THE STRUCTURE OF LIQUID METALS AND ALLOYS

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LIST OF SYMBOLS

Only the symbols frequently used are listed here. Others are defined where they occur.

$a(K)$	structure factor
C_p, C_v	specific heat at constant pressure, volume
d	density
D	diffusivity
E_D, E_η	activation energies
E_A^V	enthalpy of vaporization
f	coherent scattering factor
$g(r)$	defined as $\frac{\varrho(r)}{\varrho_0}$
G^E	excess free energy of mixing
G^M	free energy of mixing
H^F	enthalpy of fusion
H^M	enthalpy of mixing
I	X-ray beam intensity
K	dimension in K-space
k	Boltzmann constant
k_F	diameter of Fermi sphere
m	mass of one atom
N	number of atoms
$\bar{N}$	number of electrons/unit volume
r	atomic radius
R	Hall coefficient; gas constant
S^E	excess entropy of mixing
S^M	entropy of mixing
S^V	entropy of vaporization
S, s	incoherent scattering factors

$S(T), S_L, S_S$	thermoelectric power
S_K	Knight shift
T	temperature
T^B	boiling temperature
T^F	fusion temperature
V	molar volume
V^F	volume change on fusion
V_f	molar free volume
V^M	volume of mixing
Z	valency; coordination no.

GREEK

α	bulk coefficient of thermal expansion, thermal diffusion coefficient
α_L, α_S	temperature coefficient of resistivity
β_A	adiabatic compressibility
β_I	isothermal compressibility
γ	surface tension; ratio of specific heats
$\varepsilon_{ii}, \varepsilon_{ij}$	interatomic bond energies
ζ	electronegativity
η	viscosity
θ	angle of incidence
κ	thermal conductivity
λ	wavelength; interaction parameter (equation 3.4)
$\varrho(r)$	radial distribution function
ϱ_0	number density of atoms
ϱ_S, ϱ_L	resistivity of solid, liquid
σ_0	d.c. conductivity
χ	magnetic susceptibility

1. INTRODUCTION

THAT metals can exist in the molten state has been known to man for thousands of years, yet only in the last two decades has intensive interest been shown in their properties. The impetus for this has come from the organizations dealing with the design and construction of atomic reactors, both in Great Britain and in the United States.[1,2] More recently, interest has been growing in the possibilities of using liquid metals in magnetohydrodynamic applications,[3(a) (b)] in fuel cells,[4] and various other applications.[5–7] Liquid metals—normally mercury—have long been used on a small scale as boiler fluids, and it was clear that the high thermal conductivity of these materials made for good heat-transfer properties when they were employed as coolants in nuclear-power generation. A number of reactors have now been built, using either liquid sodium or a liquid–potassium eutectic alloy as coolant. The possibility of using these and other liquid metals gave rise to a very considerable effort in determining the physical properties of liquid metals and alloys. The first results of these efforts were summarized in 1950 and 1952 by Lyon.[1,2] The effort made was naturally rather specific, and did not cover the very wide range of liquid metals and alloys of no immediate use in the nuclear-reactor field. A wider field was surveyed in 1954 by Frost,[3] who attempted to relate the properties of liquid metals and alloys to their possible atomic structure. In most cases, however, far too little information was available to allow the formulation of a complete picture of structure. In the intervening decade much experimental work has been reported on liquid metals and alloys, and it is now possible to present a more comprehensive picture of the structure of these materials. This is particularly so in the fields of electronic properties, transport properties (viscosity, diffusion), and direct structural determinations, although in most areas interpretation lags far behind the experimental facts; little progress has been effected in the measurement or interpretation of surface properties, which, in any case, are unable at present to provide any information about the structure of liquids.

Considerable advances have been made in the theory of the electronic properties of liquid metals and, very recently, of alloys, but, in general, the fundamental understanding of the properties of liquid metals and alloys has remained at a very qualitative stage of development. The interpretation of, for example, transport or thermochemical properties still requires, as in the solid state, a more detailed understanding of interatomic bonding in metals and a means of applying such an understanding in a fundamental theory of the property in question. Many of these problems have been partially solved in the field of non-metallic non-electrolytes, but, curiously, there appears to have been little extension of even well-established qualitative ideas from this area to that of metallic liquids. A small attempt is made in the present work to improve the situation. An indication is given at the end of the review of some areas where more intensive effort appears to be necessary in both experimental and theoretical work.

Frost's review suggested that the behaviour of the liquid was often closely related to the type of solid, eutectic or intermetallic compound, for example, which it formed on cooling. To examine this suggestion more closely, with a view to providing a framework on which to hang a discussion of physical properties, and thus reaching some conclusions about the actual structure of the liquid formed, all binary systems for which any reliable thermodynamic or physical information is available have been classified, as indicated below, according to the type of solid-state phase diagram exhibited; reasons for this classification are discussed later.

(1) Simple solid-solution systems (SS).

(2) Eutectic systems, subdivided into:
  (*a*) Systems with neither liquidus inflected (NI).
  (*b*) Systems with one liquidus inflected (SI).
  (*c*) Systems with both liquidi inflected (DI).
  (*d*) Systems with the eutectic composition at $\sim 0\%$ of one component, and with the liquidus inflected (0% SI).

(3) Miscibility-gap (MG) systems, subdivided into:
  (*a*) Non-transition metal.
  (*b*) Transition metal.

(4) Systems containing intermetallic compounds, subdivided into:
  (*a*) Systems containing electron compounds, but not exhibiting a liquidus maximum.
  (*b*) Systems containing electron compounds, and exhibiting a liquidus maximum.
  (*c*) Systems containing non-electron compounds, and exhibiting a liquidus maximum.

(5) Miscellaneous systems.

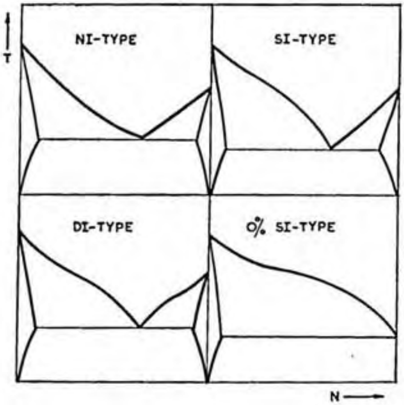

FIG. 1.—Classification of eutectic systems.

(Electron compounds[45] are regarded as those whose phase boundaries in the binary system are determined primarily by the electron-to-atom (e/a) ratio at those compositions; examples are the β, γ, and ε phases in the copper–zinc system, which, with increasing zinc content, occur at roughly $e/a = 3/2$, $21/13$, and $7/4$.)

Examples of each type of eutectic system are shown in Fig. 1, and the classification allotted to all systems discussed below is indicated in Tables I–XIII pp. 527–537, together with the size and electronegativity factors* for each system.

The review that follows is divided into sections according to the property under discussion, and each section subdivided according to the type of system involved. The conclusions reached are summarized in Section 9 (p. 504), where some suggestions are made as to the type of structure that may be exhibited in various liquid-metal systems. Because a very large amount of material has necessarily been condensed into this review, readers less conversant with the recent work in the field may first like to read this summary.

A large amount of data has been summarized in tabular form. It has not been practicable to indicate limits of experimental accuracy in the tables—such limits are often estimated, albeit optimistically, in the original papers, and there has been a very satisfactory tendency to provide a rigorous analysis of errors in all recently published experimental work. Only work that appears to be of reasonable quality, having regard to the difficulties of measurement and to the accuracy usually achieved by other workers, has been quoted; an indication is given of results that are particularly doubtful. Where it has not been possible to make a clear choice, alternative sources are indicated in parentheses. Because only selected data are quoted, the bibliography is not a complete one, but it is intended to provide a selection of the best in the field. Much earlier work has been summarized by Frost[8] and is not necessarily repeated here. Earlier references will also usually be found in the papers quoted, of course.

Most of the opinions expressed throughout the text are those of the writer, and it is hoped that they may prove controversial enough to promote discussion; the subject is still very much in its infancy, and

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* In this review, the size factor is defined as

$$SF\% = 200\,\frac{(r_A \sim r_B)}{r_A + r_B}$$

where r_A, r_B are the Goldschmidt radii of components A and B.[45] The electronegativity "factor" is defined as the difference in the electronegativities of the two components, expressed as a positive quantity. Most values of electronegativities have been taken from the paper by Teatum *et al.*[9] The exact significance of the electronegativity factor is not understood, but is here taken as a qualitative indication of the tendency of two elements to mix exothermically.

lively discussion is greatly needed, even if it is based on ideas that are subsequently proved to be ill-conceived!

2. DIRECT MEASUREMENTS OF STRUCTURE

2.1. Principles: Coherent Scattering of X-Rays and Neutrons

Direct structural investigation of liquids can be carried out by means of X-ray, neutron, or electron diffraction. The first is by far the most common technique. A short-wave, monochromatic and collimated beam of X-rays is directed on to the carefully cleaned surface of the liquid alloy, contained in a wide, shallow crucible, usually heated by a small furnace in its base. The angle of incidence, θ, is observed, as is the intensity (I) of the reflected beam. The crude results are usually presented as a plot of I vs. $(\sin\theta)/\lambda$, where λ is the wavelength of the incident beam. A typical plot is shown in Fig. 2. This curve may be obtained with great precision, using a spectrometer, but unfortunately provides no direct information about the distribution of atoms in the liquid. This can be obtained only by a method which introduces considerable possibility of calculational error.

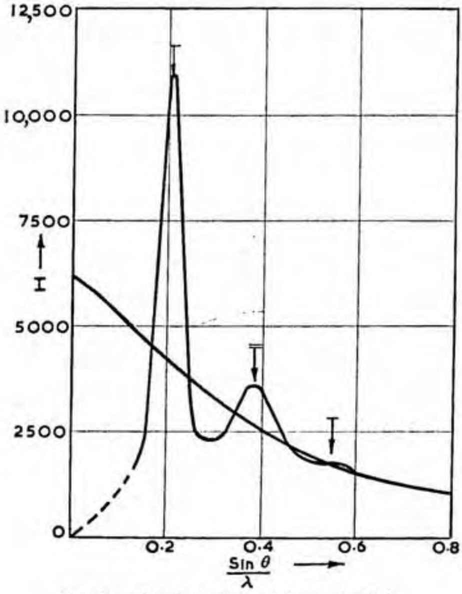

Fig 2.—Typical plot of I vs. $\sin\theta/\lambda$.

The distribution of atoms in a liquid may be represented by the atomic radial distribution function (RDF), $\varrho(r)$, which is usually expressed as the density per unit volume of atoms at a specified distance r from an arbitrary reference atom. Thus, $\varrho(r)$ also represents the 'probability per unit volume' of finding an atom at a distance r from the reference atom; it may have values between 0 and $2\varrho_0$, where ϱ_0 is the constant average density of atoms for the whole liquid. For values of r less than the atomic diameter, $\varrho(r)\rightarrow 0$, and as $r\rightarrow\infty$, so $\varrho(r)\rightarrow\varrho_0$. A typical variation of $g(r) = \dfrac{\varrho(r)}{\varrho_0}$ with r is shown in Fig. 3(a). $\varrho(r)$ may be obtained directly from a Fourier analysis of the I vs. $(\sin\theta)/\lambda$ plot by use of the Zernicke–Prins formula:[10,596]

$$4\pi r^2\varrho(r) = 4\pi r^2\varrho_0 + \frac{2r}{\pi}\int_0^\infty s\left(\frac{I}{Nf^2}-1\right)\sin sr\cdot ds\cdot dr \qquad (2.1)$$

where $s = \dfrac{4\pi\sin\theta}{\lambda}$, the scattering factor,

f = coherent scattering factor,
ϱ_0 = mean number density (atoms/Å^3)
and I = intensity.

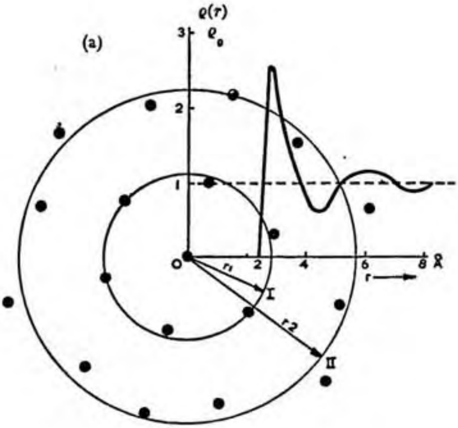

FIG. 3(a).—Variation of the radial distribution function, $\varrho(r)/\varrho_0$, with distance from reference atom.

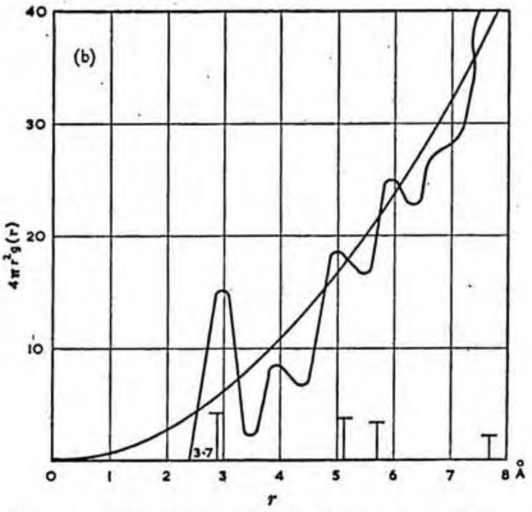

FIG. 3(*b*).—Variation of $4\pi r^2\varrho(r)$ with distance from reference atom.

The RDF is usually given as a plot of $4\pi r^2\varrho(r)$ vs. r (Fig. 3(*b*)). Clearly, high θ-values correspond to low r-values. Considerable error may arise from the use of this integral. Values of θ cannot usually be obtained outside the limits of $\theta = 5$–$75°$, and unfortunately $\varrho(r)$ or $g(r)$ is very sensitive to the arbitrarily chosen upper limit to the integral (usually $S \simeq 10$). This may result in a ripple superimposed on the RDF curve, appearing as 'ghost' peaks on either side of the main peak in $4\pi r^2\varrho(r)$. The value of Z, the coordination number or the number of nearest neighbours of the central reference atom, is determined by the area under the main peak in $4\pi r^2\varrho(r)$, and thus may be subject to considerable error. Various methods of calculation have been suggested,[11(*a*)–(*c*)] but since the I vs. $(\sin\theta)/\lambda$ curve is not subject to such errors, it is better to attempt to interpret results directly from this. Examples of this technique are discussed later.

Even the full analysis for Z and $\varrho(r)$ is capable of giving only an average distribution of atoms about a central one: no information is obtained regarding spatial configuration, because this is continually varying in a liquid, as are the values of Z, and (for any pair of atoms) r. Thus, diffraction techniques for the liquid state provide much less information than for the solid. Some progress may be made by comparison of experimental RDF curves with those calculated from assumed models of the liquid: this has been attempted by Bernal[75–78] (p. 402) and others, but the technique is extremely laborious. In principle, it is possible to calculate $g(r)$ exactly from information on the strength and nature of the interatomic bond (or vice versa), and then, from $g(r)$, the physical and thermodynamic properties of the liquid or liquid mixture. The basic theory for this has been laid down by Born and Green and others,[12–14] but these and all similar theories invoke approximation to overcome the lack of information about the *exact* nature of the interatomic potential, and the way in which it should be summed over all atom pairs to obtain the internal energy of the liquid, (see Section 2.3.5). The relationship between the interatomic forces in liquid metals (which cannot be greatly different from those in solid metals) and the radial distribution function has received some recent attention. Ling[15] has used an assumed Lennard-Jones pair potential[14] to calculate the radial distribution function for Na–K alloys from the experimental diffraction data on the pure metals; this work was remarkably successful, considering that this form of pair potential was proposed for non-metallic liquids. More recently, March and his co-workers[16–18] have used experimental X-ray diffraction data for liquid metals to calculate the dependence of the pair potential in liquid metals upon the interionic distance, using, in the main, the Born–Green theory.[12,13] Two important points arise from this work:

(1) that the use of the superposition approximation[14] to calculate the perturbing effect of a third atom upon the pairwise potential appears to be justified in liquid metals; this may be of great value in future calculations of the thermodynamic properties of liquid metals from first principles;

(2) that, unlike the situation in non-metallic liquids, the pair potential in liquid metals exhibits long-range oscillations; in a similar calculation for liquid argon, these oscillations were not observed. The long-range nature of the oscillations suggests that the Fermi surface in liquid metals is quite sharp, contrary to what is generally assumed; the extent of blurring is estimated at $\sim 10\%$ (see p. 474). March *et al.* also calculate surface energies, viscosities, internal energies, and pressures for a number of liquid metals, using their determined pair potentials in a form of the Born–Green theory; they obtain excellent agreement with experimental data, having regard to the limitations of the diffraction data and the qualitative nature of the superposition approximation. Their assumption that only central pair forces need be considered—i.e. that the ions can be regarded as point charges—may prove to be unrealistic for some of the higher-valent metals where the diffraction studies suggest a non-central contribution to the inter-ionic potential (see below).

Harrison[19] has also calculated qualitatively similar interatomic potentials for liquid zinc, but without the use of direct structural data;

while this more fundamental approach may be intellectually more satisfying, the results are so far not as good as those of March *et al.*

In the next section, it will be shown that, with no further theoretical analysis, some qualitative conclusions may be reached regarding the structure of a liquid by an examination of the detailed shape of the I vs. $(\sin\theta)/\lambda$ curve obtained by X-ray or neutron diffraction.

