a/o cerium is doubtful.

Recently Knighton has obtained solubility data below 1 a/o cerium.⁽⁶³⁾ These data also are plotted in Figure 3. They are likely to be more reliable than those of Ref. 60. A composite of the data is listed in Table IX.

The products of primary crystallization are CeZn_9 between 90 and 97.2 a/o zinc, CeZn_{11} between 97.2 and 99.9 a/o zinc and the terminal solid solution in zinc between 99.9 and 100 a/o zinc. All three phases may be present in a rapidly solidified melt.

CeZn (O_h^1 - Pm3m) is cubic, $a_0 = 3.70 \text{ \AA}$. $CeZn_{11}$ belongs to D_{2h}^{19} - I4/amd and has $a = 10.66 \text{ \AA}$, $c = 6.86 \text{ \AA}$, and 48 atoms per unit cell.(67)

Zn-Co

The system is rather complicated.(39,40) Between 70 and 100 a/o zinc the following solid phases appear at room temperature: Γ up to about 84 a/o zinc; δ_1 between 87 and 89 a/o zinc, ξ at about 92 a/o zinc, and zinc. δ_1 has an allotropic modification, δ , between 746 C and 675 C. High temperature phases appearing at higher cobalt concentrations are β and β' .

The complete liquidus has six peritectic points

δ transforms peritectoidally into δ_1 at 675 C. There appear to be no eutectics.

Primary crystallization proceeds as follows: β_1 between 66.1 and 70.9 a/o zinc, Γ between 70.9 and 93.4 a/o zinc, δ between 93.4 and 98.0 a/o zinc, and ξ between 98.0 and 100 a/o zinc. Γ , δ_1 and ξ may be formed at room temperature.

The liquidus from 63.1 to 100 a/o zinc is plotted in Figure 8. The data were taken from the diagram in Ref. 39, except for the peritectic points, and are listed in Table X.

The Γ phase is cubic with $a_0 = 8.878 \text{ \AA}$.(14) The ξ phase ($CoZn_{13}$) is monoclinic with $a = 13.47 \text{ \AA}$, $b = 7.49 \text{ \AA}$, $c = 5.06 \text{ \AA}$, $\beta = 127^\circ 5'$.(40)

A similar phase, apparently isomorphous to $CoZn_{13}$ (?), appears in the Fe-Zn system (see below) and has been assigned to the space group C_{2h}^3 - C2/m or a subgroup. In Ref. 6 this Fe-Zn phase is listed as monoclinic, but with revised unit cell dimensions and angle (shorter angle, shorter a-parameter). This could possibly apply also to ξ - $CoZn_{13}$.

Zn-Cr

There are three solid phases at room temperature: α -solid solution of zinc in chromium between 0 and 30 a/o zinc; a θ -phase (CrZn_{17}) at about 94.5 a/o zinc, and zinc.⁽⁴¹⁾

The liquidus shows a peritectic at 464 C and about 98.67 a/o zinc, and a eutectic at 415 C and 99.67 a/o zinc.^(41,42)

The liquidus between 98.67 and 99.67 a/o zinc is plotted in Figure 6, from tabulated data (Table XI). No further reliable solubility data are known.

CrZn_{17} is probably hexagonal with $a = 12.89 \text{ \AA}$, $c = 30.5 \text{ \AA}$ and $c/a = 2.37$.⁽⁴³⁾

Zn-Cu

There are five solid phases at room temperature (Ref. 2, page 1206): α -solid solution of zinc in copper between 0 and 35 a/o zinc, β' between 46 and 49.5 a/o zinc, γ between 59 and 67.5 a/o zinc, ϵ between 78 and 86 a/o zinc, and η -solid solution of copper in zinc.

β' has a high temperature modification, β . Between the γ and ϵ regions at temperatures between 557 C and 699 C there is an additional δ phase which decomposes eutectoidally to $\gamma + \epsilon$.

There are five peritectics:

There are no eutectics.

Primary crystallization proceeds as follows: Between 60 and 80 a/o zinc, γ precipitates from the melt. Between 80 and 88 a/o zinc, δ precipitates, but between 597 C and 557 C ϵ is formed from δ in the solid state and at 557 C the remainder of δ transforms into $\gamma + \epsilon$. From melt compositions between 88 and 98.4 a/o zinc ϵ precipitates and at still higher zinc contents the η -solid solution. Thus, a melt containing originally about 65 a/o zinc will eventually solidify into a non-equilibrium mixture of γ , ϵ and η .

The liquidus between 60 and 100 a/o zinc is plotted in Figure 11. The data were taken from a tabulation by Schramm,⁽⁴⁴⁾ who took special precautions in the region with less than 3.5 a/o copper. This region was re-investigated by Anderson and co-workers,⁽⁴⁵⁾ whose data do not appear to differ significantly from those of Schramm's.

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Edmunds re-investigated the region between 1.8 and 11 a/o copper by means of the sampling technique previously discussed.⁽⁷⁾ His data are from about 5 to 10 degrees higher than those obtained by thermal analysis. These data are in Figure 15. All relevant data are listed in Table XII.

The γ phase (Cu_5Zn_8 ?) belongs to the space group $T_d^3 - I\bar{4}3m$, $a_0 = 8.87 \text{ \AA}$.⁽⁶⁾

The ϵ phase is close-packed hexagonal. According to Montoro, $c = 4.288 \pm 0.001 \text{ \AA}$, independent of composition, whereas "a" varies from 2.66 to 2.673 $\text{\AA}$.⁽⁴⁶⁾ Schubert and Wall determined $a = 2.740 \pm 0.002 \text{ \AA}$, $c = 4.296 \text{ \AA}$ and $c/a = 1.567$ at 79 a/o zinc.⁽⁴⁷⁾

The η -phase is close-packed hexagonal with $a = 2.6785 \text{ \AA}$, $c = 4.8221 \text{ \AA}$, $c/a = 1.8012$ at 2.6 a/o copper (Ref. 2, page 1206).

Zn-Fe

According to Schramm there are five solid phases at room temperature: α -solid solution of zinc in iron between 0 and 5 a/o zinc, Γ ($\text{Fe}_3\text{Zn}_{10}$?) between 67 and 75 a/o zinc, δ_1 (FeZn_9 ?) between 87 and 91 a/o zinc, ξ (FeZn_{13} ?) at about 93 a/o zinc and zinc.⁽³⁹⁾ Lihl found only four phases, the δ_1 phase being absent.⁽⁹⁾ Schramm's work will be assumed to be correct here.

There are three peritectics:

There is a eutectic at about 0.05 degree below the melting point of zinc and 99.98₃ a/o zinc.

Primary crystallization proceeds as follows: γ -iron precipitates from solutions containing less than 91.4 a/o zinc. Between 91.4 and 96.5 a/o zinc the ϵ phase is the product of primary crystallization; between 96.5 and 99.5 a/o zinc the δ_1 phase crystallizes and above 99.5 a/o zinc the ξ -phase. Because of the transformations which iron and solid solutions in iron undergo, the non-equilibrium room-temperature phases which may be found after complete solidification are α -Fe, zinc, and the Γ , δ_1 and ξ phases.

Liquidus data between 11 and 0.02 a/o iron are plotted in Figure 9 from tabulated data obtained by Edmunds⁽⁷⁾ and by Truesdale and co-workers⁽⁸⁾ by means of a liquid-sampling technique. A composite of these data is shown in Table XIII.

The α phase is body-centered cubic and has a lattice parameter of around $a_0 = 2.889 \text{ \AA}$.^(2,6,39) The Γ phase is cubic with 52 atoms per unit cell and $8.9560 < a_0 < 8.9997 \text{ \AA}$. The δ_1 phase is hexagonal, space group probably $D_{6h}^4 - C6/mmc$ with $a = 12.80 \pm 0.001 \text{ \AA}$, $c = 57.6 \text{ \AA}$, $c/a = 1.130$ and 550 ± 8 atoms per unit cell.⁽⁴⁸⁾ The ξ phase is monoclinic, space group $C_{2h}^3 - C2/m$ or a subgroup, with $a = 13.65 \text{ \AA}$, $b = 7.61 \text{ \AA}$, $c = 5.06 \text{ \AA}$, $\beta = 128^\circ 44'$ and 48 atoms per unit cell.⁽⁴⁹⁾ The parameters for this phase are also given as $a = 10.76 \text{ \AA}$, $b = 7.61 \text{ \AA}$, $c = 5.06 \text{ \AA}$, $\beta = 98^\circ 26'$.⁽⁶⁾ The Metals Handbook (Ref. 2, page 1220) lists this phase as hexagonal, however.

Ekman's compound $\text{Fe}_5\text{Zn}_{21}$ ⁽¹⁴⁾ is likely to be the Γ phase designated as $\text{Fe}_3\text{Zn}_{10}$.

Zn-La

Two solid phases, δ (LaZn_9) and ϵ (LaZn_{11}), besides a terminal zinc phase, appear between 90 and 100 a/o zinc.⁽⁶⁰⁾ LaZn and LaZn_5 have also been identified.^(60,61)

The liquidus curve has a maximum at 962 C at the composition LaZn_9 , a peritectic $L + \text{LaZn}_9 \rightleftharpoons \text{LaZn}_{11}$ at 848 C and 96.25 a/o zinc, and a eutectic at 415 C and 99.73 a/o zinc.

The liquidus between 90 and 100 a/o zinc is plotted in Figure 4 from points obtained from a diagram in Ref. 60 and listed in Table XV.

The products of primary crystallization are LaZn_9 between 90 and 96.25 a/o zinc and LaZn_{11} between 96.25 and 99.73 a/o zinc. LaZn_9 , LaZn_{11} and zinc may be found in rapidly solidified melt.

LaZn is cubic ($O_h^1 - \text{Pm}3m$) with $a_0 = 3.75 \text{ \AA}$. LaZn_{11} is body-centered tetragonal, space group $D_{2h}^{19} - I4/amd$, $a = 10.68 \text{ \AA}$, $c = 6.87 \text{ \AA}$, 48 atoms per unit cell.⁽⁶⁷⁾

Zn-Li

There are several solid phases at room temperature (Ref. 1, page 858). Lithium may contain up to 1 a/o zinc in solid solution. There is a δ phase (Li_2Zn_3) which may exist between 50 and 61 a/o zinc in one of several forms, depending upon temperature and composition. At 66.6 a/o zinc the compound LiZn_2 exists, but this compound decomposes above 100 C. Between 70.5 and 72 a/o zinc there is a γ' phase. β' (LiZn_9 ?) exists between 78 and 83 a/o zinc. High-temperature γ and β phases decompose eutectoidally into γ' and β' , and into β' and zinc, respectively.

The liquidus has a maximum at the composition Li_2Zn_3 and 520 C and has two peritectics:

There is a eutectic at 403 C and 95 a/o zinc and another at 161 C and 4.5 a/o zinc.

Between 66.6 and 100 a/o zinc the following order of precipitation occurs: Between 66.6 and 71.5 a/o zinc δ precipitates, between 71.5 and 80 a/o zinc γ precipitates, and between 80 and 95 a/o zinc β precipitates. In the solidified melt one may find mixtures of two or more of the following phases: Li_2Zn_3 (δ), LiZn_2 , γ' , β' and zinc, and possibly β , since the $\beta \rightleftharpoons \beta' + \text{Zn}$ eutectoid lies at only 65 C.

A plot of the liquidus between 66.6 and 95 a/o zinc is shown in Figure 2 from data listed in Table XVI.

The δ phase probably belongs to the space group $O_h^7 - \text{Fd}3\text{m}$ with $a_0 = 6.22 \text{ \AA}$ and 16 (?) atoms per unit cell.(6) The β' phase is hexagonal ($D_{6h}^4 - \text{C}6/\text{mmc}$) with $a = 2.78 \text{ \AA}$, $c = 4.37 \text{ \AA}$, $c/a = 1.58$. The γ' phase is hexagonal with $a = 4.36 \text{ \AA}$, $c = 2.51 \text{ \AA}$, $c/a = 0.576$.(3)

Zn-Mg

Five solid phases occur at room temperature (Ref. 1, page 877): an α -solid solution of zinc in magnesium containing up to about 1 a/o zinc, compounds MgZn , MgZn_2 and $\text{Mg}_2\text{Zn}_{11}$ (MgZn_5) with little or no homogeneity range, and zinc.