2.2 INCOHERENT SCATTERING OF NEUTRONS

When studied on a time scale of $< 10^{-12}$ sec, liquids have solid-like properties in the sense that measurements are made so fast that the atomic movements are of no significance; if examined over longer time intervals liquids exhibit normal fluid-like properties. One of the most interesting features of liquid behaviour is the motion of atoms of molecules in the 'transition period' at $\sim 10^{-12}$ sec (the actual time depends upon the relaxation time of the atoms or molecules in the liquid, which is always of this order for normal liquids), between solid and liquid behaviour. 'Cold' neutrons have excellent properties for studying this time range, which cannot be investigated by any other diffraction technique.[20–22,596]

In recent years, neutron-scattering techniques have frequently been used to study the movement of atoms in liquids at very short time intervals. Van Hove[23] showed how the motion of atoms in a liquid is related to the scattering of neutrons. The total scattering may be divided into two parts—incoherent scattering due to the motion of single atoms (giving the self-correlation function, and hence providing a means of studying diffusive motion in liquids) and coherent scattering (giving the pair correlation, and hence the radial distribution function, as indicated above). The incoherent term may be obtained by subtracting the coherent term, obtained by experimental or, more usually, theoretical means, from the total.[24,25] Diffusive motion of atoms may then be studied by an analysis of the incoherent term.

A number of liquid metals have been studied in this way, viz: lead,[26–30], tin,[28–31] and sodium,[32,33] as well as water.[21] There is still considerable disagreement in the literature about the exact interpretation and significance of the results, but a number of qualitative conclusions may be reached. It appears that high-energy vibrational modes exist in the liquid as well as in the solid, and that the frequency distribution of the modes in the two states is similar. The liquid has a 'smeared-out' Debye spectrum which gradually becomes less distinct as the liquid is heated. It follows that there is only a small change in the Debye temperature on fusion in the liquids so far investigated, a deduction supported by the observation that the specific heat of most metals shows a negligible change on fusion (p. 411). It has also been suggested that diffusion in liquids cannot be represented by either a simple gas-like free-diffusion model (except perhaps at very high temperatures in the liquid range) or by a solid-like jump-diffusion mechanism; this was first concluded on different grounds by Nachtrieb.[207] An alternative model, based on a cluster model of liquid metals, has been proposed;[21,34] a similar model had been proposed independently by the present writer, but for different reasons.[324] The globules or clusters are thought to contain $\sim$ 100 atoms (see Sections 4 and 9), and may allow a qualitative interpretation of other physical properties (Section 9). Diffusion constants calculated from the model by Egelstaff give excellent agreement with experiment.[21]

2.3. Results

2.3.1. *Pure Liquid Metals*

Most simple liquids and pure liquid metals give I vs. $\sin\theta/\lambda$ curves of the type shown in Fig. 2, with a sharp, clearly defined, main peak. In recent years interest has centred on the exact shape of this main peak for a few exceptional metals. Liquid metals exhibiting a *symmetrical*, sharp maximum include the alkali metals, copper, silver, gold, and perhaps cadmium[11(a)]—the list is limited by lack of experimental evidence, rather than a lack of metals in this category. Exactly similar curves are observed for the liquid rare gases, whose structure is usually thought to be completely random. In addition, it may be shown theoretically that just such a main peak should arise from an assembly of atoms of completely random configuration, i.e. with no preferred configuration of atoms, however transient.[14,35] In such an assembly, an increase in temperature leads to a shortening and broadening of the main peak as a result of the increased thermal fluctuations of the atoms. This is observed in practice. In melts showing predominantly covalent bondng (i.e., those in which the bond is of a more rigidly fixed length than in a metal), such as liquid selenium or sulphur, a very sharp maximum is observed—the covalent bond allows less thermal 'scatter' of the interatomic distance. In vitreous selenium the peak is even narrower. In the imiting case of the crystalline solid at 0°K, the peak narrows to a line of zero width, as is well known. The position of the first peak in the iquid corresponds closely to that of the solid. This is expected, since here is no evidence of a major change in the nature or strength of the ntermetallic bond of fusion, at least in the simple metals listed above.

In several liquid metals, the first peak of the I vs. $\sin\theta/\lambda$ plot is not ymmetrical, and in some cases has a marked shoulder, usually on the igh-angle (low-r) side of the main peak. In some cases, this asymmetry may arise from poor experimental technique but there are several well-substantiated examples. Of these, the most notable are germanium[36] (Fig. 4), tin, [37, 38] gallium,[36] bismuth,[36, 39] antimony,[40] mercury,[41] and less certainly, lead and zinc.[42] In the non-metallic liquids, selenium and tellurium, the effect is particularly notable.[43, 44] The r-values corresponding to both the main and the subsidiary peaks usually tally

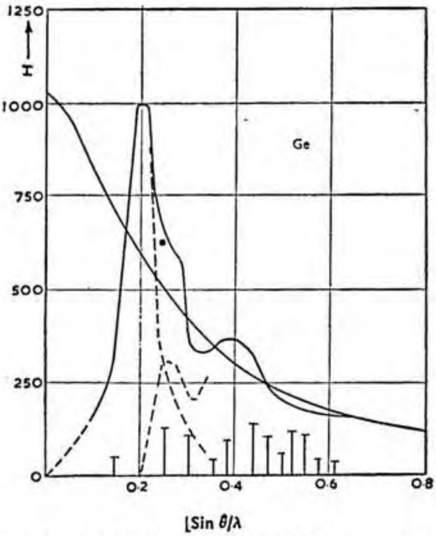

FIG. 4.—I plotted against $\sin \theta/\lambda$ for germanium.

approximately with solid-state interatomic distances. The r-value of the subsidiary maximum may often be shown to correspond to a nearest-neighbour distance characteristic of the homopolar bond in the solid state (e.g., tin[37]). It is probably significant that most of these metals have a wide range of liquid stability ($T^B - T^F$),* and a high entropy of fusion (Tables XV and XVI). It seems that the probability of finding an asymmetric maximum is greater in the elements from the numerically higher groups and lower periods of the Periodic Table; in these elements, solid-state bonding is thought to be predominantly non-metallic.[45] All this suggests that such behaviour is associated with the retention in the liquid state of a proportion of a form of 'covalent' or homopolar bonding. This bonding is probably present in the form of short-term localization

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*T^B and T^F are, respectively, the boiling and melting temperatures. The significance of ($T^B - T^F$) is discussed further on p. 413.

of valence electrons in bound states between pairs or groups of neighbouring atoms, perhaps by a resonating hybridization process as envisaged by Pauling.[46] The structure resulting from this will be stabilized by the relative stability and directionality of the non-polar bond. This predominantly 'covalently' bonded structure may appear as small clusters or 'islands' in a metallically bonded 'matrix'. If this is so, the spatial arrangements of atoms within all the clusters will probably be identical, and quite different from the more random arrangement of atoms in the metallic 'matrix'. (Unfortunately, it is not possible to determine the spatial arrangement of atoms from liquid X-ray scattering data.) The structure of the cluster need not be similar to the structure of the corresponding solid. Thus, two nearest-neighbour distances will contribute to the I vs. $\sin \theta/\lambda$ curve, one corresponding to the mean separation of atoms 'metallically' bonded, and one to that of the smaller number of atoms joined by homopolar bonds. The shoulder on the observed I vs. $\sin \theta/\lambda$ curves (Fig. 4) can now be explained by the assumption of a subsidiary ('covalent') maximum under the main peak at a slightly higher angle (closer distance of approach). An alternative explanation is that each atom may be surrounded by neighbours at two mean distances of approach, each neighbour 'resonating' between the two distances, but it is difficult to visualize how this could arise. The first interpretation has been used in various guises by several authors—for example, in the form of a two-dimensional 'layer-packet' structure (liquid Ge, Sb, Bi, &c.),[42] tetrahedral clusters of grey tin structure (liquid Sn),[37] or NaCl-structured clusters (liquid Bi and Sb).[47] Much evidence is required before any of these structures can finally be established, but the basic concept of a two-structure liquid appears to be acceptable. At high temperatures the subsidiary peak normally disappears,[37] perhaps as a result of the destruction of the homopolar-bond contribution, or of the general broadening of the main peak due to increased thermal vibration of the atoms.

Evidence for the structure of pure liquid metals is summarized in Section 9. Data for coordination numbers and nearest-neighbour distances are given in Table XIV. The need for very great care in experimental work and in the subsequent analysis of the results to obtain the nearest-neighbour distances and coordination numbers is emphasized by the very great differences between quite recent work from different sources. A classic example is the work quoted for lead; while nearest-neighbour distances agree well, the height and other details of the radial distribution curves, and hence the values of the co-ordination numbers, differ appreciably. Clearly, a reported temperature-dependence of the structure of a liquid based upon work from different laboratories must be treated with some care!

Catterall has reported soft X-ray emission spectra for liquid aluminium.[48] The data are similar to those obtained for the solid metal,[49] but with the peak characteristic of zone overlap in the solid less pronounced in the liquid. It is concluded that there is no significant change in electronic structure on fusion; the details of the Fermi surface are merely 'rounded' off in the liquid. The same conclusion is indicated by the earlier work of Skinner[50] on liquid lithium, and, of course, by the theoretical work of March *et al.* mentioned above. More evidence relating to the change of electronic structure on fusion will be discussed later (Sections 6 and 7).

2.3.2. *Solid-Solution Systems*

Disappointingly, no diffraction studies appear to have been carried out on solid-solution systems in the liquid state. As a result of the observation of certain phenomena, noted below, in early studies on eutectic and compound-containing systems, most recent work has been carried out on these groups of systems.

2.3.3 *Eutectic Systems: Miscibility-Gap Systems*

During the last decade, considerable interest has been shown in the structure of liquids of the eutectic composition. A number of workers, exclusively Russian,[51–55] report that the first peak of the I vs. $\sin\theta/\lambda$ curve for such liquids, when determined at temperatures just above that of the eutectic, contains two roughly equal subsidiary peaks. This is usually taken to indicate the presence in the liquids of two indistinguishable structures resulting from incipient immiscibility. This idea has apparently arisen by analogy with the structure of the corresponding solid, which, of course, consists of two immiscible solid solutions. It has been suggested[52] that the two structures observed in the liquid are similar to those of the pure liquid components. This interpretation is supported by the observation that the two peaks often fall at $\sin\theta/\lambda$ values corresponding to those of the main peaks of the pure components, but the technique is not of sufficient precision for this to be conclusive. The two-peak phenomenon has been observed in the Bi–Sn,[51,53] Bi–Pb,[51,54] Sn–Zn,[51,53], Pb–Sn,[50,54] and Al–Sn[55] systems. In all cases, the dual nature of the peak disappeared at higher temperatures. There is no Western work to provide direct confirmation of these observations, and it is doubly unfortunate that the Russian work invariably gives inadequate experimental detail, and a few crude results. There must, therefore, be some doubt about its reliability. However, Sharrah *et al.*[56] have determined co-ordination numbers in the liquid Bi–Pb system by neutron and X-ray diffraction, and find a value of 12 in lead-rich alloys, which falls suddenly at about the eutectic composition to 7·7 in bismuth-rich liquids. This supports the Russian view that the two structures representative of the two components are in equilibrium at the eutectic. In an interesting experiment, Samarin and his co-workers[57] centrifuged a liquid eutectic Pb–Sn alloy at just above the eutectic temperature and obtained some separation into tin-rich and lead-rich liquids. This was thought to be evidence in support of the X-ray observations. A cluster size of 3000 atoms was estimated from the rate of separation, based on the assumption that the liquid structure consisted of large clusters of lead-rich and tin-rich components. The experiment has been repeated independently, with the same result.[58]

In the absence of more detailed independent evidence to the contrary, the Russian work must be accepted. The interpretation of the results is further discussed in Section 9.3.

Miscibility-gap systems have received little attention[59–60] and no structural conclusions are possible. If a tendency to separation of the components is observed in eutectic liquids, it may also be detectable at temperatures just above the critical temperature in miscibility-gap systems, but there is no evidence from diffraction studies to support this.

2.3.4. *Compound-Containing Systems*

Hendus,[36] in a now-classic piece of work, observed that the I vs. $\sin\theta/\lambda$ curve for alloys in the gold–tin system exhibited a double main peak. More recent work[61–63] has shown that only the pure metals and an alloy of 25 at.-% tin have a single main peak; in all other alloys there are two peaks whose relative intensity depends upon the composition, and whose positions are those of the peak at 'Au_3Sn' and of the weighted mean of the peak positions of the two pure metals. It may be concluded that the structure at 'Au_3Sn' is in some way unique, and that all other liquids have a dual structure, consisting perhaps of clusters of atoms of the 'Au_3Sn' composition in equilibrium with a 'matrix' of more randomly arranged gold and tin atoms. It is possible that the structure at 'Au_3Sn' arises out of the proposed clustered structure of liquid tin;[37] it may consist of quadrivalent tin clusters in which bonding is partially homopolar (i.e., with some electrons in bound states, or 'localized') and in which one in every four tin atoms has been replaced by a gold atom. The structure 'Au_3Sn' does not appear in the solid state; on the other hand, there are M_3Sn compounds—the ε phases—in the Cu–Sn and Ag–Sn systems. In the Au–Sn system, the ε phase is prevented from forming by the high electronegativity factor,[45] which favours the NiAs structure that appears at AuSn. In the liquid state, it seems that the electronegativity factor has less influence, and the factors which in the solid fail to bring about the ε phase can operate with more success. It is interesting that none of the compounds AuSn, $AuSn_2$, $AuSn_4$, that appear in the solid state, seems to be reflected to a detectable extent in the liquid, although the factors which bring them about are presumably still able to operate.

Exactly similar phenomena are reported in the X-ray diffraction curves of the Cu–Sn and Ag–Sn liquid systems, according to preliminary studies at the Fulmer Research Institute.[62] The structure of these systems is discussed in more detail in Section 6.

Orton *et al.* investigated two liquid alloys in the Na–K system, one of which corresponded exactly with the incongruent compound Na_2K.[64] They found no evidence of a double peak in the I vs. $\sin\theta/\lambda$ curve, in contrast with the tentative conclusions of earlier work.[65] This compound is an 'ideal' Laves phase—i.e. its existence depends upon the size factor—and both liquid and solid alloys have a very small positive enthalpy of mixing (Section 3) so that any short-range order in the liquid would probably remain undetected by relatively structure-insensitive diffraction measurements. Evidence from physical measurements on this system are inconclusive and will be discussed later. Orton *et al.* also examined liquid alloys of eutectic composition, and found only 'a statistical mixture of atoms', which raises doubts about the Russian work on liquid eutectics referred to earlier.*

Little reliable diffraction work is available for other compound-containing systems. Orton and Williams[62] report a shouldered I vs. $\sin\theta/\lambda$ peak in the Cd–Sb liquid system at about 'Cd_3Sb_2'. This system is discussed in more detail later (p. 448). Asymmetric first peaks are reported in In–Sb,[47] Ag–Al,[51] and Bi–In[66,67] liquid alloys; in the last case, there is possibly some evidence from physical properties of clustering in the liquid.[66] Finally, to emphasize the relative insensitivity of diffraction techniques to slight short-range order in the liquid, Smallman and Frost[68] were unable to detect with certainty any effect upon the liquid of the factors giving rise to the compound Hg_5Tl_2 in the Hg–Tl system, although short-range order was detected by later thermodynamic measurements.[69] Similar results were obtained in X-ray studies of Hg–In liquids[93] (compounds Hg_7In and HgIn in the solid state) but in this case measurements were made at temperatures too far above the liquidus for any asymmetry of the first peak in I to be detectable.

In this group of systems the factors—electronegativity, relative atom size, for example—that decide the formation and stability of a solid-state compound should have a detectable effect upon the structure, and therefore the properties, of the liquid because their magnitude is not changed by fusion. If (as in the case of an electron compound) the

* See note added in proof (p. 590).

major factor producing the compound requires a solid-state lattice, and if this lattice is completely destroyed on fusion, the liquid properties should not reflect the solid-state characteristics. The electron-to-atom ratio may, however, be important in the liquid state, but not at the same *e/a* value, and therefore composition, as in the solid (Section 6.2.2.).

It is not possible to reach any conclusion regarding the *spatial* arrangements of atoms from diffraction work on liquids; only the spacing and number of nearest neighbours can be obtained, although too often this information cannot be calculated with any accuracy from the inadequately detailed results published. Keating[70] has shown that by a suitable combination of three separate sets of scattering data on the same liquid mixture it is, in principle, possible to determine uniquely the A–A, B–B, and A–B distances and co-ordination numbers—only an averaged figure may be obtained from a single experiment. If this can be achieved in practice, a considerable forward step will have been made; it is understood that the necessary experiments are planned in at least two laboratories.

To summarize, it is disappointing that so little definite information has resulted from the considerable effort which has been put into the determination of scattering data for metallic liquids; the limitations lie both in the inadequate precision of much of the published data, and in the difficulties involved in its quantitative analysis. Recent theoretical work has shown that accurate diffraction data are of the greatest importance in interpreting the electronic properties of liquid metals and in calculating the form of the interionic bond. It is to be hoped that much more useful data will soon be forthcoming.

2.3.5. *Structural Models*

A number of models of liquid structure have been suggested, most of which are based, necessarily, upon a limited amount of evidence. The test of such models lies in the extent to which they are able to predict physical and thermodynamic properties; so far, at least for liquid metals, they have had little success in this respect. Models of this type usually involve insupportable assumptions which make them either applicable only to a very limited range of real liquids, or totally unrealistic. They have, however, been of some value in correlating measurements of physical properties of simple non-metallic liquids, and it is probable that the only way in which some of the anomalous X-ray scattering data on liquid metals and alloys may be interpreted successfully is by fitting to the experimental data scattering curves calculated from assumed structural models. This has already been done for a number of simple non-metallic liquids with some success, but in such cases, the model assumed need only in principle be very simple—e.g. a fluid of random hard spheres,[35] or one with an assumed interatomic-pair potential.[14,79] It is in the latter case that, in practice, calculation of even the radial distribution function becomes extremely difficult; the calculation from this of thermodynamic properties has been attempted by many workers with limited success for simple liquids, and none at all for liquid metals and alloys. March *et al.*,[16–18] whose work has been referred to earlier, reversed this process and attempted with some success to calculate the pair potentials in liquid metals from the experimental radial distribution function. Before the intellectually more satisfying process of calculating thermodynamic properties of liquid metals and alloys from an *assumed* structure and pair potential can be carried out, we need to know much more about the structure of the liquids, and the nature of the pair potential. In this sense, any structural model of a liquid metal is bound to be of limited value, because it can only make assumptions based on non-existent evidence. In all cases, liquid-metal models have set out to achieve much less than a fundamental calculation of liquid properties.