The liquidus has a maximum at 590 C at the composition MgZn_2 . At higher zinc concentrations there is a peritectic, $\text{L} + \text{MgZn}_2 \rightleftharpoons \text{Mg}_2\text{Zn}_{11}$, at 380.5 C and 91.4 a/o zinc, and a eutectic at 364 C and 92.4 a/o zinc.

The primary crystallization proceeds in the order: MgZn_2 between 66.6 and 91.4 a/o zinc, and $\text{Mg}_2\text{Zn}_{11}$ between 91.4 and 92.4 a/o zinc.

At room temperature one may find MgZn_2 , $\text{Mg}_2\text{Zn}_{11}$ and Zn.

The liquidus between 66.6 and 92.4 a/o zinc has been plotted in Figure 3 from data tabulated by Hume-Rothery and Rounsefell(50) and listed in Table XVII.

The structure of MgZn_2 is hexagonal, space group $D_{6h}^4 - \text{C}6/\text{mmc}$ with $a = 5.15 - 5.21 \text{ \AA}$, $c = 8.48 - 8.60 \text{ \AA}$, $c/a = 1.644 - 1.651$, and 12 atoms per unit cell.(6)

$\text{Mg}_2\text{Zn}_{11}$ has the space group $T_h^1 - \text{Pm}3$ with $a_0 = 8.535 \pm 0.005 \text{ kX}$ (51,52) and 39 atoms per unit cell, but has also been reported as hexagonal.(6)

Zn-Mn

There are a number of solid phases at room temperature (Ref. 2, page 1229): zinc, β between 92.5 and 92 a/o zinc (MnZn_{13} , MnZn_{11} ?), γ' (MnZn_9 ?) between 89 and 91 a/o zinc, ϵ (MnZn_4 ?) between 85 and 79 a/o zinc, ξ between 75 and 70 a/o zinc, and others at higher manganese content. γ' transforms into γ and ϵ , and ξ into δ at higher temperatures.

There are three peritectics known:

There is a eutectic at 417.25 C and about 99.5 a/o zinc.⁽⁴²⁾

Primary crystallization occurs in the following order: δ precipitates between 63 and 97.5 a/o zinc, γ between 97.5 and 99 a/o zinc and β between 97 and 99.5 a/o zinc. At room temperature one may find mixtures of zinc, β , γ' , ξ and a high manganese phase.

Liquidus data between 63 and 99.5 a/o zinc are plotted in Figure 7 from data by Schramm⁽⁷⁴⁾ and unpublished data from the New Jersey Zinc Co., both quoted by Edmunds.⁽⁷⁾ Edmunds' data, obtained by the sampling technique, are also shown in Figure 15. A composite of these is given in Table XVIII.

The ϵ phase is cubic (O_h^9 , T_d^1 or T_d^3) with $a_0 = 9.14$. The γ' phase is hexagonal (probably D_{6h}^4 - C6/mmc) with $a = 12.8 \text{ \AA}$, $c = 57.6 \text{ \AA}$, $c/a = 4.50$, and the β phase is monoclinic with $a = 13.7 \text{ \AA}$, $b = 7.6 \text{ \AA}$, $c = 5.1 \text{ \AA}$ and $\beta = 127^\circ 5'$.

Zn-Mo

Although it had been reported that molybdenum does not dissolve in zinc at 1350 C,⁽¹³⁾ Knighton has been able to obtain solubility data between 800 C and 500 C.⁽⁶³⁾ These are plotted in Figure 6 and listed in Table XIX. These data were obtained, however, in zinc saturated with uranium.

Zn-Ni

There are six solid phases at room temperature (Ref. 2, page 1236): α -solid solution of zinc in nickel between 0 and about 20 a/o zinc, β' (NiZn) between 47 and 52 a/o zinc, γ' (including the composition NiZn₃) between 72 and 76 a/o zinc, γ (including the compositions NiZn₄, Ni₅Zn₂₁) between 77 and 85 a/o zinc, δ at about 88 a/o zinc and a terminal zinc phase (NiZn₈?). At elevated temperatures β' decomposes peritectoidally into $\alpha + \beta$, whereas β decomposes eutectoidally into $\beta' + \gamma$. γ' decomposes peritectoidally into $\beta' + \gamma$. The distinction between γ' and γ may be artificial.

There are two peritectics:

The liquidus curve has a maximum at 882 C and about 75 a/o zinc.

Between 75 and 99.1 a/o zinc the γ phase is the product of primary crystallization, and between 99.1 and 100 a/o zinc it is the δ phase. At room temperatures the phases γ , δ and zinc may occur after non-equilibrium solidification of a melt containing more than 76 a/o zinc.

The solubility curve has been plotted in Figure 8 from data tabulated by Heike and co-workers⁽⁵³⁾ and listed in Table XXI.

The γ phase ($\text{Ni}_5\text{Zn}_{21}$) is cubic, possibly body-centered, with $a_0 = 8.904 \text{ \AA}$.^(2,14) The δ phase is hexagonal, $a = 8.873 \text{ \AA}$, $c = 14.63 \text{ \AA}$, $c/a = 1.649$.⁽²⁾

Zn-Pd

There are eight solid phases at room temperatures:⁽⁵⁴⁾ α -solid solution of zinc in palladium between 0 to 16 a/o zinc, a ξ phase between 34 and 35 a/o zinc, a θ phase between 38 and 50 a/o zinc, a ξ_1 phase between 60 and 61 a/o zinc, a γ_1 phase ($\text{Pd}_5\text{Zn}_{21}$?) between 76 and 80.5 a/o zinc, γ_2 between 82 and 85 a/o zinc, η between 92 and 93 a/o zinc, and a terminal zinc phase. At higher temperatures ξ transforms into a β phase (Pd_2Zn), which itself shows a eutectoid decomposition into $\xi + \theta$. The situation is similar with ξ_1 , forming β_1 (Pd_2Zn_3) at higher temperatures, β_1 decomposing eutectoidally into $\xi_1 + \gamma_1$.

The liquidus is known only between about 77 and 94 a/o zinc. There is a eutectic at about 77.5 a/o zinc and two peritectics:

and a maximum at about 78 a/o zinc and 895 C.