Models of particular interest are those of Stewart *et al.*[71,72] of Mott and Gurney,[73] and, more recently, of Bernal.[75–78] Some of the ideas have been reviewed by Temperley.[74*]

(1) *Stewart* et al.[71,72]

This model treated the liquid, for the sake of quantitative calculation, as equivalent to an equilibrium mixture of 'crystallites' of all sizes and of solid-state structure, which are packed together in such a way that no long-range order is possible. Although originally proposed purely for convenience of calculation (the partition function of the liquid may be expressed as the averaged partition functions of all the crystallites), the model has often been thought to have some physical significance. This is unrealistic, since an important aspect of the Stewart approach is that it assumes the crystallites to have the solid-state structure; if this were so, the supercooling observed in most liquids would be impossible, owing to the nucleating effect of the crystallites.

(2) *Mott and Gurney*[73,74]

These authors suggested an extension of the Stewart model to the calculation of the communal entropy of the liquid—this quantity takes account of the fact that in a liquid an atom does not have easy access to all parts of the fluid, as it would in a gas, but is confined by its 'community' of surrounding atoms to making relatively short excursions away from its equilibrium position. This restriction is carried to its extreme in the solid, where, at least at low temperatures, the atom can

[*] See also D. Turnbull, Ref. 596, p. 6.

be considered to be immobile. In the Stewart model, the communal entropy will depend upon the mean number of molecules, n, in a crystallite; it may then be shown that for N/n crystallites, where N is the total number of atoms in the liquid, the communal entropy is

$$S_c = (N/n)k \log (n^{1/3}) \quad . \quad . \quad . \quad . \quad (2.2)$$

provided that n is fairly large. This condition may be observed at temperatures near the melting point. (It is interesting that the Mayer[79] cluster theory of gases requires that clusters of liquid-like structure appear in the gas simultaneously with the appearance of the liquid state; perhaps the same may be considered to occur in the liquid at temperatures near the freezing point (see Section 8)). One particularly interesting result of the Mott and Gurney theory, pointed out by Temperley,[74] is that once the mean crystallite size has fallen to $n = 10$ or so, any further reduction in cluster size will not affect the communal entropy. It follows that any direct entropy measurements will probably not detect clusters smaller than this (see Section 3).

There is considerable evidence, for example from diffraction studies (above), to indicate that clusters may really exist in liquid metals; these clusters need not have the structure of the corresponding solid, since there is no longer any need to pack the clusters together in the form of a lattice with long-range order. The structure of the cluster will be determined by the nature of the inter-ionic bond, i.e. its directionality or any other special feature, and by other factors that control the ease of packing (e.g. the size factor). The structure taken up will be that which results in the lowest possible internal energy of the liquid; this structure certainly need not be that of the solid.

Mott and Gurney's model also gives, in principle, a physical theory of melting, since solidification may occur when the crystallites grow to such a size that a significant volume of the liquid is occupied by any one of them (Section 8).

The more recently proposed 'significant structure' model of liquids due to Eyring *et al.*[80–81] appears to be essentially similar to that of Stewart. The liquid is effectively considered as a mass of submicroscopic crystals with relative order within the crystals and disorder between them; the crystals are not assumed to have the solid-state structure, so that in this respect the theory may be more applicable to liquid metals. The theory has had considerable success in predicting thermodynamic properties of simple liquids, including a few liquid metals.

(3) *Bernal*[75–78, 82]

This model is essentially in direct opposition to those of Stewart and of Mott and Gurney. A completely random liquid structure is proposed which is said to consist of "homogeneous, coherent, and essentially irregular assemblages of atoms or molecules containing no crystalline regions or holes large enough to admit another molecule"; the structural units or 'assemblages' are thought to vary widely within a given liquid. At present the model is not mathematically handleable, but it has been possible to calculate from it an 'experimental' radial distribution function.[78] In an extension of this important work, Bernal[78] and Scott[83–85] have determined experimentally the radial distribution function of large collections of hard spheres (usually steel balls). The $g(r)$ so determined agrees very well with that obtained experimentally for structurally simple liquids such as liquid argon.

An attempt has been made by Fürth[86] to treat the Bernal liquid mathematically in order to calculate thermodynamic data. One interesting result is that the theory predicts a temperature below which it should be impossible to supercool pure liquids; this is just what has been observed in practice for many metallic and non-metallic liquids (Section 8). A further consequence of the experimental work on the Bernal 'liquid' was that the model showed that relatively large holes could occur infrequently in the liquid; perhaps the earlier 'hole' models of the liquid structure[14,87–91] were not so unrealistic as they have often been claimed to be.

None of the structural models have had any real success for liquid metals unless some information about the structure of the liquid is 'fed' into them. It seems unlikely from the experimental evidence that the Bernal liquid bears much resemblance to liquid metals, with the possible exception of the metals from Groups 1 A and I B. In fact it is doubtful whether any structural model of liquids will apply to *all* liquid metals in view of the very large differences in structure between metallic liquids that are apparent from diffraction studies. (The conclusion of Furukawa[11(a),92] that all liquid metals have essentially the same structure is not supported by the diffraction evidence now available.)

In conclusion, it seems that the only profitable approach to establishing a fundamental relationship between the structure of metallic liquids and their physical properties must come through a physically realistic model of liquid structure, such as that of Born and Green,[12(a)] combined with a more fundamental understanding of inter-ionic forces in liquid metals. This is a road along which there is still a long way to travel!

3. THERMODYNAMIC PROPERTIES

Of all the properties of liquid metals and alloys that may be measured, thermochemical and thermodynamic properties have received the greatest attention. For this reason, the section that follows is necessarily a long one, but in justification it is clear that at present more indirect information about the structure of liquid metals, and especially alloys, may be deduced from thermodynamic parameters than from any other properties. It is unfortunate that, because of the inadequate state of the theory, such deductions must at present be qualitative.

3.1. PRINCIPLES

For pure liquid metals there are five thermodynamic properties of primary interest: the specific heat, the vapour pressure, the compressibility, and the enthalpies of fusion and evaporation. For liquid alloys there must be added the changes that take place in the thermodynamic parameters of the materials on mixing—the free energy, entropy, enthalpy, volume, &c., of mixing. The latter data may then be examined in two ways, called here for convenience the 'direct' and the 'indirect' methods. The first method involves the examination of the manner in which the thermodynamic properties of the mixture vary with composition and temperature for a particular system, or group of similar systems. This may give some indication of the structure of the individual liquids, usually when considered together with other data. The second method investigates the manner in which the thermodynamic quantities for a wide range of systems of all types vary with changes in solute and solvent at fixed composition and temperature, and attempts to explain the variation in terms of changes in size, electronegativity factor, or other parameters. The basic thermodynamic principles are common to both methods, and are outlined only briefly here. More detail will be found in the many standard texts on the subject.[100, 101]

3.1.1. *Specific Heats*

One of the most important thermodynamic properties of pure metals is the heat capacity at constant pressure, C_p. At room temperature most solid metals have values of C_p lying around $6{\cdot}2 \pm 0{\cdot}4$ cal. mole^{-1} deg^{-1} (Dulong and Petit's Law) compared with 7–10 cal. mole^{-1} deg^{-1} for liquid metals (Table XV). The origin of the specific heat of solids is well understood at low temperatures as a result of the work of Einstein,[94] Debye,[95] Blackman,[96] and others,[97] and is the temperature derivative of the energy associated with the frequency spectrum of vibration of atoms about lattice sites. At higher temperatures, and therefore greater amplitudes and more complex modes of vibration, the elementary theory is no longer applicable, and so far no more rigorous treatment has become available. It is thus unlikely that a successful theoretical treatment of the specific heat of the liquid state will be forthcoming in the near future. The heat capacity of a liquid metal is still related to the energy associated with the vibration spectrum (about which little is known), but to this must be added any energy arising from rotation and translation of the constituent particles. Various attempts have been made to account theoretically for the much more complex situation in liquids.[98, 99] None have been more than superficially successful, even for the structurally simple liquid rare gases. In view of the difficulties involved in producing a rigorous treatment, a purely empirical approach is used here.

The specific heat of a *mixture* often exhibits linear dependence upon composition, i.e. it obeys the Neumann–Kopp Law. Deviations from Neumann–Kopp behaviour in liquid alloys may be either negative or positive, and such deviations usually arise either through a change in the vibration spectrum on alloying, or through a variation in the electronic contribution to the specific heat.

Neither is quantitatively predictable in liquid alloys. It is, however, possible to estimate qualitatively the effect of large differences in atom size or co-ordination number between the components. Since these factors are more important in their effect upon the entropy of solution, they are discussed in the next section.

3.1.2. *Mixtures*

In addition to the specific heats of an alloy system, measurements may be made of the free energy, entropy, and enthalpy of mixing, respectively G^M, S^M, H^M, and the corresponding partial quantities $G^M_{i.j}$, $S^M_{,i.j}$, $H^M_{i.j}$, for binary components i, j.[100,101] If bond energies between the possible pairs of atoms in a binary mixture of components i, j are ε_{ii}, ε_{jj}, and ε_{ij}, positive values of H^M are associated with $\varepsilon_{ij} < \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$, or a preference for like-atom pairs, and a negative H^M with $\varepsilon_{ij} > \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$, or a preference for unlike-atom pairs. Similarly, a positive value of G^E, the excess free energy of solution, is usually associated with a positive H^M, and positive activity deviations from ideality (the relative signs of G^E and H^M may be modified by the entropy term, TS^E).

Various attempts to produce a more quantitative relationship between the ε_{ij}'s and the measurable thermodynamic parameters have met with considerable success in dealing with mixtures of non-metallic non-electrolytes.[102–103] Attempts [104–106] to extend these treatments to metallic solutions have been no more than qualitatively successful because of the lack of information about the nature of the interatomic bond in metals, and therefore about the manner in which ε_{ij}'s should be treated mathematically. An exact treatment must await an adequate quantum-mechanical treatment of the bonding forces in metals; this will be made more difficult by the apparently homopolar or heteropolar contribution to these forces in many metals and alloys.

Some limited progress may be made in the qualitative interpretation of data using the quasi-chemical approximation of Guggenheim.[107] This approach assumes additivity of pairwise interactions (i.e. that the total energy of an assembly of atoms may be calculated by a simple summation of the isolated bond energies between each pair of atoms, any perturbation due to neighbouring atoms being ignored), and that the atoms are arranged on a cubic lattice, so that only qualitative conclusions are possible when the model is applied to liquid mixtures. Only the configurational effect upon the thermodynamic properties is considered. The excess thermodynamic parameters may be shown to be:

$$G^E = N_i N_j \lambda \left(1 - N_i N_j \frac{\lambda}{ZRT}\right) \tag{3.1}$$

$$S^E = -N_i^2 N_j^2 \frac{\lambda^2}{ZRT^2} \tag{3.2}$$

and hence

$$H^M = N_i N_j \lambda \left(1 - N_i N_j \frac{2\lambda}{ZRT}\right) \tag{3.3}$$

where:

$$\lambda = -ZN_0[\varepsilon_{ij} - \tfrac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})] \tag{3.4}$$

and is positive for $\varepsilon_{ij} < \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$. Z is the co-ordination number, and N_0 is the total number of lattice points per mole. N_i, N_j are the numbers of atoms of types i, j respectively. Note that both H^M and G^E are predicted to be negative when λ is negative. The types of free-energy curves obtained for various values of λ are indicated in Fig. 5. The special case of $\lambda = 2RT$ is the limiting case of incipient immiscibility, for which $\varepsilon_{ij} \ll \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$.

The value of the simple model is obviously rather limited; it fails, for example, to account for solutions in which the excess free energy and enthalpy are of different sign, and it predicts that the excess entropy must be negative unless $\varepsilon_{ij} = \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$. Many examples of positive excess entropies are known in metallic and non-metallic solutions, and these must be accounted for in some other way. The model also ignores the fact that the values of all three pair potentials may be composition-dependent because the perturbing effect upon them of neighbouring atoms may vary with the type and number of those atoms. It will be shown that the asymmetry observed in the excess thermodynamic parameters of a large number of liquid metallic solutions may be explained in this way. However, for all its shortcomings, the Guggenheim model does provide a basis for discussing the effects of a number of variables upon the excess quantities and will be used below.

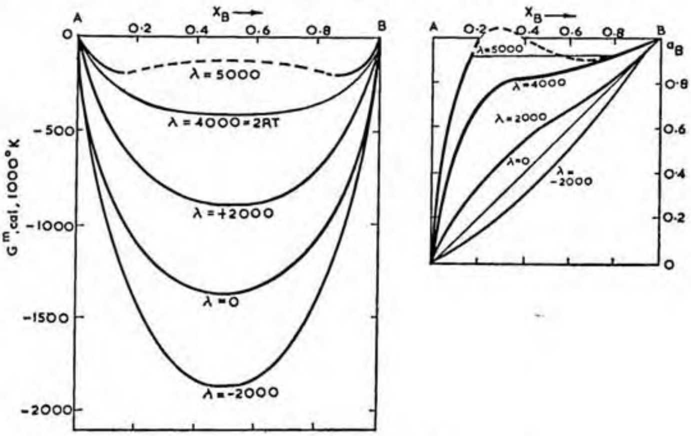

FIG. 5.—Dependence of G^M upon λ (see p. 406).

Excess quantities have also been discussed in detail by Scatchard[108] and by Barker.[110] The latter, using classical thermodynamics, proposed a series expansion for the excess quantities based upon:

$$G^E = N_1N_2[A + B(N_1 - N_2) + C(N_1 - N_2)^2 + \cdots] \quad (3.5)$$

and showed that it was possible to interpret the shape of the curves for the excess entropy and enthalpy in terms of the relative magnitudes of the terms in $A, B, C \ldots$; this provides a convenient means of classifying and analysing the data, although little is learnt about the reasons for the asymmetry of S^E and H^M. The simplest class of non-ideal solutions are those for which all coefficients higher than A in equation (3.5) vanish; these are the 'regular solutions':

$$\begin{aligned} G^E &= A.N_1N_2 \\ S^E &= N_1N_2\left[-\left(\frac{\partial A}{\partial T}\right)_P\right] \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.6) \\ H^E &= N_1N_2\left[A - T\left(\frac{\partial A}{\partial T}\right)_P\right] \end{aligned}$$

Now if $(\partial A/\partial T) = 0$, then $S^E = 0$, and $H^E = G^E = A.N_1N_2$. This is the condition for Hildebrand's[112] so-called 'regular solution', which is thus a special case arising from equation (3.6). The term 'regular solution' is better kept for solutions obeying equation (3.6); such solutions are, in any case, rare, and possibly even non-existent, although regular solutions are often assumed to exist for the sake of easy calculation, especially of thermodynamic data from phase diagrams. (This is never a very satisfactory way of obtaining data, because minor discrepancies in the phase diagram may greatly affect the results; the reverse process is not subject to such errors, and recently Kubaschewski and his co-workers[111] have been able to correct a number of phase diagrams in this way.)

The application of classical thermodynamics to solutions of non-metallic non-electrolytes has advanced further than its use for metallic solutions; it is hoped to show in what follows that some of the ideas obtained are of use in discussing liquid-alloy thermodynamics.

The Entropy of Solution

From equation (3.3) a finite negative value of S^E must result from a finite difference between ε_{ij} and $\frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$. The Guggenheim theory takes no account of non-configurational contributions to the entropy of mixing, arising from changes in the density of states on mixing or from changes in magnetic moment; in liquid alloys these contributions are usually small, but in many solid systems they may completely outweigh the configurational term.

The following factors may affect the configurational or other contributions to S^E in liquid mixtures:

1. A finite volume of mixing, V^M.
2. A difference in the molar free volume of the components.
3. A change in coordination number on mixing.
4. Deviations from Neumann–Kopp behaviour resulting from the following:
   - (*a*) changes in the density of states,
   - (*b*) changes in magnetic moment,
   - (*c*) changes in atomic vibration frequencies or modes.

Some of these effects (e.g. 2 and 4(*c*)) may be closely connected, and some care is required when estimating the contribution arising from each.

(1) *Volume of Mixing*

Scatchard[108] has shown that the contribution to the excess entropy of solution arising from a finite volume of mixing, V^M, is:

$$S^E_{\text{vol.}} \simeq V^M \qquad \ldots\ldots \quad (3.7)$$

with $S_{\text{vol.}}$ in cal. deg.$^{-1}$ mole^{-1}, and V^M in c.c. mole^{-1}. In most liquid metallic systems, $V^M = \pm 0{\cdot}2$ c.c. mole^{-1}, so that the effect on S^E is small. In some systems, strong unlike-atom interactions (high ε_{ij}) lead to a drastic change in bonding on mixing and thus result in strong volume contractions (e.g. Hg–K, $V^M_{\text{max.}} = -25{\cdot}4\% = -5$ c.c. mole^{-1}). Kubaschewski and Evans[101] have shown that there is an approximate correlation between S^E and V^M in some liquid alloy systems (Section 3.2.3.D).

(2) *Difference in Molar Free Volumes*

Scatchard[108] also showed that a difference between the molar free volumes of the components must lead to an increase in S^M as a result of a decrease in the mean atomic vibration frequency. The molar free volume may be estimated approximately from:

$$V_f = RT \exp\left(\frac{S^V}{R}\right) \qquad . \quad . \quad . \quad . \quad (3.8)$$

at one atmosphere pressure. S^V is the entropy of vaporization at the boiling point. In systems that exhibit a very large difference in free volumes, e.g. a transition-metal–alkali-metal system, a positive S^E may be observed through this effect, but normally its contribution is insignificant or masked by other factors.

(3) *Change in Coordination Number*

The effect of a composition-dependence of Z may be determined qualitatively from equation (3.2). A value of Z_{alloy} which is above the mean of those of the components results in a less negative value of S^E. Changes in Z may be significant across many systems (e.g. Bi–Pb alloys: for the pure components, $Z_{\text{Pb}} \simeq 11$ and $Z_{\text{Bi}} \simeq 8$), and may result in a composition-dependent contribution to S^E.