The liquidus between 78 a/o and 98 a/o zinc, which includes an estimate of the section between 94 and 98 a/o zinc, is plotted in Figure 10 from a curve in Ref. 54. Two points obtained by Knighton are also shown in Figure 10. The data are listed in Table XXII.

The products of primary crystallization are: γ_1 between 78 and 94 a/o zinc, γ between 94 and 98 a/o zinc and η between 98 and 100 a/o zinc. One may obtain mixtures containing γ_1 , γ , η and zinc from a solidified melt.

A γ -phase composition of 81.6 a/o zinc has a lattice parameter of $9.107 \text{ \AA}$. The phase is cubic and has 52 atoms per unit cell.⁽¹⁴⁾ The η phase is close-packed hexagonal with $c/a = 1.55$.⁽⁵⁴⁾

Pt-Zn

The phase relationships at room temperature are similar to those in the system Pd-Zn.⁽⁵⁵⁾ The α phase lies between 0 and 22 a/o zinc, θ between 32 and 41 a/o zinc, ξ_1 between 63 and 64 a/o zinc, γ_1 (PtZn_2)

between 73.5 and 77 a/o zinc, (PtZn_4 , $\text{Pt}_5\text{Zn}_{21}$?) between 77.5 and 80.5 a/o zinc, and Γ (PtZn_9 ?) between 89 and 90 a/o zinc. At higher temperatures ξ_1 transforms into ξ , which itself decomposes eutectoidally into $\xi_1 + \gamma_1$. The liquidus curve is known only between 87 and 97 a/o zinc. There is a peritectic

and probably another at 425 C and 99.5 a/o zinc.

Between 85 and 94.5 a/o zinc, γ_1 is the product of primary crystallization, γ between 94.5 and 99.5 a/o zinc, and Γ between 99.5 and 100 a/o zinc.

The liquidus curve between 87 and 97 a/o zinc has been plotted in Figure 10 from data taken from a curve in Ref. 55. The data are listed in Table XXIII.

Mixtures of γ_1 , γ , Γ and zinc may be found in a solidified melt.

$\text{Pt}_5\text{Zn}_{21}$ has been reported to be cubic with $a_0 = 18.079 \text{ \AA}$.⁽¹⁴⁾

Zn-Rh

A solid $\text{Rh}_5\text{Zn}_{21}$ -phase with a body-centered cubic structure has been identified.⁽¹⁴⁾ Knighton has obtained some solubility data between 800 C and 550 C,⁽⁶³⁾ which are listed in Table XXIV and plotted in Figure 10.

Zn-Ru

Knighton has obtained tentative solubility data between 750 C and 600 C,⁽⁶³⁾ which are listed in Table XXV and plotted in Figure 10.

Zn-Sb

There are three intermediate phases at room temperature: SbZn , Sb_3Zn_4 and Sb_2Zn_3 . Sb_3Zn_4 undergoes one, Sb_2Zn_3 two, transformations as the temperature is raised (Ref. 1, page 1057).

The liquidus shows two peritectics:

There is a maximum at 566 C and the composition Sb_2Zn_3 .

The eutectics are at 505 C and 32 a/o zinc, and at 413.75 C and 98.4 a/o zinc.⁽⁴²⁾

The liquidus between 60 and 98.4 a/o zinc is plotted in Figure 13 from points taken from the diagram in Ref. 1 (Table XXVI).

Zn-Si

No phase diagram is available. A few points on the liquidus curve between 96 and 100 a/o zinc are mentioned in Ref. 1, page 1074. These points are plotted in Figure 12 and listed in Table XXVII.

Zn-Ti

Information is available concerning the portion of the phase diagram between 90 and 100 a/o zinc. According to Gebhardt there is a compound TiZn_{15} and two peritectics: at 460 C and 99.2 a/o zinc, and at 490 C and 98.9 a/o zinc.⁽⁵⁶⁾ According to Anderson and co-workers there is in addition a compound TiZn_{10} , but no peritectic at 460 C whereas the 490 C peritectic was found at 485.⁽⁵⁷⁾ Gebhardt finds a eutectic at 99.4 a/o zinc and 418 C whereas Anderson finds it at 99.8 a/o zinc and 418.5 C. Other compounds which have been identified are TiZn_3 and TiZn_2 .^(58,59)

The products of primary crystallization are not quite certain. TiZn_3 , TiZn_{10} and TiZn_{15} may all be involved in the high zinc region.

Liquidus data have been taken from a curve in Ref. 56 and are plotted in Figure 5. They are listed in Table XXVIII.

The crystal structures of TiZn_{10} and TiZn_{15} are unknown. TiZn_3 belongs to the space group $\text{O}_h^1 - \text{Pm}3\text{m}$ with $a_0 = 3.9322 \pm 0.0003 \text{ \AA}$ and 4 atoms per unit cell⁽⁵⁸⁾ or with $a_0 = 3.023 \pm 0.005$.⁽⁵⁹⁾ TiZn_2 probably belongs to the space group $\text{D}_{6h}^4 - \text{C}6/\text{mmc}$ with $a = 5.064 \pm 0.002 \text{ \AA}$, $c = 8.210 \pm 0.002 \text{ \AA}$, $c/a = 1.621$.

Zn-U

Chiotti and co-workers have constructed a phase diagram in which, aside from the terminal phases, a compound UZn_9 appears. The compound melts congruently at $1050 \pm 20 \text{ C}$ and 5 atm.⁽⁶²⁾ The zinc-rich portion of the phase diagram was determined by sampling and other means, including vapor pressure measurements. Knighton has redetermined the solubility of uranium in zinc⁽⁶³⁾ by sampling method. His data are more consistent than Chiotti's data, as is evident from Figure 14. The sampling data are listed in Table XXIX.