(4*a*) *Change in the Density of States*

Little progress has been made towards a means of measuring or calculating the effect of this for a liquid alloy. The electron specific-heat term, except in the transition metals, is usually $\sim 2\%$ of the total C_p, so any variations through $N(E)$ should have little effect.

(4*b*) *Change in Magnetic Moment*

This is not likely to be significant in any liquid alloy; it is only large enough to affect C_p, and hence S^E, significantly when ferromagnetic transformations are involved.

(4*c*) *Change in Vibration Frequencies or Modes*

This may make a significant contribution, through C_p, if a drastic change in the nature of the interatomic bond takes place on mixing—as is apparently the case in the Hg–K system, mentioned earlier—leading to major changes in bond length or strength. These changes result in negative deviations from Neumann–Kopp behaviour, and hence make S^E more negative. A large change in packing efficiency on mixing, perhaps as the result of a considerable difference in atomic size, will have a similar effect, which also may be significant in systems containing the very large alkali-metal atoms. S^E is large and negative in many of these systems (Section 3.2.3 and Table XXIII). In some alloy systems—possibly those exhibiting strong short-range order at temperatures near the liquidus—there may be a considerable temperature-dependence of the vibration modes and hence of C_p. This will appear as a contribution to both the enthalpy and entropy of mixing.

In addition to the thermodynamic consequences of a large value of $[\varepsilon_{ij} - \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})]$, there is also the physical result of positive (like-atom, $\varepsilon_{ij} < \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$), or negative (unlike-atom, $\varepsilon_{ij} > \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$), clustering or short-range order, which is reflected in the negative contribution to S^E through the configurational entropy of mixing (equation 3.2) and which also affects a number of physical properties. If the extent of this contribution to S^E is invariant across the system, a smooth S^M/N* or S^E/N curve will be observed. If, however, there is an optimum composition for short-range order of either kind, such as might be expected at a composition of maximum total bonding energy, perhaps corresponding to the liquidus maximum of an intermetallic compound,[8] then the S^M/N and S^E/N curves will contain a section which is flattened or depressed in a negative sense at about that composition. This will also result in wide deviations from the ideal curve of the *partial* entropies of solution, since these are determined, at any composition, by the intercepts of the tangents to the S^M/N or S^E/N curves with the entropy axis. It follows that such deviations are an indication of positive or negative clustering; the type of clustering will be indicated by the sign of H^M, which will be positive for like-atom, negative for unlike-atom, clustering. A number of examples of this type are discussed in Section 3.2.2. Ölander[109] has calculated the shape of the S^E/N curve, and the corresponding partial curves, for the specific case of a b.c.c. structure at nearly complete order. A similar treatment should be possible for the liquid state;[113,114] by comparison of experimental and calculated S^E/N plots, one should then be able to estimate a degree of order, but so far such a treatment has proved impossible without unrealistic simplifying assumptions. A less ambitious but very interesting treatment of the problem has been given by Kehiaian,[115] who has considered the special case of a solution with association of the AB type; the predicted

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* This form of shorthand denotes a plot of S^M, &c., against the mole-fraction of solute, N.

composition-dependence of the integral excess entropy of solution is just that discussed above, with a minimum value in S^E at the composition AB which becomes more pronounced with increasing enthalpy of formation of the association AB. The same author has also considered the case where one of the components is associated, or has an exceptionally strong pair potential.[116] This results in asymmetric G^M/N and H^M/N plots, and this will be referred to later. It should be emphasized that these approaches to the problem do not tell us *why* the associations occur, but only indicate what happens *when* they occur.

The fluctuations in S^E and its corresponding partials are, of course, also reflected in the H^M/N and partial-enthalpy curves. Thus the H^M/N curve will show a sharp minimum at the optimum ordering composition; this has been observed in a number of systems (Section 3.2.3). In addition the *symmetry* of the H^M/N and S^E/N curves (equations 3.2 and 3.3) may give a qualitative indication of any changes in the nature of the intermetallic bond or other factors with composition[103] (p. 430).

3.2. RESULTS

Details of experimental methods are given in Ref. (101).

3.2.1. *Pure Metals*

The known specific-heat data of pure metals, together with details of the enthalpies of fusion and sublimation and change of specific heat on fusion, are summarized in Table XV. The information on those metals and alloys for which the specific heat has been measured through the melting point is collected in Figs. 6 and 7, from which the following conclusions are possible:

(1) The specific heat of a liquid metal may be greater or less than that of the solid at the melting point. (In many cases the difference recorded in Table XV is less than the total error ($\sim \pm 8\%$) in the figures for solid and liquid).

(2) The temperature coefficient of the specific heat of most liquid metals for which data are available is small and negative, and often invariant with temperature. In several cases the sign of $d(C_p)/dT$ changes as the temperature is increased, becoming positive at higher temperatures (K, Na, Hg, In, probably Li). Since in most metals C_p shows little change on fusion, it seems that neither the vibrational spectrum nor the valence-electron configuration of most liquid metals changes significantly on melting (see Section 6.2). This is confirmed by the evidence from incoherent scattering of neutrons (p. 393).

The negative $d(C_p)/dT$ immediately after fusion, which is common to most liquid metals, could result from a gradual post-melting modifica-

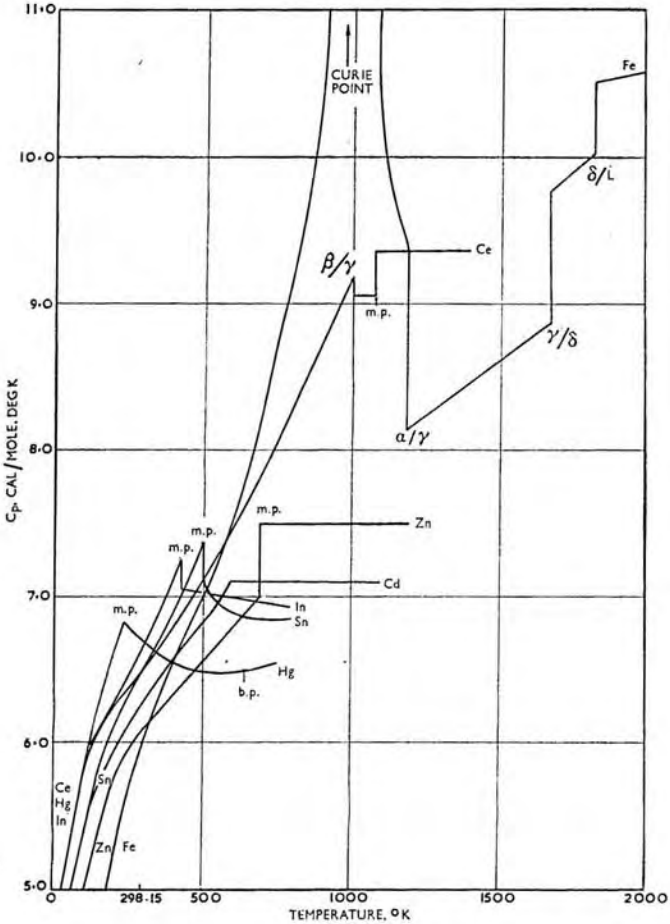

FIG. 6.—Specific heats of pure solid and liquid metals.

tion of the liquid structure, or from impurities (see also Section 8). On the other hand, both this and the subsequent positive $d(C_p)/dT$ observed in some metals (the latter may be confined to atoms of large radius, and large free volume, e.g. the alkali metals) may be due to a varying vibrational contribution to C_p which may arise from a change in the vibration spectrum with increasing temperature. Neutron scattering indicates that the Debye spectrum is little changed on fusion, apart from a degree

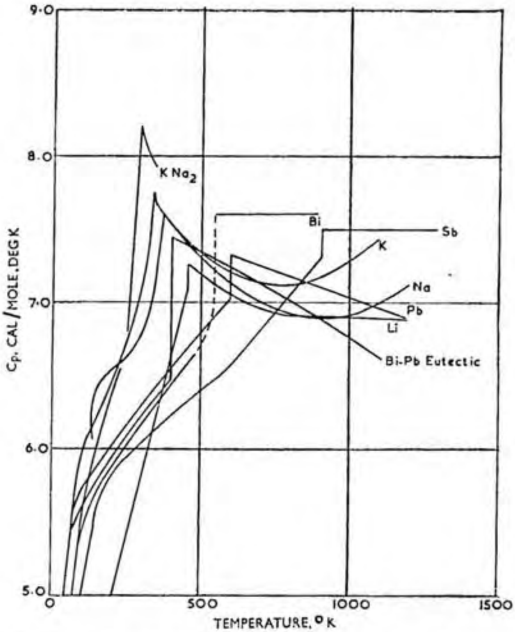

Fig. 7.—Specific heats of liquid metals and alloys.

of 'smearing'; many of the high-frequency modes of the solid must therefore remain at temperatures just above the melting point but may disappear as the temperature is increased. A similar increase in C_p may ultimately be observed when measurements on other liquid metals are extended to high superheats.

The abnormally high values of C_p for the liquid transition and alkaline-earth metals are probably the result of a high electronic contribution to C_p.

Hume-Rothery has shown that some indication of the structure of pure metals may be obtained from their melting and boiling points.[117] If these are T^F and T^B, respectively, the 'liquid range' R_p may be defined as $(T^B - T^F)$. The range of existence of the condensed state may be divided into the 'solid fraction' $S_p = T^B/T^F$ and the 'liquid fraction' $L_p = R_p/T^B$. (The subscripts 'p' indicate measurements, particularly of T^B, at a constant pressure of 760 mm.) Values of T^F, T^B, R_p, and L_p, for the metallic elements are given in Table XVI. The value of R_p is often high in Groups I and III, A or B, and low in Groups II and IV, A or B. It seems possible that the stable nature of the pair of *s*-electrons in elements from Groups II and IV results in these electrons contributing relatively little to the bonding of the liquid: thus the boiling points (Table XVI) and enthalpies of volatilization (Table XV) are low. In the odd Groups the unpaired electrons are able to form bonds, possibly of the Pauling hybrid-orbital type. The very high liquid fractions of the Group III liquids suggest that the three electrons in s^2p combination provide optimum bonding conditions and stabilization of the liquid.

There are a number of special cases. The boiling points of some of the Group IV and V elements are relatively low because the formation of a polyatomic vapour stabilizes the gas phase relative to the liquid and thus reduces the liquid range. In the transition metals, bonding in both solid and liquid is very strong as the result of *spd* hybridization of valence electrons, and both melting and boiling points are high. The IB metals are also strongly bonded as the result of interactions between the *d*-electrons in the ion core. Hume-Rothery[117] suggests that indium and thallium may be incompletely ionized, thus giving lower boiling points than the apparently completely ionized gallium; other anomalies in the properties of these metals may be explained in the same way. Incomplete ionization may also explain the anomalous behaviour of mercury (see also Section 6).

It appears, both from X-ray and thermodynamic evidence, that the liquid state of the elements in the odd groups of the Periodic Table and possibly those in Group IVB (tin has a very wide liquid range), is stabilized in some way, perhaps by homopolar bonding resulting from the hybridization of valence-electron orbitals proposed by Pauling.[46] As Hume-Rothery suggests, the Pauling model of metallic bonding may be more applicable to liquid than to solid metals, since, with the removal of the necessity to pack in the form of a long-range lattice, the atoms may be free to take up positions relative to one another which can more easily satisfy the 'spatial' requirements of the Pauling theory.

3.2.2. *Liquid Alloys: Specific Heats*

Here interest lies mainly in deviations from Neumann–Kopp behaviour, rather than in the absolute value, or the temperature-dependence, of C_p. Very few direct measurements of C_p are reported, and those available are of low accuracy.[118] The Hg–Tl,[119] Bi–Pb[120] (Fig. 7), In–Sn,[121] K–Na,[122] Au–Zn,[123] Bi–Sb,[124] and Na–Tl[125] systems show zero or small positive ΔC_p values. In the case of NaTl, an anomalously large value of $d(C_p)/dT$ is observed from ~ 40 degC below the melting point, as in In, KNa_2, Bi, Ca, Sb_2Te_3, Bi_2Te_3 and other materials (Figs. 6 and 7 and Section 8). This phenomenon is probably due to an anomalously high vacancy concentration, or possibly premelting due to impurities; it requires further investigation. In all the alloys studied the temperature-dependence of the specific heat is similar to that of the pure liquid metals (see above).

Values of ΔC_p, the deviation from Neumann–Kopp behaviour, may also be determined by observing the variation in H^M with temperature.[126, 127] Then:

$$\Delta(H^M) = \Delta C_p . \Delta T \qquad . \quad . \quad . \quad . \quad . \quad (3.9)$$

Very little calorimetric work (H^M values from equilibrium measurements are not sufficiently accurate) has been carried out over a range of temperature. The total information available is summarized in Table XVII.

Values of ΔC_p for solid alloys are usually smaller than those for the corresponding liquid. ΔC_p for many intermetallic compounds is small and negative;[128] similar, but less pronounced behaviour may be expected of the liquid as the result of the influence of the relatively tighter packing in the alloy upon the vibrational spectrum.

3.2.3. *Liquid Alloys: The 'Direct' Method*

The 'direct' method consists in the investigation of the composition-, or temperature-dependence of thermodynamic parameters (G^M, S^M, H^M, &c.) in a system, or group of similar systems.

The thermodynamic data quoted in Tables XVIII–XXIII have been taken mainly from the assessments of Kubaschewski and Catterall[129] and of Hultgren *et al.*[130] and the data on volumes of mixing from the reviews by Sauerwald;[136] in such cases no reference is given. In cases where new data have made a re-assessment necessary the sources are indicated.*

A. *Solid-Solution Systems*

The available data are summarized in Table XVIII. Data on size and electronegativity factor have already been quoted in Table I. The formation of a solid solution with no solid immiscibility (as in eutectics) or intermetallic compounds, and the form of the solidus and liquidus curves, indicate that the liquid state of such systems should show small positive or negative H^M values with excess entropies of mixing of about zero ('regular solutions'). The sign of the enthalpy term depends upon the balance of size, valence, and other factors. Table XVIII shows that this is approximately the case. In the Ag–Au, Au–Cu, and Cd–Mg systems the relatively high electronegativity factors produce fairly high

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* The author is extremely indebted to Dr. O. Kubaschewski for providing him with the results of some of his recent assessments before publication.

enthalpies of mixing (partially offset in the Au–Cu system by a high size factor) and, in the Cd–Mg and Au–Cu systems, solid-state ordering. The thermodynamic parameters are nearly symmetric (the data for the Au–Cu system are in some doubt[130] but here the asymmetry may arise from the large size factor) indicating, as expected from the similarity of the components of each of these systems, negligible composition-dependence of bond characteristics, co-ordination number, or other influencing factor. Excess free energies of mixing may be either positive or negative.

The data suggest that the factors thought to control ease of miscibility in the solid also exert a major influence after fusion, e.g. the size factor may apparently control the ease of packing of two dissimilar atoms, even in the liquid. The electronegativity factor should, of course, operate regardless of structure or phase.

Analogous systems amongst non-metallic non-electrolyte systems are those between non-polar non-associated liquids of similar molecular size and structure, such as the paraffin hydrocarbons,[103] but here the excess quantities are very small by 'metallic' standards—enthalpies of mixing are usually < 50 cal. Molecular asymmetry may result in asymmetry of H^M and S^E for non-metallic solutions, but structural effects are unlikely in the simple metallic liquids discussed here.

B. *Eutectic Systems*

The eutectic systems listed in Tables II–V show an increasing size factor in the order

$$\text{NI} < \text{SI} < \text{DI} < 0\% \text{ SI} \quad \text{(see p. 387 and Fig. 1)},$$

which suggests that a strongly inflected liquidus may result from a large size factor. The limiting case of incipient immiscibility is the eutectic system with a horizontal liquidus which corresponds to a linear section in the G^M/N curve at the liquidus (Fig. 5). Thus, a less strongly inflected liquidus may also indicate a tendency to immiscibility, as has been suggested elsewhere.[131] Once again, it appears that the size factor determines the ease of insertion of a solute atom into the liquid solvent 'structure'.

The available thermodynamic data for the various groups of eutectic (and a few peritectic) systems are summarized in Tables XIX A–F. The suggestion of an increasing difficulty of liquid-state mixing in the order NI, SI, DI, 0% SI, is supported by the general increase in the positive enthalpies of mixing in the same order, although more data are required to establish this with certainty.

It is interesting that in the alkali-metal systems, the liquid-state enthalpies of mixing become more positive as the components become further separated in the Periodic Table, suggesting a size-factor effect. The positive enthalpy of mixing in the K–Na system supports the conclusion from diffraction studies that no short-range order should be observed in the liquid state. The enthalpies of mixing are considerably less positive in the 'complex' eutectic and peritectic systems in which the size factors are smaller and electronegativity factors higher; this suggests that the feeble unlike-atom interactions in these systems, which result in intermediate phases that are unstable at the liquidus temperature, also operate to a small degree in the liquid.

Excess entropies of mixing are generally positive in eutectic systems, and thus result in excess free energies of mixing that are slightly less positive than the enthalpies. Exactly similar behaviour is observed in a very wide range of non-metallic mixtures in which there is a considerable size or structure difference between the otherwise inert components, e.g. mixtures of paraffin and aromatic hydrocarbons,[103] emphasizing that mechanical rather than chemical differences between the components are of primary importance in these liquid mixtures. There is little information on the type of equilibrium diagram exhibited by non-metallic mixtures of the type referred to, but it is very probable that eutectic systems are common; in molten-salt mixtures there is a similar correlation between the thermodynamic parameters and the type of phase diagram produced—indeed, the basic thermodynamic principles of the phase rule indicate that this must be so.