UZn_9 was found to be hexagonal, symmetry class D_{6h} with $a_0 = 8.99 \text{ \AA}$, $c = 8.98 \text{ \AA}$ and $c/a = 0.999$.⁽⁶²⁾ Some modification of these numbers may be necessary, however.⁽⁷⁶⁾

Zn-Zr

Tentative phase relations are shown by Lustman and Kerze.⁽⁶⁵⁾ The following room temperature phases have been identified: ξ (ZrZn_{15} ?), ϵ (ZrZn_{10} ?), δ (ZrZn_3 ?), γ (ZrZn) and the two terminal phases.⁽⁶⁵⁾ The zinc-rich liquidus has probably three peritectics:⁽⁶⁵⁾

Chiotti also reports a definite peritectic horizontal at 750 C, and a less definite one at 850 C.⁽⁷⁵⁾ X-ray data show the composition of the ξ phase to be ZrZn_{14} rather than ZrZn_{15} . No clarification could be given as to whether one or two compounds exist between 85 and 90 a/o zinc (ZrZn_6 and ZrZn_{10}). X-ray work indicates that both formulas may be incorrect. The δ phase has a decomposition pressure of one atmosphere at about 910 C.

Gebhardt reports two peritectics, one at 545 C and 99.5 a/o zinc, and one at 970 C and 97.6 a/o zinc.⁽⁵⁶⁾ He also reports a eutectic at 416 C and 99.9₃ a/o zinc.⁽⁵⁶⁾

Knighton has recently obtained liquidus data between 550 C and 750 C by a sampling method.⁽⁶³⁾ He found solubilities considerably higher than Chiotti's and Gebhardt's. No explanation can be offered at this time, and a program is underway in which an attempt will be made to determine the reason for this and other discrepancies between thermal analysis and sampling results.

The liquidus data of Gebhardt (taken from his curve in Ref. 56) and of Knighton are tabulated in Table XXX. Both sets of data are shown in Figure 5. The straight line representing Knighton's data has been drawn without regard to the possible existence of peritectics in this range.

ZrZn_3 has a complicated X-ray pattern which was not analyzed.⁽⁷⁵⁾ An intermediate composition between " ZrZn_6 " and " ZrZn_{10} " shows hexagonal symmetry, $a = 8.02 \text{ \AA}$, $c = 7.31 \text{ \AA}$, $c/a = 0.901$. ZrZn_2 belongs to the group $O_h^7 - \text{Fd}3m$, with $a_0 = 7.3958 \text{ \AA}$, ZrZn_{14} is cubic, with unknown space group, $a_0 = 14.11 \text{ \AA}$.

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APPENDIX I

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APPENDIX II

SOLUBILITY CURVES

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FIGURE 1

LIQUIDUS CURVES FOR THE SYSTEMS ALUMINUM, CADMIUM,
GALLIUM, GERMANIUM, INDIUM, MERCURY AND TIN WITH ZINC

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APPENDIX III

TABLES OF SOLUBILITIES

Table I

MISCIBILITY GAP IN THE ZINC-BISMUTH SYSTEM

Temp (C)	Bi - Branch		Zn - Branch	
	a/o Bi	w/o Bi	a/o Bi	w/o Bi
~605	15	36.06	15	36.06
597	19.72	43.98		
595	23.58	49.65		
567	39.39	58.25		
~550			5.49	15.65
536	39.58	67.68		
520	44.77	72.14		
500			2.59	7.83
482	50.11	76.24		
475	53.45	78.59		
420	60.55	83.07		
416	63.0	84.47	0.66	2.20

Table II

MISCIBILITY GAP IN THE ZINC-LEAD SYSTEM

Temp (C)	Pb - Branch		Zn - Branch	
	a/o Pb	w/o Pb	a/o Pb	w/o Pb
790	24	50	24	50
775	47.3	74	13.0	32
750	57.3	81	9.1	24
700	69.9	88	5.3	15
650	78.5	92	3.0	9
600	83.2	94	2.0	6
550	88.4	96	1.3	4
500	91.1	97	0.73	2.3
450	93.1	97.7	0.46	1.44
417.8	93.9	98	0.02	0.63

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Table III

SOLUBILITY OF SILVER IN ZINC

Temp (C)	a/o Ag	w/o Ag
660.6	37	49.2
631.2	29.1	40.4
623	25	35.5
605	20	29.2
~ 580	15	22.6
545	10	15.5
495	5	8.0
430.7	1.9	3.1
419	0	0

Table IV

SOLUBILITY OF ALUMINUM IN ZINC

Temp (C)	a/o Al	w/o Al
562	70.8	50
537	61.8	40
507	50.9	30
472	37.7	20
420	21.2	10
382	11.3	5

Table V

SOLUBILITY OF ARSENIC IN ZINC

Temp (C)	a/o As	w/o As
1015	40	43.4
1006	36.8	40
970	30.4	33.5
955	27.2	30
883	17.9	20
815	11.7	13.2
792	8.8	10
725	5.8	6.6

Table VI

SOLUBILITY OF GOLD IN ZINC

Temp (C)	a/o Au	w/o Au
644	33.53	60.33
634	32.67	59.40
635	31.52	58.12
632	28.91	55.08
630	27.68	53.57
627	27.08	52.82
624	26.04	51.49
619	25.28	50.50
617	25.03	50.17
609	23.69	48.35
589	22.00	45.96
572	18.92	41.30
540	13.30	31.63
503	10.99	27.13
491	9.75	24.58
485	9.16	23.31
479	8.70	22.32
441	5.02	13.75
423	3.23	9.14
419	0	0

Table VII

SOLUBILITY OF BARIUM IN ZINC

Temp (C)	a/o Ba	w/o Ba
797	1.09	2.27
748	0.49	1.02
693	0.14	0.290
645	0.046	0.097
600	(0.009 ₅)	(0.02)

Table VIII

SOLUBILITY OF CALCIUM IN ZINC

Temp (C)	a/o Ca	w/o Ca
717	9.0	5.7
710	7.8	4.9
698	5.6	3.5
677	4.5	2.8

Table IX

SOLUBILITY OF CERIUM IN ZINC

Temp (C)	Schramm(60)		Knighton(63)	
	a/o Ce	w/o Ce	a/o Ce	w/o Ce
972	10	19.2		
964	9.1	17.7		
960	8.3	16.2		
950	7.7	15.2		
942	7.1	14.0		
916	5.8	11.6		
874	4.4	9.1		
840	3.4	7.0		
786	2.8	4.7		
780	2.0	4.2		
755	1.42	3.0		
742			0.825	1.75
728	0.99	2.1		
698			(0.153)	(0.326)
642			0.110	0.245
599			0.046	0.098
549			0.013	0.028
501			0.0044	0.0094
423	(0.11)	(0.24)		