In all the eutectic systems listed, the electronegativity factor is small, but a number of the systems containing Al, Ge, Ga, Sn, Bi, and Sb have an abnormally small size factor. It may be significant that these elements, with the exception of aluminium, are those which (Section 2.3.1) may have a 'dual' structure as a result of the homopolar contribution to the interatomic bond. Aluminium does not fall into this group, but exhibits homopolar bond characteristics in many of its compounds with non-metals; further work may indicate a degree of non-metallic bonding in the pure metal or its alloys. The difficulty of mixing in these 'small-size-factor' systems may result from the task of breaking the strong interatomic bond in the homopolar-bonded components. This characteristic may even be observed in systems where the miscibility is improved by a high electronegativity factor (e.g. in the IB–VB metal alloys, although here it may also be caused by strong interatomic bond in the IB metals).

An inflected liquidus can result only from a flattening of the G^M/N curve for the liquid. The centre of the flattened section will correspond approximately to the maximum value of G^E, since this represents the deviation of the observed curve from the ideal plot. Thus, the composition at which $G^E_{\text{max.}}$ falls should be the same as that of the axis of symmetry of the inflection in the liquidus. This is approximately true, at least for the well-documented systems (Tables II–VI and XIX).

The Cu–Fe and Cu–Co systems approximate to the limiting case of a horizontal liquidus; Nakagawa[132] has induced separation into two liquids in these alloys by supercooling to below liquidus temperature, the extra cooling being sufficient to produce a G^M/N curve characteristic of the miscibility-gap system ($\lambda > 2RT$ in Fig. 5). In these liquids at just above the liquidus temperature, $\frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj}) \leqslant \varepsilon_{ij}$; it may therefore be possible to detect positive like-atom clustering in the liquid along the critical curve, perhaps through anomalous composition-dependence of S^M or $S^M_{i,j}$. Similar phenomena might even be observed in systems with less strongly inflected liquidus curves. Recently Pratt and Morris[133] have observed anomalous behaviour of the excess entropy of solution of tin in liquid Ag–Sn alloys at ~ 65 at.-% Sn. This composition closely corresponds to the axis of symmetry of an inflection in the liquidus of this rather complex eutectic system, suggesting that structurally incompatible clusters of the type proposed may be present in the liquid, although in this case the two incompatible structures may arise from the structures of pure liquid tin and of the Ag–Sn liquids at ~ 25 at.-% tin, both of which have been shown by diffraction studies to be abnormal (Section 2). A more detailed thermodynamic investigation of 'inflected' eutectic systems would be welcome to determine whether such 'foreshadowing' of immiscibility is a real effect, and to establish the factors that affect the shape of the G^M/N curve in liquid alloys. Immiscibility is probably caused by the increasing difficulty at lower temperatures of packing unequal-sized atoms, as a result of thermal contraction and the reduced randomizing effect of thermal vibrations.

The size factor may be supplemented in some of the systems containing IB solvents by an extension of the relative valency factor to the liquid state. In the solid state the IB metals are only slightly soluble in metals of higher valence, but usually act as a fairly good solvent for those metals, for reasons which may be connected with the homopolar bond in the high-valent metal.[45] The same phenomenon is often observed in the liquid, and manifests itself as a positive contribution to the enthalpy of mixing in the alloys rich in the high-valent metal, thus producing an asymmetric H^M/N curve. In some cases the enthalpy of mixing may be positive at one end of the system (that rich in the high-valent metal) and negative at the other. Systems exhibiting such behaviour include Ag–Bi, Ag–Sn, Ag–Sb, and Cu–Sn. In most of these systems the phase diagram also clearly reflects the positive enthalpy contribution at the end rich in the high-valent metal by possessing an inflected liquidus. Similar behaviour is observed in mixtures of non-metallic non-electrolytes in which one component contains a hydrogen bond; examples are alcohol/hydrocarbon mixtures such as methanol/benzene, or aqueous mixtures such as water/dioxan.[103] In these, the enthalpy of mixing is more positive or less negative in mixtures *weak* in the hydrogen-bonded component, and it is usually argued that this results from the difficulty of breaking hydrogen bonds in such mixtures; this must happen in order to disperse the relatively small number of alcohol molecules in the inert solvent. At high alcohol or water concentrations this is not necessary, and a more negative enthalpy results. The same arguments may apply to metallic solutions; in this case the lower-valent metal apparently behaves as the more strongly bonded component, thus giving more negative or less positive enthalpies of mixing in alloys rich in the low-valent metal. The enthalpies of sublimation (Table XV), which are an approximate measure of bond strength, are certainly higher for the low-valent metals in the alloy examples given above. In dilute alloys, the process of mixing for each solute atom approximates to the breaking of the solute/solute bond, and its replacement by a solute/solvent bond; solute/solute interactions in the alloy may be ignored at high dilution. It follows that, in general, if $\varepsilon_{ii} > \varepsilon_{ij}$ and $\varepsilon_{jj} < \varepsilon_{ij}$ (p. 405), then an asymmetric enthalpy-of-mixing curve should be observed, with the more positive enthalpies at the end of the system rich in component j. If the pure-metal pair potentials are estimated in terms of the enthalpy of sublimation, this should be the case for a fairly large proportion of the systems listed in Tables XVIII–XXIII, but there are many exceptions, and clearly there are other factors to be taken into account in many systems. Some of these are discussed later. The main difficulty lies in estimating the strength of the bond between unlike atoms; if this is high (large negative H^M), then the asymmetry of the enthalpy of mixing is determined by the composition of maximum bonding energy and hence the maximum negative H^M in the liquid—this usually corresponds to a solid-state compound—and not by the 'balance' between the bond strengths. If $\varepsilon_{ii} > \varepsilon_{ij} > \varepsilon_{jj}$, then ε_{ij} cannot be very large, and the effects of this 'balance' should be sought only in systems in which $\varepsilon_{ij} \simeq \frac{\varepsilon_{ii} + \varepsilon_{jj}}{2}$, i.e. in which H^M is small, and positive *or* negative, and indeed it is only in such systems that the particular form of asymmetry in the H^M/N curve discussed here is found. In a number of systems containing the IIB metals, asymmetry in H^M is observed for different reasons (see below).

An alternative approach to the structure of eutectic systems has been used by Hume-Rothery and Anderson,[134] who surveyed all eutectics (irrespective of the type of system involved) reported in Hansen and Anderko's book.[135] They noted that eutectics prefer to fall at certain compositions (0, $8\frac{1}{2}$, 17, 25, $33\frac{1}{3}$, 40 at.-% solute) and suggest that at these compositions packing in the liquid state of the two components is easy. Very few eutectics are observed at 50%, and packing is therefore thought to be exceptionally difficult at this value. A number of negatively clustered arrangements are suggested, mostly based on the dodecahedron.[137] However, such structures, which indicate an apparent preference for A–B bonding, are not compatible with the positive enthalpies of mixing in these systems, and take no account of the widely varying size factor which must also affect the ease of packing (see Section 9.4).

C. *Miscibility-Gap Systems*

The thermochemical and other properties of partially miscible non-metallic liquids have been studied fairly extensively.[144] Both upper and lower critical solution points are possible (the latter give a 'closed loop' containing two immiscible liquid phases on the temperature/composition diagram), but in metallic mixtures which are thermodynamically capable of showing lower critical points, solidification occurs before the lower critical temperature is reached. Closed loops are known in a number of non-metallic liquid mixtures—nicotine/water is the most frequently quoted example.

The thermodynamic criteria for immiscibility have been discussed by various writers and a number of formal expressions have been proposed.[103, 139, 141–143, 152] These generally have the disadvantage of being difficult to relate to experimental data; a more qualitative guide to immiscibility is usually needed. Copp and Everett[139] have pointed out that a rough guide is available in the size of the excess free energy of mixing; if this exceeds $+\frac{1}{2}RT$ then phase separation is likely, provided that H^M is positive and S^E is more positive than $-\frac{1}{2}R$. This is, in fact, the behaviour predicted for the rather unlikely combination of a partially miscible but regular mixture, but it serves as a good rough guide, even for metallic solutions, as will be seen from Tables XVIII–XXIII. It is also possible to distinguish thermodynamically between the criteria for an upper and a lower critical solution point;[103] from this it may be shown that it is unlikely that a metallic solution will be found that exhibits a lower critical point. The nearest non-metallic approximation to metallic-system thermodynamic behaviour is provided by fluorocarbon mixtures with non-polar hydrocarbons or with other non-polar organic halides.[140] These invariably exhibit high positive excess free energies, entropies, and enthalpies, and form mixtures with only upper critical points. However, none of this thermodynamic information on metallic or non-metallic partially miscible liquids has anything to say about the reasons for immiscibility; these are still a matter for speculation, particularly in metallic systems.

The thermodynamic information for metallic systems is summarized in Table XX. H^M is, of course, universally positive, as are the excess entropies of solution. Both apparently arise, as in the eutectic systems, from the generally large size factor in the systems investigated, which decreases the mean vibration frequency and thus makes a positive contribution to the alloy specific heat and to the excess entropy of mixing. The maximum values of G^E and H^M fall, as expected, at compositions close to those of the maximum in the miscibility gap.

The systems listed in Tables VIII and IX fall into two groups with a few exceptions—those with large size factors (group I), and those containing the transition metals (group II); (the latter systems may also have a large size factor). The mean size factor of group I is just (but not significantly) smaller than that of the 0% SI systems.

In the first group the size factor is apparently the major influence in producing immiscibility; as in the case of the eutectic systems, exceptions occur in systems containing aluminium, germanium, and, particularly, uranium. On the other hand, the transition-metal systems (group II) appear to exhibit liquid immiscibility, or near-immiscibility, for two different reasons, depending upon the second component. In systems with the Group IB metals, in which the size factor is nearly always small, it is possible that strong, partially homopolar and directional bonds in the transition metal[145] resulting from hybridization of *s*-, *p*-, and *d*-orbital electrons are not easily broken down, and involve a high degree of *d*-participation. In the IB metals, however, the *d*-shells are full, and the *d*-electrons are unable to take part in the electron-sharing bonds. Thus, the bonding characteristics, and therefore the structure, of the transition metal cannot be achieved by the IB metal, and immiscibility results. In the remaining transition-metal systems, the size factor is high and is the major factor in producing immiscibility. Several of these systems also contain elements to which some degree of homopolar bonding has been ascribed (e.g. bismuth, gallium, Section 2.2.1). These may also provide a strongly bonded structure incompatible with that of the transition-metal component.

Mott[138] has used as a criterion for miscibility a modified version of the Hildebrand rule[112] for non-metallic non-electrolytes:

$$\tfrac{1}{2}(V_A + V_B)\left[\left(\frac{E_A^V}{V_A}\right)^{1/2} - \left(\frac{E_B^V}{V_B}\right)^{1/2}\right]^2 > RT \qquad (3.10)$$

where V_A, V_B are atomic volumes of components A and B, and E_A^V, E_B^V are their heats of vaporization. The terms $\left(\frac{E_A^V}{V_A}\right)^{1/2}$, &c., were termed by Hildebrand 'solubility parameters' (δ_A) and are an empirical measure of the bonding energy of the components, i.e. of ε_{ii} and ε_{jj} (p. 405). Thus the rule becomes:

$$\tfrac{1}{2}(V_A + V_B)(\delta_A - \delta_B)^2 > 2RT \quad . \quad . \quad . \quad (3.11)$$

as a condition for miscibility. Mott modified this to:

$$\tfrac{1}{2}(V_A + V_B)(\delta_A - \delta_B)^2 - 23{,}060\eta(\zeta_A - \zeta_B)^2 > 2RT \quad (3.12)$$

where ζ_A, ζ_B are the electronegativities of the two elements, and η is the maximum number of Pauling[46] valence bonds which they can form. A 'Mott Number' was thus derived:

$$N_M = \frac{\tfrac{1}{2}(V_A + V_B)(\delta_A - \delta_B)^2 - 2RT}{23{,}060(\zeta_A - \zeta_B)^2} \quad . \quad (3.13)$$

for comparison with η. If $N_M > \eta$, liquid immiscibility was predicted. Considerably better agreement was obtained between prediction and practice than with the original Hildebrand criterion. Agreement may be further improved by taking some rather unconventional valency and electronegativity values for certain elements.[9, 146] The Mott theory takes into account three of the factors that have been discussed—the size and electronegativity factors, and an approximate measure of the interatomic bond strength—but, because of its empirical nature, it reveals no fundamental information about the influence of these parameters.

The positive enthalpies of mixing in the miscibility-gap systems indicate that the tendency for immiscibility does not disappear when the critical temperature is exceeded; thus, evidence of positive clustering, or at least of long-range compositional fluctuations, may be observed in the homogeneous liquid phase at temperatures just greater than critical. No adequate work is reported in this range on the properties of metallic systems, but evidence of clustering has been obtained in the form of anomalies in the viscosity/temperature plots,[147] specific heats,[148] molar volumes,[148] light scattering,[149] and absorption of ultrasonic waves[150] in mixtures of organic liquids. The evidence indicates that the liquid mixtures at temperatures just above the critical temperature may be considered as very finely divided emulsions; the viscosity measurements[147] have been treated successfully by means of a model[151] based on the assumed existence in the liquid of long-wavelength variations in composition of the kind that would be observed in such an 'incipient emulsion'. The same sort of structure may exist in liquid metallic mixtures under these circumstances, although at the higher temperatures and therefore greater amplitudes of atomic vibration involved the structure may be detectable only at temperatures very close to the critical curve. It is clear that more detailed thermodynamic and physical investigations of immiscible metallic systems are needed.

D. *Compound-Containing Systems*

These have been arbitrarily divided into: (*a*) systems containing electron compounds, subdivided into those with and without a liquidus maximum, and (*b*) systems not containing electron compounds, and showing a liquidus maximum. The well-established systems, together with size and electronegativity factors,* are listed in Tables X, XI, and XII; the available thermochemical data are summarized in Tables XXI–XXIII. Miscellaneous systems, including some which also contain a miscibility gap (Table XIII), are discussed briefly later.

As expected (Section 3.1.2), all compound-containing systems exhibit negative enthalpies of mixing in the liquid state, indicating, as in the solid, a tendency to form A–B bonds preferentially. The enthalpies are smallest for the electron-compound systems and increase with the tendency to form a liquidus maximum; again, this reflects exactly the characteristics of the solid. Correspondingly, excess free energies and entropies of solution are negative, the composition-dependence of the latter suggesting a tendency to short-range order in these systems; the negative enthalpies of solution indicate that this is of the negative (unlike-atom) type. The exceptions of Au–Sn and Cd–Sb have no logical explanation and may result from incorrect measurement.[130]

For the simple electron-compound systems, the low negative H^M values ($\sim -1{\cdot}5$ kcal) and the small change in H^M on fusion (most of which is accounted for by the change in the standard state) suggest that the change in Fermi energy on alloying is still the main contribution to H^M. The electronegativity factor is small in all these systems, and thus is unlikely to contribute significantly to the enthalpies of mixing or to produce any appreciable degree of negative clustering in the liquid (except, perhaps, in the Cu–Sn system, where H^M has a very sharp minimum). The randomness of the liquid structure is reflected in the relatively small negative excess entropies of solution. Critical electron-concentration effects will not be observed in the liquid, since fusion will remove any effects due to Brillouin-zone/Fermi-sphere interactions by destroying the Brillouin zone. Zone effects are, however, possible in liquid alloys (Sections 6.1 and 6.2), but not at the same composition as in the solid state.

The enthalpies of mixing in the 'simple' electron-compound systems vary approximately with the electronegativity factor. In the second group of 'electron' systems, which have liquidus maxima, the electro-

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* Defined on p. 388.

negativity factors are greater and are clearly becoming an over-riding factor. With the exception of Cd–Cu, the enthalpies of mixing are higher (~ 3 kcal), and the change on fusion rather more marked. In both liquid and solid states, the interatomic force has a more 'chemical' nature, involving, perhaps, a proportion of homopolar or heteropolar bonding. Some negative short-range order may be expected in the liquid, especially at the liquidus maximum, where bonding is strongest in the solid. Thus some anomalous composition-dependence of S^M and S_i^M is expected, and is observed in the Au–Sn system in which it indicates some degree of ordering at 25 at.-% Sn.[155] This composition does not correspond to any known solid-state compound, but is approximately the ordering composition suggested by X-ray (Section 2.3.4), resistivity (Section 6.2.2D), and viscosity (Section 4.2.3D) data on this system. There is some evidence of similar behaviour in the Cu–Sn and Ag–Sn systems,[153, 156] where the electronegativity factor is smaller. In Cu–Cd[157] the 'γ-brass' δ-phase is apparently only a partial electron compound, with bonding enhanced electrochemically.

The remaining compound-containing systems and their thermodynamic properties have been listed in Table XXIII. Many of these systems form liquids of high negative enthalpy of mixing and many, mainly those with the higher H^M values, show anomalous composition-dependence of S^M and S^E (p. 410), even in the case of Hg–Tl alloys, for which H^M is very small.[69] The data usually indicate a maximum degree of short-range order at the compound composition. This short-range order, especially if H^M is very high, may even take the form of clusters of the compound structure in a more random liquid 'matrix', although this particular cluster structure seems unlikely because such liquids could not be supercooled. The structure of the clusters, if they exist, need not be that of the solid compound, and is probably quite different, since the restriction of having to pack to form a long-range lattice is now removed (Section 9.6).

The observation of an inflected entropy-of-mixing curve in the Hg–Tl system, in which the enthalpy of fusion and hence the degree of ordering is small, indicates that the entropy is a sensitive measure of short-range order in liquid metallic mixtures. The main problem at higher temperatures is the difficulty of making sufficiently precise entropy measurements for any inflection in the partial curves to be statistically significant. It seems probable that an inflected entropy curve would be found by careful work on all the systems listed.