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Table X

SOLUBILITY OF COBALT
IN ZINC

Temp (C)	a/o Co	w/o Co
966	36.9	34.5
924	33.9	31.5
895	29.1	27
855	16.4	15
805	11.0	10
746	6.6	6
725	5.5	5
675	3.0	2.7
566	1.1	0.9

Table XI

SOLUBILITY OF CHROMIUM
IN ZINC

Temp (C)	a/o Cr	w/o Cr
463	1.33	0.98
455	0.99	0.79
440	0.78	0.64
415	0.26	0.22

Table XII

SOLUBILITY OF COPPER IN ZINC

Temp (C)	Schramm(44)		Anderson(45)		Edmunds(7)	
	a/o Cu	w/o Cu	a/o Cu	w/o Cu	a/o Cu	w/o Cu
834	40.7	40				
833	39.7	39				
832	39.2	38.5				
816	33.2	32.5				
768	26.6	26				
759	25.6	25				
719	21.5	21				
706	20.5	20				
659	16.4	16				
601	12.3	12				
595					10.82	10.55
587					9.98	9.72
577	10.2	10				
543	7.2	7				
530					5.87	5.69
457	3.1	3	3.0	2.9		
448	2.8	2.7				
440					2.09	2.04
433.4	2.3	2.2				
430			2.16	2.08		
429					1.83	1.77
427.2	2.0 ₃	2.0				
425.4	1.9 ₆	1.9				
424.5			1.9 ₆	1.9		
424	1.8 ₅	1.8	1.7 ₅	1.7		
423.5	1.7 ₅	1.7				
423.1	1.6 ₅	1.6				
422.7			1.3	1.3		
422.6	1.5	1.5				
421.9			1.0	1.0		
421.3	1.0	1.0				
420.1			0.55	0.55		
419.4	0	0	0	0		

Table XIII

SOLUBILITY OF IRON IN ZINC

Temp (C)	Edmunds(7)		Truesdale(8)	
	a/o Fe	w/o Fe	a/o Fe	w/o Fe
(900)			(11.22)	9.75
875			10.54	9.15
850			9.77	8.65
825			9.41	8.15
800			8.89	7.70
782			8.55	7.40
775			8.03	6.95
750			6.55	5.65
725			5.40	4.65
700			4.48	3.85
675			3.55	3.05
672	3.51	3.02	3.49	3.00
650			2.04	1.75
625			1.28	1.10
600	1.01	0.86	0.82	0.70
575	0.63	0.53	0.53	0.45
550	0.37	0.31 ₆	0.35	0.30
525	0.22	0.19	0.23	0.20
500	0.12	0.10 ₃	0.11	0.10
475	0.065	0.056	0.070	0.06
450	0.033	0.029	0.035	0.03
425	0.020	0.014 ₃	0.024	0.02
419.4	0.013	0.012	0.020	0.018

Table XIV

SOLUBILITY OF
GERMANIUM IN ZINC

Temp (C)	a/o Ge	w/o Ge
958.5	100	100
905	89	90
840	73	75
770	67.5	60
720	48.4	51
615	22.7	35
585	27.9	30
540	23.1	25
480	13.7	15
398	5.4	6

Table XV

SOLUBILITY OF
LANTHANUM IN ZINC

Temp (C)	a/o La	w/o La
962	10	19.1
960	9.31	18.0
959	9.10	17.5
947	8.19	16.0
940	7.62	15.0
912	5.99	12.0
870	5.49	8.0
848	3.75	7.7
832	2.85	5.9
762	1.33	2.8
714	0.99	2.1
415	0.27	0.45

Table XVI

<u>SOLUBILITY OF LITHIUM IN ZINC</u>		
<u>Temp (C)</u>	<u>a/o Li</u>	<u>w/o Li</u>
520	40	6.61
516	35	5.40
513	33	4.97
501	28	3.96
498	27	3.78
496	26	3.59
479	18	2.28
471	15	1.84
446	10	1.17
403	5	0.56

Table XVII

<u>SOLUBILITY OF MAGNESIUM IN ZINC</u>		
<u>Temp (C)</u>	<u>a/o Mg</u>	<u>w/o Mg</u>
590	31.0	16.7
585	30.5	16.3
580	26.8	13.6
579	26.3	13.3
519	17.9	8.1
487	14.9	6.5
427	11.4	4.8
396	9.9	4.1
378	8.9	3.6
369	8.25	3.3

Table XVIII

SOLUBILITY OF MANGANESE IN ZINC

<u>Temp (C)</u>	<u>Schramm(74)</u>		<u>New Jersey Zinc(7)</u>		<u>Edmunds(7)</u>	
	<u>a/o Mn</u>	<u>w/o Mn</u>	<u>a/o Mn</u>	<u>w/o Mn</u>	<u>a/o Mn</u>	<u>w/o Mn</u>
800	34.5	30.7				
798					26.75	23.45
780			29.5	26.0		
760			27	23.7		
712			23.5	20.5		
700	23	20.1				
690			19.5	16.9		
660	17.5	15.1				
632	15.5	13.3				
611			14	12.0		
592			12	10.3		
582	11.9	10.2			10.10	8.61
576					9.91	8.45
567			10	8.5		
553			9	7.7		
535	8.9	7.6				
532			7.7	6.5		
527					6.45	5.47
498	5.95	5.04	4.95	4.19		
485					4.03	3.40
475	4.45	3.76				
446					2.14	1.80
442					2.01	1.69

Table XIX

SOLUBILITY OF
MOLYBDENUM IN ZINC

<u>Temp</u> <u>(C)</u>	<u>a/o Mo</u>	<u>w/o Mo</u>
800	0.024	0.035
750	0.020	0.029
700	0.015	0.022
650	0.014	0.021
600	0.010	0.015
550	0.010	0.015
500	0.0068	0.010

Table XX

SOLUBILITY OF SODIUM
IN ZINC

<u>Temp</u> <u>(C)</u>	<u>a/o Na</u>	<u>w/o Na</u>
557	11.5-6.8	4.4-2.5
550-545	5.5	2.0
550-535	3.7	1.3 ₃
543-523	2.9	1.0 ₄
530-518	2.2	0.78
495-470	1.1	0.39

Table XXI

SOLUBILITY OF NICKEL IN ZINC

<u>Temp</u> <u>(C)</u>	<u>a/o Ni</u>	<u>w/o Ni</u>	<u>Temp</u> <u>(C)</u>	<u>a/o Ni</u>	<u>w/o Ni</u>
880.9	25.0	23	791	11.0	10
880.5	23.9	22	760	8.8	8
879	22.8	21	732	7.7	7
862	19.7	18	700-692	5.5	5
854	17.5	16	664	4.4	4
837	15.3	14	630	3.3	3
835	14.8	13.5	585	2.2	2
818	13.2	12	518	1.1	1
			485	0.83	0.75

Table XXII

SOLUBILITY OF PALLADIUM IN ZINC

Temp (C)	Nowotny ⁽⁵⁴⁾		Knighton ⁽⁶³⁾	
	a/o Pd	w/o Pd	a/o Pd	w/o Pd
892-	22.5	32.1		
860	15.0	22.4		
823	12.5	18.9		
805	11.4	17.4		
760	9.0	13.9		
550			1.27	2.07
500			0.82	1.35
(420)	(3.5)	(5.9)		

Table XXIII

SOLUBILITY OF PLATINUM
IN ZINC

Temp (C)	a/o Pt	w/o Pt
869	12.6	30.1
825	9.2	23.2
762	6.9	18.1
728	5.5	14.8
688	3.5	9.8

Table XXIV

SOLUBILITY OF RHODIUM
IN ZINC

Temp (C)	a/o Rh	w/o Rh
700	1.70	2.66
650	0.81	1.27
600	0.32	0.495
550	0.15	0.241

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Table XXV

SOLUBILITY OF
RUTHENIUM IN ZINC

Temp (C)	a/o Ru	w/o Ru
750	0.55	0.86
700	0.29 ₅	0.46
650	0.13 ₅	0.210
600	0.071	0.110

Table XXVI

SOLUBILITY OF
ANTIMONY IN ZINC

Temp (C)	a/o Sb	w/o Sb
566	40	55.4
550	34.9	50
535	30.5	45
520	26.4	40
505	22.4	35
497	18.7	30
482	15.2	25
477	11.8	20
457	5.6	10
411	1.6 ₅	2.5

Table XXVII

SOLUBILITY OF
SILICON IN ZINC

Temp (C)	a/o Si	w/o Si
850	3.7	1.62
800	2.1	0.92
730	1.3	0.57
650	0.35	0.15
600	0.14	0.06

Table XXVIII

SOLUBILITY OF
TITANIUM IN ZINC

Temp (C)	a/o Ti	w/o Ti
1000	6.7	5
990	6.1	4.5
950	5.4	4
910	4.7	3.5
860	4.0	3
770	3.5	2.5
710	2.7	2
625	2.0	1.5
~418	0.2	0.12

6
Table XXIX

SOLUBILITY OF URANIUM IN ZINC

Temp (C)	Chiotti ⁽⁶²⁾		Hayes ⁽⁶²⁾		Kaufmann ⁽⁶²⁾		Knighton ⁽⁶³⁾	
	a/o U	w/o U	a/o U	w/o U	a/o U	w/o U	a/o U	w/o U
800							1.87	6.47
750							0.79	2.81
700	0.87	3.1					0.347	1.25
680					1.13	4.0		
650	0.36	1.3					0.129	0.467
600	0.14	0.45					0.051	0.186
550	0.083	0.30					0.014	0.052
500	0.077	0.28	0.33	1.2	0.061	~0.22	0.0058	0.021
450	0.055	0.20						
419	0.0069	0.025						

Table XXX

SOLUBILITY OF ZIRCONIUM IN ZINC

Temp (C)	Gebhardt ⁽⁵⁶⁾		Knighton ⁽⁶³⁾	
	a/o Zr	w/o Zr	a/o Zr	w/o Zr
1027	1.44	2.0		
970	1.26	1.7 ₅		
843	0.90	1.2 ₅		
800	0.79	1.1 ₀		
757	0.68	0.95		
745			5.45	7.44
742	0.65	0.90		
700			3.94	5.41
676			3.25	4.48
657			2.42	3.35
628			1.70	2.36
600	0.37	0.52		
595			1.37	1.90
575			1.07	1.48
558			0.88	1.22
545	0.27	0.37		
540	0.24	0.33		
500	0.19	0.27		
416	0.07	0.1		

APPENDIX IV

SUMMARY OF CRYSTALLOGRAPHIC DATA

Cubic

Space group O_h^1 - Pm3m. Structure type B2(CsCl), 2 at/u.c.*

CuZn(β^1) $a_0 = 2.94^{**}$

AuZn(β) $a_0 = 3.12$

PrZn $a_0 = 3.67$

CeZn $a_0 = 3.70$

LaZn $a_0 = 3.75$

TiZn

Space group O_h^1 - Pm3m. Type L1₂(Cu₃Au) 4 at/u.c.

TiZn₃ $a_0 = 3.9322$ or 3.023

Space group O_h^6 - Fm3c. Type D2₃(NaZn₁₃) 112 at/u.c.

CaZn₁₃ $a_0 = 12.13$

SrZn₁₃ $a_0 = 12.215$

NaZn₁₃ $a_0 = 12.2836$

BaZn₁₃ $a_0 = 12.33$

KZn₁₃ $a_0 = 12.360$

Space group O_h^7 - Fd3m. Type C15(MgCu₂) 24 at/u.c.

ZrZn₂ $a_0 = 7.3958$

Space group O_h^7 - Fd3m. Type B32(NaTl) 16 at/u.c.

δ -(LiZn) $a_0 = 6.22$

Space group T_h^1 - Pm3. Structure type unknown 39 at/u.c.

Mg₂Zn₁₁ $a_0 = 8.552$

Space group T_d^2 - $F\bar{4}3m$. Type B3(ZnS, zinc blende) 8 at/u.c.

ZnS $a_0 = 5.42$

ZnSe $a_0 = 5.661$

ZnTe $a_0 = 6.089$

*Atoms per unit cell

**All parameters given in Angstrom units ($\text{\AA}$).

6:

Space group $T_d^3 - I\bar{4}3m$. Type $D8_2(\gamma\text{-brass})$ 52 at/u.c.