A number of the systems listed in Table XXIII are of particular interest. The positive enthalpy of mixing in the Cd–Na system supports the suggestion of a miscibility gap or, at least, a strongly inflected liquidus in this system;[135] the gap or inflection may arise because of a difficulty in mixing pure liquid sodium with the complex liquid alloy structure arising from the fusion of the compound Cd_2Na, although it is surprising that the enthalpy of mixing does not become negative in cadmium-rich alloys. Thermodynamic data are not available for other similar systems listed in Table XIII. The very high negative enthalpies and volumes of mixing in the transition-metal–silicon systems emphasize that an exceptionally strong A–B bond (high ε_{AB}) can lead to very considerable shrinkage on mixing; the same characteristic is observed in the mercury–alkali-metal liquids, although the nature of the A–B bond is probably very different in the two cases (see below). From Table XXIII it is clear that a close qualitative relationship exists between the enthalpies, excess entropies, and volumes of mixing; generally, a large negative enthalpy of mixing is associated with a large negative entropy and a large negative excess volume.

The crystal structure of the main compound in the solid state may give some clue to the type of bonding prevalent in both solid and liquid.[154] The structures taken up by compounds in the alkali-metal amalgams, for example, are characteristic of ionic materials, as are those of the compounds between magnesium and the Group IVB elements silicon, germanium, tin, and lead; it is reasonable to suppose that a proportion of heteropolar bonding may be found in the liquid alloys of these systems. On the other hand, the structures of the antimonides of the Group III elements are characteristically homopolar; thus, the liquids may also contain a proportion of homopolar bonding—or at least, non-free electrons in weakly bound states. A further clue to the type of bonding in the liquid may be obtained from the change in the enthalpy of mixing upon fusion. For example, the very large change in $H^M_{\text{max.}}$ on fusion in the In–Sb system indicates a major change in bonding on fusion. Solid InSb is a semiconductor, with a high proportion of homopolar bonding, i.e. with a high proportion of the valence electrons localized into bound states. It becomes considerably more metallic in all its properties on fusion, probably as a result of partial destruction of the homopolar bond in favour of metallic bonding. On the other hand, the small changes in H^M on fusion in the systems with C-type structures (these are usually related to known ionic structures, such as CaF_2 [C1]), give an indication of a slight change in the nature of the interatomic bond on fusion. In this case the bond is likely to be partly ionic, with an identifiable 'anion' and 'cation', although the charges on the latter are probably much smaller than those possible according to normal valency rules. The ionic bond is not associated with directionality, and is not usually affected by any alteration in structure, at least in truly ionic materials, so that only small changes in thermodynamic properties should be observed on fusion. This should be particularly notable in those systems with very high enthalpies of mixing, and 'ionic' solid-state structures (e.g. Hg–K, Hg–Na, Na–Pb, Bi–Mg, or possibly Na–Tl (see below)). Where enthalpy values are small errors in determination may be relatively significant, and nothing can be concluded from the change in H^M on fusion.

The excess entropies are high and negative in many of those systems which show little change in H^M on fusion and, in extreme cases, the entropy change on mixing, S^M, is negative. In some of these, a high negative volume of mixing accounts for the large negative S^E (Hg–Na, Hg–K, in particular) (equation 3.7). The partial and integral entropies of solution exhibit the usual anomalous composition-dependence, which is an indication of negative short-range order, perhaps due to the clustering of 'ions'.

Summary: The (Direct) Method

Thermodynamic data on individual liquid systems, and in particular entropies of mixing in cases where they are determined with sufficient precision, may provide considerable qualitative information on the degree of short-range order present in the liquid. The current state of the theory of metallic liquids does not permit a quantitative estimate of the degree of order prevailing, although in principle this is possible. However, when combined with other information, particularly that derived from physical measurements on the same liquids, thermodynamic data can allow the construction of a fairly complete picture of the bonding characteristics of liquid metallic alloy, although at present the results cannot be considered unambiguous. It is certainly true that the information obtained in this way is no more ambiguous than that available from direct structural measurements; the two approaches should clearly be considered as complementary.

3.2.4. *Liquid Alloys: The 'Indirect' Method*

A. *Free Energies*

From a limited number of *solid* solutions in Group IB solvents, the partial excess free energies of solution of the solute at infinite dilution show an approximately linear dependence upon the electronegativity difference between solvent and solute.[158] A similar correlation is shown for various solutes in *liquid* solvents from Groups IB, IIB, IIIB, IVB, and VB (Fig. 8), together with what appears to be a progressive relationship upon moving from Group IB → VB solvents. The usefulness of the correlation is limited by the accuracy of the thermodynamic and electronegativity data.

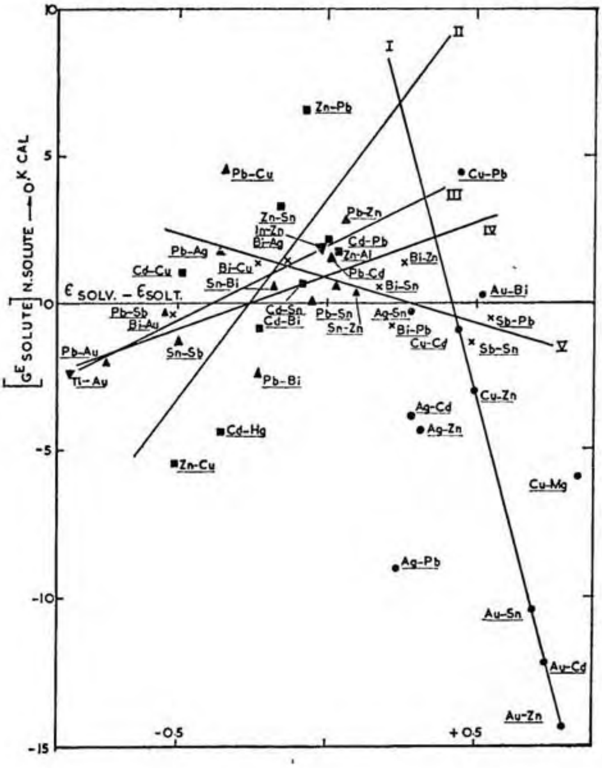


FIG. 8.—Dependence of G^E_{solute} upon the electronegativity factor. Data from Ref. (130) corrected to 1000°K.

	Solvent Group
●	I
■	II
+	III
▲	IV
×	V

Only the difference between solute/solute, and solute/solvent interactions are involved at high dilution—there are no solute/solute interactions in the solution. Thus, the limiting partial excess free energy of the solute is a measure of this difference, $\varepsilon_{ij} \sim \varepsilon_{ii}$, where i is the *solute.* From Fig. 8, the strength of the i–j bond is determined by the 'chemical' difference between the components, as indicated qualitatively by the electronegativity difference. The resulting configurational effect should be evident in the limiting partial excess entropies of mixing, but these are seldom obtained with sufficient precision to show the necessary correlation.

It was found convenient to extrapolate the partial excess free energies to zero solute concentration by plotting G_i^E against electron: atom ratio (e/a). Examples are shown in Fig. 9. For most solutes in Group IB and IIB solvents, the plots are linear; the exceptions are the plots for Group IV and V solutes in liquid zinc. These plots are smoothly curved over the entire composition range, as are the plots for Tl–Au, Sn–Bi, and Pb–Sn alloys. The remaining systems based on Group IVB elements give linear plots, as do those with Group V solvents. Curved plots appear to be associated mainly with the Group IV and V *solutes*. The non-linearity of some of the e/a plots may arise from a wrongly assumed valence for one of the components, or from an additional factor contributing to the excess free energy. Valencies of 4 and 5 were assumed for the IVB and VB elements, respectively, when calculating e/a values, so that the concave-upward curvature of these plots suggests the first interpretation. The otherwise linear dependence of G_i^E upon e/a, even

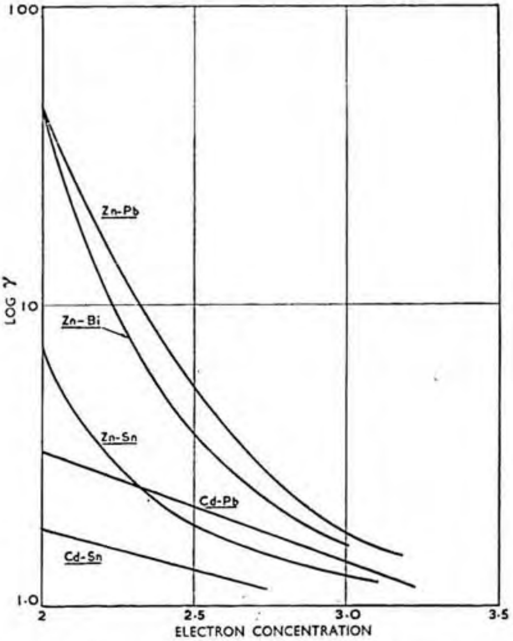


FIG. 9.—Typical plots of $\log \gamma$ ($=G^E_{\text{solute}}/RT$) vs. electron concentration.

in systems containing compounds, indicates that a major source of the excess free energy in solutions of components of different valence may be the energy associated with the Fermi electrons. This contribution to G_i^E is negligible at infinite dilution, and is distinct from that arising from the electronegativity factor.[163]

No correlation of the slopes of the *e*/*a* plots with size factor was observed, in contrast with the solid-state observations.[158] Generally, for any solvent the slope became more negative or less positive the higher was the group of the solute, and thus may depend upon the difference in bond mechanism, and therefore structure, of the two liquids.

B. *Entropies*

Kleppa[159] has claimed some correlation between partial excess entropies of solution of zinc and solute valence in zinc-based systems, the value of S_{Zn}^E at a given mole fraction (including zero) being more positive for large differences in valence between solute and solvent. The correlation is ascribed to 'deviations' of the electronic-heat capacities from the linear mixing rule. The electronic contribution to the total heat capacity is probably too small at $\sim 3\%$ for this to be acceptable, although there is evidence that the Fermi level in molten zinc is abnormally increased by solutes of higher valence than zinc (see p. 470). The change in solute–solute and solute–solvent bond mechanism with valence may affect the vibrational spectrum upon alloying, and give rise to a contribution to S^E. This probably positive contribution will give way to a much stronger negative contribution due to short-range order with higher-valent solutes. Thus, in order to observe a correlation with valence difference alone, allowance must be made for terms, probably much larger, due to changes in electronegativity difference or misfit. Aldred and Pratt[160] have noted such limitations in attempting with some success to correlate excess entropies with valence difference in various lead-based liquid alloys.

Kleppa[161] has also investigated liquid mercury alloys, finding excess entropies that are mostly small and negative, and that do not correlate with valence difference between solute and solvent. The large size factor in some of these systems may contribute in the positive sense to the excess entropy of solution through a reduction in atomic vibration frequencies.

C. *Enthalpies*

In moderately dilute solutions, the enthalpy of mixing may be expressed as:

$$H^M = ax + bx^2 + cx^3 + \cdots \; (x = \mathrm{conc^n\ of\ solute}) \quad (3.14)$$

from which:

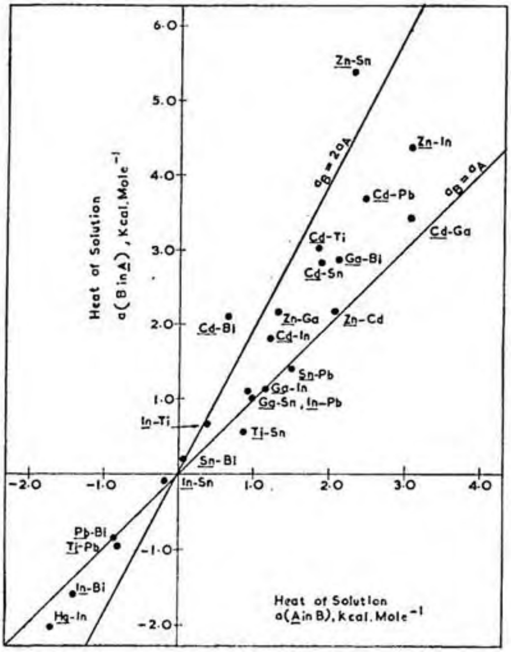
$$H_1^M = a + 2bx + (3c - b)x^2 + \cdots \qquad . \quad . \quad (3.15)$$
$$H_2^M = -bx^2 + \cdots$$

where 1 = solute, 2 = solvent.

The terms *a* and *b* thus represent, respectively, the limiting partial molar heats of solution at infinite dilution, and the limiting curvature of H^M. *b* always has the same sign as H^M.[163]

Kleppa[162] has tabulated *a* and *b* for a large number of liquid metallic solutions, and has plotted (Fig. 10) *a* (for *A* in *B*) against *a* (for *B* in *A*). For systems in which the two are equal, this plot has a slope of unity, and the system is said to be 'energetically symmetric'. There is a rough correlation between the energetic asymmetry of a system and the difference in valence of the components.

Symmetrical integral enthalpy-of-mixing curves are shown by alloys of metals in the same Group of the Periodic Table or, if both valencies



[*Courtesy Amer. Soc. Metals*

FIG. 10.—Correlation between limiting heats of solution for B-Group solvents. (*Kleppa.*[162])

are > 2, by alloys of metals from neighbouring Groups. In other systems, valency and position in the Periodic Table are major factors in determining the magnitude and sign of H^M. Alloys of a Group IB metal with metals of higher Groups from the Fourth (Zn, Ga, Ge) and Fifth (Cd, In, Sn) Periods are usually exothermic, as are alloys between metals in the Sixth Period, regardless of Group. Most other alloys are endothermic, especially those between metals from the Fourth and Sixth Periods; these alloys frequently contain miscibility gaps owing to the almost universal combination of a large size factor with a small electronegativity factor.

The extreme asymmetry of the enthalpy curve in the IB–IVB, VB, systems, as a result of a positive contribution to H^M through difficulty of mixing in alloys rich in the higher-valent element, has been discussed previously (p. 418) in terms of the relative valency effect. The effect is exhibited by the Ag–Sn, Ag–Bi, Ag–Sb, Au–Bi, and Cu–Sn systems. In Ag–Sn, the enthalpy of mixing actually becomes positive above 77 at.-% Sn.[153] The Au–Pb and Au–Sn systems, which do not show this effect, are dominated by the large electronegativity factor, and the Cu–Pb system, in which the size factor is very high, has a miscibility gap. No thermodynamic data are available on the remaining IB–IVB, VB, or VIB systems. Of the IB–VIB alloys, Ag–S, Ag–Se, and Ag–Te all have a miscibility gap at the VB-rich end of the system. In some of these cases miscibility gaps are formed on either side of a strongly bonded compound (Table XIII); this seems to represent the extreme case of total incompatibility of structure between both constituents and the molten compound (which often has a salt-like character[154]).

The Group IIB solvents are also anomalous in some respects. Zinc and cadmium usually give positive enthalpies of mixing with metals of the next two higher Groups, often with an extensive energetic asymmetry which increases in rough proportion to the difference in valence of the two components. The maximum value of the enthalpy of mixing usually falls at a composition nearer the IIB component (Zn with Ga, In, Tl, Sn, and Pb; Cd with Ga, In, Tl, Pb, and possibly Sn). All these are either eutectic or miscibility-gap systems; both the miscibility gaps and any inflections in the liquidus lie at the IIB-rich end of the system. Of the II–V systems, both Cd–Sb and Zn–Sb, in which the size factor is small, and the electronegativity factor fairly high, contain compounds, but the generally negative enthalpy of mixing becomes positive at the IIB-rich end of the system. Cd–Bi and Zn–Bi, in which the size factor is larger, form eutectic and miscibility-gap systems, respectively. Again, the maximum value of H^M (positive) is strongly biased toward the IIB-rich end of the system in each case. The miscibility gap in the Bi–Zn system is similarly positioned.

In many of these systems there is a considerable change in coordination number with composition (Table XIV) but this cannot explain the extreme asymmetry observed in the enthalpies of mixing. The explanation might, perhaps, lie in the bonding characteristics of zinc and cadmium; for these metals Wallace has suggested partially homopolar bonding in the solid state.[164] A more acceptable explanation[162] is that addition of a higher-valent element to liquid zinc or cadmium abnormally raises the Fermi level of the solvent, and leads to the observed large positive partial enthalpy of mixing of the solvent metal. Neither account is very satisfactory; measurements sensitive to the Fermi energy are required (Section 6).

Mercury-based systems do not conform to the behaviour pattern of the other IIB-based alloys; it appears that the properties of these systems are determined primarily by their size factor.[161] Essentially similar conclusions to those of Kleppa have been reached by Wittig *et al.*,[165] who have investigated a very wide range of liquid alloys by calorimetric methods. They made considerable use of the so-called ζ-function, by which H^M may be related to the number of statistically distributed A–B bonds, $N_A N_B$; $\zeta = H^M / N_A N_B$. The quantity ζ should be constant for all values of N_A in strictly regular solutions, but it is shown that this is rarely the case. If ζ is plotted against N_A, the intercepts on the vertical axes represent the limiting partial enthalpies of solution of the solute, A, in pure B, and of B in pure A. The partial enthalpies of mixing of solutes *in* zinc or cadmium are always greater than those of zinc or cadmium in the solute; this confirms that the asymmetry observed in the enthalpy-of-mixing plots in the IIB metals is due to a large partial enthalpy of mixing of the solute in pure zinc or cadmium. In cases where the plots are linear the slopes depend non-linearly upon the difference in valence between the components. Curved ζ-plots are usually observed only at the IIB-rich end of alloys with the 'covalent' metals, tin, antimony, bismuth, &c.; since the curvature is concave upwards, it also results in or from the large asymmetry in H^M in these systems. For solvents from Groups IIIB, IVB, and VB, the ζ-plots again depend upon the relative positions of solute and solvent in the Periodic Table, confirming the observations of Kleppa. Mercury-based systems are again found to be exceptional. The characteristics of the phase diagram follow the same general rules as would be expected from the arguments used earlier. The difficulty in discussing the variation in thermodynamic or other properties solely in terms of the position of the components in the Periodic Table is that several important factors—size, electronegativity, valence—vary according to the Group or Period of the elements, and it is not easy to separate their effects.