$\gamma\text{-(Cu-Zn)(Cu}_5\text{Zn}_8)$	$a_0 = 8.87$
$\gamma\text{-(Au-Zn)(Au}_5\text{Zn}_8)$	$a_0 = 9.242 - 9.287$
$\gamma\text{-(Ag-Zn)(Ag}_5\text{Zn}_8)$	$a_0 = 9.3407$

Space group O_h^2 (Type $D8_1 \text{ Fe}_3\text{Zn}_{10}$), T_d^1 (Type $D8_2, \gamma\text{-brass}$) or T_d^3 (Type $D8_3 \text{ Cu}_9\text{Al}_4$) 52 at/u.c.

$\gamma\text{-(Ni-Zn)(Ni}_5\text{Zn}_{21})$	$a_0 = 8.904$
$\Gamma\text{-(Co-Zn)(Co}_5\text{Zn}_{21})$	$a_0 = 8.878$
$\Gamma\text{-(Fe-Zn)}$	$a_0 = 8.9560 - 8.9997$
$\gamma_1\text{-(Pd-Zn)(Pd}_5\text{Zn}_{21})$	$a_0 = 9.09$
$\gamma\text{-(Pt-Zn)(Pt}_5\text{Zn}_{21})$	$a_0 = 18.08$
$\epsilon\text{-(Mn-Zn)(Mn}_5\text{Zn}_{21})$	$a_0 = 9.14$

Space group unknown

$\gamma\text{-(Zr-Zn)(ZrZn)}$	$a_0 = 3.336$
$\xi\text{-(Zr-Zn)(ZrZn}_{15}\text{?)}$	$a_0 = 14.11$
$\gamma_1\text{-(AuZn}_3\text{)(AuZn}_3\text{)}$	$a_0 = 7.880 \text{ 32 at/u.c. ?}$

Hexagonal

Space group $D_{6h}^1 - C6/mmm$, Type $D2_x(\text{CaZn}_5)$, 6 at/u.c.

CaZn_5	(1)	$a = 5.405$	$c = 4.183$	$c/a = 0.774$
	(2)	$a = 5.371$	$c = 4.242$	$c/a = 0.789$
LaZn_5		$a = 5.416$	$c = 4.217$	$c/a = 0.778$
$(\text{Th}_{0.6}\text{Zn}_{0.4})\text{Zn}_5$		$a = 5.248$	$c = 4.451$	$c/a = 0.848$

Space group $D_{6h}^4 - C6/mmm$, Type $A3(\text{Mg})$

Zn	$a = 2.659$	$c = 4.936$	$c/a = 1.856$
$\text{CuZn}_5(\epsilon\text{-brass})$	$a = 2.740$	$c = 4.296$	$c/a = 1.567$
	$a = 2.663 - 2.673$	$c = 4.288$	$c/a = 1.604 - 1.610$
$\beta^1\text{-(Li-Zn)(?)}$	$a = 2.78$	$c = 4.39$	$c/a = 1.58$
$\epsilon\text{-(Au-Zn)(AuZn}_6\text{?)}$	$a = 2.81$	$c = 4.37$	$c/a = 1.56$
$\epsilon\text{-(Ag-Zn)(AgZn}_3\text{?)}$	$a = 2.81$	$c = 4.42$	$c/a = 1.57$

Space group D_{6h}^4 - C6/mmc, Type C14(MgZn₂) 12 at/u.c.

MgZn ₂	a = 5.15-5.21	c = 8.48-8.60	c/a = 1.644-1.651
TiZn ₂	a = 5.064	c = 8.210	c/a = 1.621

Space group D_{6h}^4 - C6/mmc, Type unknown. 550 ± 8 at/u.c.

δ_1 -(Fe-Zn)(FeZn ₉ ?)	a = 12.8	c = 57.6	c/a = 4.50
γ_1 -(Mn-Zn)(MnZn ₉ ?)	a = 12.8	c = 57.6	c/a = 4.50*

Space group unknown

δ -(Ni-Zn)	a = 8.873	c = 14.63	c/a = 1.649
γ^1 -(Li-Zn)(Li ₃ Zn ₇)	a = 4.36	c = 2.51	c/a = 0.576 28 at/u.c.
CrZn ₁₇	a = 12.89	c = 30.5	c/a = 2.73 288 at/u.c.
Hg ₃ Zn ₈	a = 2.7132	c = 5.4801	c/a = 2.0198
ξ -(Ag-Zn)(AgZn?)	a = 7.62	c = 5.65	c/a = 0.741 54 at/u.c.
UZn ₉ **	(a = 8.99)	(c = 8.98)	(c/a = 0.999)
Zr-Zn(88 a/o Zn)	a = 8.02	c = 7.31	c/a = 0.901

Tetragonal

Space group D_{2h}^{15} - P4/nmc, Type D5₉(Zn₃P₂) 40 at/u.c.

Zn ₃ P ₂	a = 8.09 ₇	c = 11.45	c/a = 1.41 ₈
Zn ₃ As ₂	a = 8.31 ₆	c = 11.76	c/a = 1.41 ₈

Space group D_{2h}^{19} - I4/amd (BaCd₁₁ type) 48 at/u.c.

LaZn ₁₁	a = 10.68	c = 6.87	c/a = 0.643
CeZn ₁₁	a = 10.66	c = 6.86	c/a = 0.644
PrZn ₁₁	a = 10.65	c = 6.85	c/a = 0.644

*Space group assignment not certain

**Symmetry group D_{6h}

RhombicSpace group D_{2h}^{17} - Amam 24 at/u.c.BaZn₅ a = 5.37 b = 10.85 c = 8.50Monoclinic β -(Mn-Zn)(MnZn₁₃?) a = 13.7 b = 7.6 c = 5.1 $\beta = 128^\circ 44'$ ξ -(Co-Zn)(CoZn₁₃?) a = 13.46 b = 7.49 c = 5.01 $\beta = 127^\circ 5'$ ξ -(Fe-Zn)(FeZn₁₃?) a = 13.65 b = 7.61 c = 5.06 $\beta = 128^\circ 44'$
a = 10.76 b = 7.61 c = 5.06 $\beta = 98^\circ 26'$