Kubaschewski (private communication) has recently shown that a plot of maximum excess entropies against maximum enthalpies of mixing for a wide range of liquid metallic solutions (i.e. using data taken directly from Tables XVIII–XXIII) is approximately linear; the correlation may be expressed as:

$$H^m = 2373\ S^E$$

i.e. by a line passing through $H^M = S^E = 0$, at which point all solutions are ideal. The scatter of results about the line is fairly great, and the fact that a number of systems are reliably reported to have H^M and S^E of different sign, suggests that the line may not in fact pass exactly through the origin, i.e. that ideal metallic solutions are improbable. The correlation is, however, good enough to allow the approximate calculation of excess entropies and excess free energies of mixing from calorimetric data alone. The significance of the correlation is not clear; there seems little point in attempting an interpretation in terms of approximate relationships such as equation (3.3).

Wagner[100, 166, 167] has argued that the shape of the plot of the partial enthalpy of mixing against composition may give a qualitative guide to the bond mechanism in a metallic solution. An example is the Mg–Bi system; this contains a compound Mg_3Bi_2 of high (−7·4 kcal) heat of formation, forming an 'ionic' M_2O_3 structure in the solid state. According to Wagner, addition of magnesium to the liquid in excess of 'stoichiometry' provides free electrons and positively charged magnesium ions. There will be no transfer of electrons to form negatively charged bismuth 'cations', or to form any type of Mg–Bi bond, since these are fully saturated. Thus, there will be only a small partial enthalpy of mixing of magnesium and the added electrons can contribute to conduction. In alloys containing less magnesium than the stoichiometric composition, addition of magnesium provides electrons which either are immediately absorbed by the undersaturated bismuth 'anions' or are involved in Mg–Bi bonds. There will be relatively little contribution to the conduction band from the magnesium and a high partial enthalpy of mixing of magnesium results. (Some of the bismuth atoms can contribute to conduction, thus, avoiding, in this case, complete semiconducting behaviour). There is thus a sharp increase in H^M_{Mg} at the stoichiometric composition. A number of systems behave in this way (e.g., the Ag–Te system[100]). In some cases, the less-metallic component—tellurium, selenium, sulphur—is able to provide only a very few conduction electrons when present in excess of stoichiometry, and the conductivity shows little variation with composition in this range: positive hole conduction is possibly predominant (see, for example, Ag–S,[168] Cu–S,[169] and Cu–Te, Sn–Te, Ag–Te[170]).

Associated solutions are also common among non-metallic liquid mixtures, but, as expected at the lower temperatures involved, enthalpies of mixing are much smaller. In some cases, a complex composition-dependence of the thermodynamic properties which is of a form exactly similar to that in metallic liquids, is observed. Because of the simpler atomic or molecular species involved, and hence the much simpler form of the interatomic potential, such mixtures are much more amenable to theoretical treatment; unfortunately, the results are seldom applicable to metallic systems.

Summary: The (Indirect) Method

It has been shown that an analysis of the dependence of the thermodynamic parameters of a series of alloys upon size, electronegativity, and other factors can provide useful support for structural models, and permits to some extent the separation of the various contributions to the excess functions, and hence to non-ideality. A number of correlations have been suggested in this section which, when further developed, may allow an estimate to be made of thermodynamic properties of alloys on which direct measurements are difficult. It has been demonstrated that the thermodynamic properties of any alloy depend primarily upon the position of the constituents in the Periodic Table, and hence upon two main factors: the size factor (elements from widely differing periods have a large size factor) and the nature of the bond formed between unlike atoms (which is determined by the electronegativity factor, and hence by the separation of the Group and Period Numbers of the two elements). In some alloys, especially those with Group IIB solvents, the change in the Fermi energy on alloying may also make a large contribution to the partial enthalpy and excess free energy of mixing; this change also depends upon the relative valence of the components. In many systems, the partial excess free energies of mixing are a linear function of the valence-electron concentration at all concentrations; in others, a simple curved relationship is observed. This suggests that at least the excess free energy is determined primarily by the Fermi energies of solute and solvent in the alloy.[163]

3.2.5. *Solubilities in Liquid Metals and Alloys*

This section deals only with the problem of the solubility of solid metals in pure liquid metals at high dilution; the more general problems of solubilities in binary alloys, and the properties of the ternary alloy so produced, are too complex to cover in a review of this type. In the next section there is a short discussion of the solubilities of interstitials in liquid binary alloys.

An understanding of the factors controlling the solubility of solid metals in a liquid metal is of obvious importance in determining, and hence predicting, the rate of corrosion of the solid by the liquid;[171] it is all the more surprising, therefore, that the literature shows an almost complete lack of both experimental and theoretical information on the subject (other than the relatively crude data from direct corrosion studies or from phase-diagram determinations). The factors that control the solubility of sparingly soluble solutes in liquid metals are far from being understood.[182]

Two quantities are important in corrosion studies in liquid metals: the isothermal rate of solution of solid in liquid, and the temperature-dependence of the solubility. The latter is easily shown to depend upon the partial enthalpy of solution of solute in solvent; if the solute is a pure metal (or in practice a very dilute solid solution) then for solute B in solvent A:

$$\frac{d(R \ln N_B)}{d(1/T)} = H_B^F + H_B^M \quad . \quad . \quad . \quad (3.16)$$

If the solid solute is an alloy or intermetallic compound, then equation (3.16) must be modified to take account of the activity of B in the solid state. The left-hand side of equation (3.16) may be obtained from the expression:

$$\frac{d(R \ln N_B)}{d(1/T)} = \frac{RT^2}{N_B} \cdot \frac{dN_B}{dT} \quad . \quad . \quad . \quad (3.17)$$

Strauss *et al.*[172] have claimed a correlation between the quantity represented by the left-hand side of equation (3.16) and the size factor for a wide range of liquid solvents and solid solutes, but the correlation is a very poor one. Later work of Weeks[171] has shown that it does not apply to solutions in liquid bismuth and cadmium. However, the size factor has been shown earlier to be a major factor in determining the thermodynamic properties of more concentrated solutions, and it will certainly contribute to the difficulty of solution of solid metals in liquid metals. Strauss *et al.*[172] suggested that H_B^M was dependent upon the size factor defined as r_B/r_A (H^F being roughly constant for the solutes considered), and was low (and hence the temperature-coefficient of solubility was low) in solutions with a size factor of ~ 1, and reached a maximum in solutions with a size factor of $\sim 1{\cdot}4$. At higher size factors, the temperature coefficient again fell, perhaps as the result of the formation of interstitial solutions. The poor quality of the correlation suggests that other factors are involved. In a later note, Strauss[173] claims an analogous correlation between S_B^M (and hence S_B^E) and the size factor; this shows that S_B^M also reaches a minimum value at a size factor of ~ 1. Weeks and Klamut,[171] on the other hand, have suggested that electronic effects may be more important than the size factor, at least in solutions in bismuth and cadmium. In these solvents, H_B^M is approximately a linear function of the size factor over a small range of size differences, with the larger atoms tending to give lower H_B^M values. Kerridge[182] has reviewed the data on the solubilities of solid in liquid metals, and has shown that, for any solvent, the solubility of the solute varies according to its atomic number; maximum solubilities generally occur at or near Li, Na, K, Mn, Ga, Rb, In, Cs, Hg, with a smaller maximum at Bi, but the maxima vary by one or two atomic numbers from this generalization in several solvents.* This dependence upon position in the Periodic Table is not particularly enlightening, since it tells us nothing about the fundamental atomic factors that determine solubility. Correlations have also been reported with other properties that are themselves periodic functions of the atomic number, but again, nothing is learnt that is fundamentally useful. Some of these correlations may be used to predict solubilities.[182] It should be remembered that there is often considerable disagreement in the literature about the exact values of solubilities.

It was shown earlier that the partial molar excess free energy of solution of a solute was determined at infinite dilution by the position of the solvent in the Periodic Table and by the electronegativity difference between solvent and solute; similarly, the composition-dependence of G_B^E was determined by the electron:atom ratio. It is clear that any unified theory of solubilities in liquid metals must take account of *all* the factors discussed here; little progress will be made by considering one factor alone, unless experiments are designed so that each factor may be investigated separately. It seems probable that the limiting value of $\dfrac{d(R \ln N_B)}{d(1/T)}$ at zero concentration of solute may be determined by a combination of size, valence, and electronegativity factors, while the subsequent shape of the solubility curve may be affected by the rate of change in the valence-electron concentration, and hence the Fermi energy, with composition. This, in turn, will be affected by the extent to which the valence electrons are 'free', and hence by the position of solute and solvent in the Periodic Table. Once the significance of the various factors is established, an investigation of the solubility curve may give some indication of the number and extent of freedom of valence electrons in, say, the transition metals, when dissolved in a simple, near-free-electron, solvent such as an alkali metal. The *kinetics* of the solution of solid in liquid is also affected by the parameters discussed above and by the diffusivities of the dissolving species

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* See also Ref. 595.

through the stagnant boundary layer of liquid that surrounds the solid. In practice, this rate of solution will also be affected by any protective film that develops on the solid—this may be used as a means of controlling the rate of attack by the liquid.[171] In most cases, the liquid-state diffusivities are the controlling factor and other factors may be ignored. In the relatively unlikely[171] absence of a diffusion-controlled mechanism, the partial molar free energy of solution of the solute must be the rate-controlling factor. The parameters that determine this and its composition-dependence have been discussed above. The initial solution kinetics in the pure solvent will be determined primarily by the electronegativity factor and the position of the solvent in the Periodic Table, while the composition-dependence of the reaction kinetics will be determined primarily by the composition-dependence of the Fermi energy of the solvent. In normal liquid-metal corrosion practice, several solute species may be involved, and the situation becomes very much more difficult to analyse. A great deal more experimental work is required on all aspects of the solubility of solid metals in liquid metals at high dilution. Only a few recent studies are reported.[174–181] Earlier data have been summarized by Kerridge.[182]

3.2.6. *Solution of Interstitial Atoms in Liquid Alloys*

Wagner[100] has shown that the solubility, $x_c^{(\text{soln.})}$, of a slightly soluble interstitial, c, in a near-ideal solution of components A, B, is given by

$$\ln x_c^{(\text{soln.})} = (1 - x_B) \ln x_c^A + x_B \ln x_c^B \quad . \quad (3.18)$$

where x_B = mole fraction of B in A–B.

x_c^A, x_c^B = solubilities of c in pure A, B, respectively.

If $x_c^A = x_c^B$, then $\ln x_c^{(\text{soln.})}$ is a linear function of x_B. In arriving at equation 3.18, the coordination number of the interstitial in the solution, Z_c, is assumed to be large, so that $1/Z_c$ may be neglected. In view of the simplifications, it is surprising that $\ln x_c^{(\text{soln.})}$ is linear in x_B for many alloys and interstitials. The solubilities of hydrogen in Cu–Sn[183] and Fe–Si[184] alloys may be each represented as two linear plots, intersecting to give a minimum at "Cu_4Sn" and "FeSi". For carbon in Cu–Mn[185] and Fe–Ni[186] there are similar discontinuities in $\ln x\binom{\text{alloy}}{\text{carbon}}$, corresponding to minima in the solidus and liquidus curves. Similar results are reported for Fe–Cu, Fe–Mn, Fe–Co alloys.[187] The strong Fe–Si bond, which causes a 30% contraction on mixing, may exclude the interstitial by reducing the amount of free space in the liquid structure; the same process may occur in Cu–Sn alloys, where other evidence indicates strong bonding at 20–25 at.-% tin (p. 475). The other examples cannot be attributed to this effect, and may be connected with the electronic anomalies suggested in some of the transition-metal liquid alloys by the magnetic-susceptibility measurements of Samarin (Section 6). Little is known of the interaction between the transition metals and hydrogen, even in the solid state.[188] Hydrogen solubilities in the liquid transition metals and their alloys have received some recent attention. Weinstein and Elliott,[189] Bagshaw *et al.*,[190] and Gunji *et al.*[191] have independently measured solubilities in Fe, Co, Ni, Cr, Cu, and in Fe–Co, Fe–Ni, Fe–Mo, Fe–Si, Fe–Cr, Fe–V, and Fe–W binary liquid alloys with excellent agreement. The earlier work of Busch and Dodd[192] is apparently in error. The sharp minimum solubility at 'FeSi' is quantitatively confirmed in the Fe–Si system. Bagshaw *et al.* attempt, with limited success, to interpret their results in terms of the possible localization of hydrogen in the liquid alloys as H^- ions, in contrast to the screened H^+ ions usually proposed.[193] Possible coordinate structures which could accommodate such ions are proposed for the liquid alloys. If they do exist, such structures would have a very transient existence indeed at the high temperatures, and hence high atomic vibration amplitudes, involved.

4. ATOMIC-TRANSPORT PROPERTIES

4.1 PRINCIPLES

Transport processes in liquid metals include viscous flow, concentration- and thermal-gradient diffusion, and electro-diffusion, of which the first two are the most important.

A complete theoretical treatment of transport properties in liquids[195] requires a more exact knowledge of interatomic forces in liquid metals than is available at present, and only an empirical approach is of practical value. Metallic interatomic forces may be estimated from diffraction data by using the Born–Green or a similar theory, and viscosities calculated from pair potentials through the same theory.[18] Many more empirical methods have been suggested for calculating the viscosities and diffusivities of liquid metals but none are successful for more than few metals.[80, 87, 195–203] These approaches have usually involved a discussion of the analytical relationships between viscosity and diffusion, which are, of course, mechanically similar processes in liquids.[204–207]

A discussion of electro-diffusion will be found in Section 6.2.10.

4.1.1. *Viscosity*

Both viscosity and diffusion obey approximately the general form of the Arrhenius equation; for viscosity this is:

$$\eta = C \exp\left(\frac{E_\eta}{RT}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where C, E_η, are constants. A similar expression may be used for the diffusivity. Many pure metals, however, do not show exactly linear plots of $\log \eta$ vs. $1/T$ over wide temperature ranges,[194] and it is doubtful whether the expression has any fundamental significance.[195] A number of alternatives to equation (4.1) have been proposed[98] which are more successful for particular groups of liquids, but even if these have greater significance, the accuracy of the available data probably does not justify a more complex equation than (4.1).

Batschinsky[208] suggested on empirical grounds that for many liquids,

$$V = a + \frac{c}{\eta} \qquad \ldots\ldots \qquad (4.2)$$

where V is the specific volume, a and c are constants. Thus plots of V vs. $1/\eta$, or more usually d/η vs. d, where d is the density, should be linear. These "Batchinsky plots", which have no fundamental significance, are linear for a wide range of non-metallic liquids, and for In, Sb, and Ga; Cd, Zn, Hg, Na, and Pb all give smooth curves.

The mechanism of an activated process in a liquid is not well understood, but a jump process, such as is usually visualized in solids, does not seem likely and is certainly not supported by the evidence from neutron-diffraction experiments (Section 2). Nachtrieb[207] calculates that the mean unit of movement in a liquid metal is $\sim 0{\cdot}6$ Å, compared with the 3–5 Å of a solid. Probably a complex cooperative movement of a number of atoms produced by local fluctuations in density is involved in the liquid, allowing a 'low-geared' movement of the diffusing atom. A suitable cooperative movement might be the opening of a disc or ring of atoms to allow the passage of a moving atom through its centre, or the rotation of a cluster or disc of atoms carrying the moving atom on its surface or circumference. A number of models of this type have been proposed.[198, 200, 202] The activation energy, E_η (or E_D for diffusion), may involve the energy needed to stretch the bonds in the disc of atoms to allow an atom through, or to rotate the cluster and attach and detach atoms to and from it, i.e. the energy required to produce the necessary density fluctuation in the liquid. Because such a process involves the making and breaking of interatomic bonds, E_η or E_D, and hence η and D, are likely to reflect the bond strength of the melt modified for each metal to an extent depending upon the amount of free space between atoms—the free volume—which will dictate the degree of cooperative movement required. Thus, the viscosity or diffusivity will depend upon three fundamental parameters: the interatomic bond strength (pair potential), the atom size, and the coordination number. In alloys, the situation is more complex because three pair potentials now have to be considered, together with the size and other factors, and the effect of these upon atomic configuration. In all liquid metals and alloys, high E_η and E_D values (and hence high viscosities and low diffusivities) should result from high bond energies, and low free volumes, if other factors can be ignored. Hence the viscosity should show a close relationship with the 'cohesive energy density',[112] E^V/V, where E^V is the enthalpy of evaporation and V the atomic volume; such a relationship is observed.

4.1.2. *Self-Diffusion*

An analogous Arrhenius expression to that used for viscous flow is found to fit all available data:

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad . \quad . \quad . \quad . \quad . \quad (4.3)$$

Because similar mechanisms are involved, E_D and E_η should be closely similar. The semi-empirical Stokes–Einstein equation:[87]

$$D = \frac{kT}{6\pi\eta r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.4)$$

was originally derived for a sphere moving freely in a viscous medium, but it is found to hold approximately for liquid metals provided that r is the radius of the ion.[209] From this, it may be shown that, approximately:

$$E_D - E_\eta \simeq RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.5)$$

(Compare with values of E_D and E_η from Tables XXIV and XXV.) Several more complex expressions have been produced to relate viscosity and diffusion in metallic liquids.[205] Saxton and Sherby,[205] in an interesting analysis of viscosity and diffusion data for liquid metals, have used

$$D_{\text{calc.}} = STd_i(\eta)^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.6)$$

to calculate diffusivities from viscosity data. S has the value 2×10^{-17} ergs. deg^{-1} and d_i is the Pauling univalent ionic diameter. T is in degK. There seems little point in using a more complex expression. Saxton and Sherby conclude from their analysis of the experimental and calculated (from viscosities) diffusion data that diffusion in liquids is a thermally activated process, as in the solid state, and obeys the equation:

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.7)$$

The activation energy, Q, may be calculated from:

$$Q = RKT^F \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.8)$$

where R is the gas content, T^F the melting temperature (degK), and K is a constant equal to 3 for typical metals and 2·75 for the 'semi-metals' Ga, Bi, Sb, Sn, &c., which are again shown to be abnormal (Section 2). The quantity D_0 is apparently dependent upon the atomic mass M, and upon the crystal structure taken up by the metal on solidification; it may be expressed as

$$D_0 = C \, . \, M^{-1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.9)$$

where the constant C is twice as large for the b.c.c. metals as for the close-packed metals and decreases with increasing coordination number of the 'semi-metals'. The probable explanation of this is that C is sensitive to the position of a metal in the Periodic Table and hence to the nature of the interatomic bond, which controls the coordination number, packing density of atoms, and hence the free volume and structure in both the solid and liquid states. Hence, those metals which are close-packed in the solid state are more likely to be so in the liquid state than the more open-structured metals, and C appears to show a relationship with the solid-state structure. Low C-values result from closer packing; hence diffusivities are low and viscosities are high in those metals with a high interatomic bond strength and low free volume, as was suggested earlier on more empirical grounds.

The empirical methods used for determining viscosities may also be used to obtain diffusivities through an equation of the form of (4.6). Correspondingly, the arguments of Saxton and Sherby may be applied to the mechanism of viscous flow. Diffusivities, like viscosities, may be calculated from a fundamental theory of the liquid state such as the Born–Green[12] theory, provided that details are available of the interatomic potentials. Alternatively, diffraction or other 'direct' structural data may be used as a source of information. Egelstaff,[21] for example, has used the cluster model referred to earlier (p. 394) in a successful attempt to calculate liquid-metal diffusivities from neutron-scattering measurements.

Mixtures

Various empirical expressions have been derived to express the viscosity of a mixture in terms of those of the components; these have usually been of the form:

$$\eta_{ij} = q_i \eta_i + q_j \eta_j \quad . \quad . \quad . \quad . \quad . \quad (4.10)$$

where q_{ij} may be mole or volume fractions. Log η_i, or $1/\eta_i$ (the fluidity), may be used in place of η_i. Vandor[210] has extended these expressions in a partially successful attempt to allow for the difference in strength between the solute–solvent, solute–solute, and solvent–solvent bonds, by using a form of regular solution theory. As will be seen in Section 4.2.3, the expression (4.10) usually applies quite well for metallic systems, with positive deviations if $\varepsilon_{ij} > \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})$, and negative deviations for the reverse situation, until the extreme case of immiscibility is reached. In principle, a precise formulation for the viscosity of a mixture is possible through the Born–Green theory.[12] So far, this has proved impossible to use in practice.

4.1.3. *Thermal Diffusion*

If an alloy is placed between, and in contact with, two surfaces at different temperatures, a small separation of the components takes place, as a result of the difference in chemical potential induced by the thermal gradient. The results may be expressed in terms of a coefficient, α, defined by:

$$\ln\left(\frac{x}{1-x}\right)_H + \left(\frac{1-x}{x}\right)_C = \alpha . \ln\frac{T_H}{T_C} \quad . \quad . \quad (4.11)$$

where x is the mole fraction of the component under investigation, and T_H, T_C are the temperatures of the hot and cold surfaces (H and C).

Winter and Drickamer[211] have attempted to relate α to the partial molar volumes of the components, and the chemical potential (activity) of the solute:

$$\alpha = \frac{M_i V_j + M_j V_i}{2M}\left(\frac{\Delta U_j}{V_j} - \frac{\Delta U_i}{V_i}\right)\frac{1}{x_i\,\dfrac{d\mu_i}{dx_i}} \quad . \quad (4.12)$$

where V_i = partial molar volume of component i.

M_i = molecular weight of component i.

μ_i = chemical potential of component i.

ΔU_i = an activation energy.

and have met with some success with both metallic and non-metallic liquids, using values of ΔU_i calculated from reaction-rate theory.[197]

4.2 RESULTS

Experimental methods have been reviewed by Thresh.[593]

4.2.1. *Viscosity of Pure Metals*

It is important to remember that viscosity results are often presented as kinematic viscosities, i.e. as η/d. The determination of the absolute viscosity requires precise density data which are often not available, particularly for liquid alloys. To obtain absolute viscosities, densities have often been estimated; for alloys this usually involves the assumption of Vegard's law. Care is required when using these results, since this law is often *not* obeyed, especially in alloys with high negative enthalpies of mixing.

Because considerable disagreement has been reported amongst viscosity measurements made close to the melting point, the selected data in Table XXIV are quoted at a temperature 50 degC above this. Values of E_η, calculated using equation (4.1) are also given.

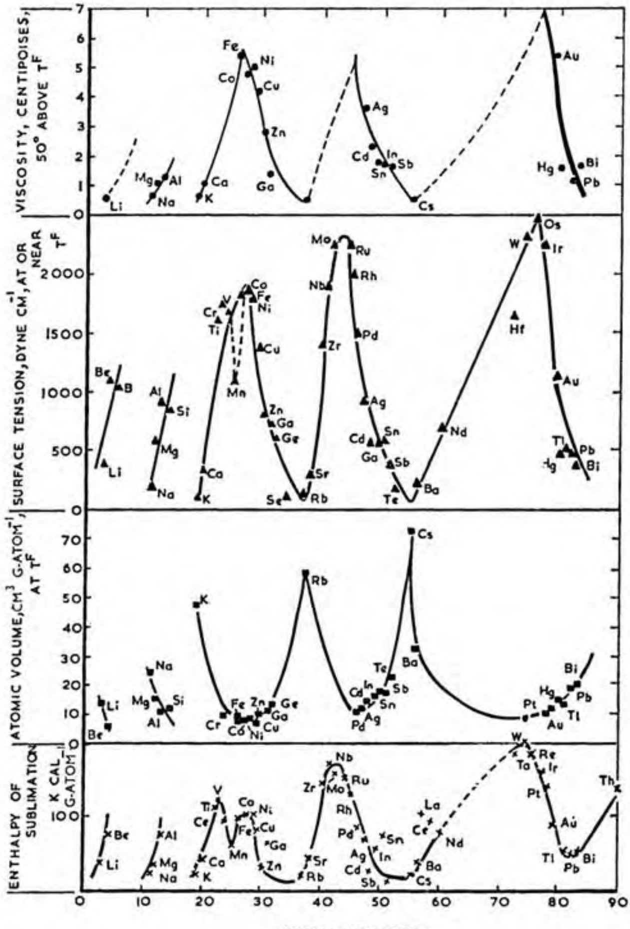

Fig. 11.—Correlation between viscosity, surface tension, atomic volume, and atomic number.

The viscosity of the elements varies periodically with the atomic number (Fig. 11), the transition metals occupying the peaks and the alkali metals the valleys of the curve, and with the *A* group metals on the rising sections of the curve and the *B* groups on the falling side. This relationship suggests that viscosity is a function of a parameter, perhaps the bond strength, which is itself a periodic function of atomic number. An exactly similar periodic behaviour is observed for the heats of sublimation, melting points, and free volumes and compressibilities of the elements,[45] all of which confirm that those metals with highest bonding energy and lowest free volume have the highest viscosities. Thus, the approximately linear relationships between viscosity and the free volume, or the cohesive-energy density,* indicate that the strength of the interatomic bond is a major factor in determining the viscosity of a liquid. Another factor may be the size of the unit moving in the velocity (or chemical, thermal) gradient; a large unit gives rise to a high viscosity.[218]

The activation energy, E_η, shows a similar correlation with the interatomic bond strength and factors reflecting it. The abnormally high values of E_η for magnesium and calcium require confirmation. They may be spurious, probably on account of oxide suspended in the melt, or they may result from an anomalous structure—possibly inefficient screening of the ion by electrons, which could modify the effective interatomic forces acting on a moving atom.

A number of liquid metals have been reported to exhibit extensive deviations from an Arrhenius plot. Gallium shows a discontinuity in the slope of the Batchinsky plot at 350°C, corresponding to an inflection in the less sensitive Arrhenius plot.[212] This is not supported quantitatively by earlier work[213] which has a similar discontinuity at 430°C, or by any other physical measurements.[214] Liquid tin has a completely smooth, but curved, Batchinsky plot,[215] but has an anomaly in the temperature coefficient of resistivity at 520°C. The evidence is not sufficient to indicate whether the anomalies noted could be due to the disappearance with increasing temperature of the 'second structure' observed in these liquids (Section 2). Similar phenomena are found in the electrical properties of certain molten intermetallic compounds (Section 6).

Several metals have been reported to show an anomalously high viscosity over a range of ~ 50 degC above the melting point, which has been claimed[216,217] as an indication of a 'foreshadowing' of solidification. These data, which are almost certainly incorrect, have been used by at least two authors to calculate the size of clusters in the liquid

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* Cohesive-energy density $= (E^V/V)$, where E^V is the enthalpy of sublimation and V the atomic volume, and is a qualitative measure of bond strength.

which are supposed to result from the 'prefreezing'.[218, 219] In a few metallic and non-metallic liquids (see below) the phenomenon may be real but in others it is due either to oxide or impurities suspended in the melt, or to temperature gradients in the apparatus leading to premature solidification. The phenomenon has been reliably observed in a number of non-metallic liquids in which a random arrangement of atoms seems unlikely on other grounds.[220] Particularly notable in this respect are the long-chain aliphatic hydrocarbons and other molecularly complex liquids in which the degrees of rotational and positional freedom increase progressively with increasing temperature after fusion. Some of the structurally complex elements—examples are sulphur, tellurium, and selenium—and perhaps some structurally complex 'intermetallic' compounds in which the metallic bond is not predominant in the solid state, may exhibit similar characteristics through a slow post-melting disordering of the structure. In such cases, the viscosities should exhibit hysteresis, those measured just after fusion being greater than those measured just before solidification but after superheating the liquid. The viscosities may also be time-dependent. Such phenomena have been reported for a number of tellurides and similar complex compounds.[221] Unfortunately, the same source reports similar phenomena for structurally simple liquids such as the antimonides in which such effects would not be expected; indeed some of this work is not supported by later, more careful studies, and it seems that the earlier observations were probably invalidated by suspended impurities in the melts. This casts considerable doubt on the results for more complex liquids (see also Section 6).

4.2.2. *Self-Diffusion*

Coefficients and activation energies for self-diffusion have been determined for a number of pure liquid metals and alloys. Because of the considerable difficulty of the experimental techniques, particularly at high temperatures, the available data listed in Table XXV are subject to an error of $\nless \pm 50\%$. The close connection between diffusion and viscosity has been discussed earlier; diffusivities should exhibit the same dependence upon factors reflecting the bond strength and free volume of the liquid as do the viscosities. The work of Saxton and Sherby[205] suggests that this is the case.

4.2.3. *Viscosity of Alloys*

Since the viscosity of a liquid is apparently determined primarily by the strength of the interatomic bond and the packing efficiency of the atoms, the composition-dependence of the viscosity in a binary system should provide a sensitive qualitative guide to the manner in which the *mean* interatomic bond strength varies with composition.

Several liquid alloys of low melting point are well documented; the data are subject to the same sources of error as those for the pure metals, particularly at high temperatures. The warning given on p. 443 regarding the need for good density measurements in order to convert the directly determined kinematic viscosities into absolute viscosities should be borne in mind when considering data. In some systems the density (Section 5) is by no means a simple function of composition.

A. *Solid-Solution Systems*

A number of the systems listed in Table I have been investigated and the results are summarized in Table XXVI. If an ideal system is defined, quite arbitrarily, as one obeying a linear mixing rule for viscosity (equation 4.10), the activation energy and viscosity isothermals of the systems investigated show insignificant positive or negative deviations from 'ideal' composition-dependence. This confirms the conclusion suggested by thermodynamic measurements that in these alloys the unlike-atom pair potential is not greatly different at any composition from those of the components, and that the atomic arrangement is near-random.

B. *Eutectic Systems*

As Table XXVII indicates, there is considerable disagreement between sources of data for the better documented systems.

It appears that most eutectic systems show small negative deviations from a linear mixing rule, and that many of these systems may exhibit a sharp minimum in the viscosity isotherm at the eutectic composition. Generally, as the temperature is increased, the deviations from linear mixing behaviour are reduced, and any anomalous composition-dependence disappears. There is some inconclusive evidence that eutectic viscosity minima may be observed only at near-eutectic temperatures, and that deviations from linear behaviour may be greater in systems containing elements from the higher groups of the Periodic Table. In some systems, viscosity maxima have been reported to occur at compositions corresponding to solid-solubility limits in the solid state. Eutectic viscosity maxima have been reliably reported for at least one system.[222] In all cases investigated, E_η shows the same composition-dependence as η. More precise measurements, on a wider range of systems, are required before a systematic investigation of any relationship of η or E_η with size factor or thermodynamic parameters can be carried out. However, it does seem that negative deviations from linear mixing are associated with positive enthalpies of mixing, as originally predicted by Vandor.[210]

C. *Miscibility-Gap Systems*

No systematic investigation over the entire composition range has been reported for any of the systems listed in Tables VI and VII. Patterson reports measurements up to the solid-solubility limit of lead in zinc in the Pb–Zn system. Negative deviations from linear mixing are observed.

Reed and Taylor[147] have measured viscosities of binary mixtures of organic liquids which exhibit miscibility gaps—notably in iso-octane*/perfluoroheptane †mixtures—and find a sharp maximum in the viscosity isotherm at temperatures just greater than the critical temperature. This maximum disappears rapidly with increasing temperature. A possible interpretation is that the liquid is forming *A*-type and *B*-type groups or clusters as a prelude to separation into two layers, and that the viscosity is raised by the increase in size of the 'flow' unit. McLaughlin and Ubbelohde[218] have shown that cluster formation would have such an effect and it is possible that similar results may be obtained for metallic systems. Other evidence on non-metallic systems supports the suggestion of clustering or emulsion formation at temperatures just greater than critical (p. 422).

D. *Compound-Containing Systems*

The effect of molecular associations upon the viscosity of a liquid mixture has often been discussed.[223–226] It is generally agreed that a positive 'excess viscosity' should result, with a maximum value corresponding to the composition at which the degree of association reaches a maximum.

Measurements on compound-containing systems indicate almost universally that the presence of a liquidus maximum gives rise, at least at temperatures close to the liquidus, to a maximum in the isotherms of both viscosity and activation energy for viscous flow (Table XXVIII). If there is no liquidus maximum, but a negative enthalpy of solution, viscosity deviations from linear composition-dependence are usually positive.

The viscosity maxima at ~ 20 at.-% tin in the Cu–Sn and Ag–Sn systems fall at about the same compositions at which X-ray investigations have indicated short-range order (Section 2). In Au-Sn, the compounds AuSn and $AuSn_2$ have little influence on the viscosity of the liquid, but unfortunately measurements have not been reported below

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* C_8H_{18}. † C_7F_{16}.

30 at.-% tin. None of the IB–Pb systems behave in this way, which suggests that the short-range order may be a result of the two-structure nature of tin[37] (see Section 6, p. 475).

In the Cd–Sb system, the structure of Cd_3Sb_2, metastable in the solid state, may be stabilized in the liquid by the removal of the need to pack on a long-range lattice. Recent resistivity measurements in the writer's laboratory support this view.

Comparison of the Mg–Pb and Mg–Sn systems shows that the viscosity maximum at Mg_2Pb is much less persistent with increasing temperature than that at Mg_2Sn, reflecting the stronger bonding in the Mg–Sn system. The maximum activation energies are 4800 and 7600 cal. mole^{-1} respectively, and therefore also indicate much stronger bonding in the Mg–Sn system, in agreement with the maximum enthalpies of formation of the liquids of $-2{\cdot}3$ and $-3{\cdot}5$ kcal.mole^{-1}, respectively. There is insufficient information on activation energies to observe any general correlation between E_η and enthalpies of mixing, but qualitatively both H^M and E_η show a sharper maximum in those systems with high negative enthalpies of mixing; for example, in liquid Hg–K alloys ($H^M_{\text{max.}} = -5{\cdot}3$ kcal.mole^{-1}), there is a very sharp viscosity maximum at Hg_2K. The maximum negative enthalpy of mixing in liquid alloys such as this also falls at the compound composition, indicating that this is the composition of maximum bonding energy in the liquid. It follows that the viscosity maximum is associated with this energy maximum, confirming that the viscosity is determined primarily by the bond strength in the liquid. The viscosity may also be magnified by any increase in the size of the flow unit caused by negative clustering[218] which, if it occurs, will also reach its maximum extent at the 'maximum bonding' composition (p. 424). Exactly similar behaviour has been observed in a number of non-metallic, compound-containing systems.[227, 228]

It is interesting to speculate on the relationships between the interatomic potentials that might give rise to these results.[229] If all three pair potentials are equal, and if the atomic sizes are not greatly different, the viscosity, which is approximately a function of $(N_{AA}.\varepsilon_{AA} + N_{BB}.\varepsilon_{BB} + N_{AB}.\varepsilon_{AB})$, will be linearly dependent upon composition; this is the situation in the 'solid-solution' group of systems, as is indicated by the thermodynamic data. If $\varepsilon_{AB} > \dfrac{\varepsilon_{AA} + \varepsilon_{BB}}{2}$, then N_{AB} will be greater than its random value at all concentrations, since short-range order will result. The viscosity will reach a maximum in this case at a composition at which the maximum number of A–B bonds is produced; this will not necessarily occur at the equiatomic composition because associations of, say, p A atoms and q B atoms may be formed preferentially in the liquid, perhaps at the composition at which the compound A_pB_q is formed in the solid state. This situation (see above) is commonly observed. In eutectic and miscibility-gap systems in which $\varepsilon_{AB} < \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}$ and $\varepsilon_{AB} \simeq \varepsilon_{BB}$ the viscosity will exhibit generally negative deviations from 'ideal' behaviour; the exact relative values of the interatomic potentials will determine the degree of symmetry of the 'excess-viscosity' curve. The very simple picture presented so far will be affected, perhaps extensively, by any size or other differences between the two atoms which can modify the interatomic potentials. Additionally, in eutectic or miscibility-gap systems for which ε_{AB} is relatively small, the viscosities of the A-rich and B-rich liquids will be controlled primarily by A–A and B–B bonds, respectively, which will be present in greater numbers than predicted for a random structure. Thus, starting with pure liquid A, addition of B may produce only a few A–B bonds—B may perhaps be considered to have a small 'solubility' in the A-type structure; this could account for the viscosity maxima reported at solid-solubility-limit compositions. Addition of more B will result in a structure in which A atoms are associated mainly with A atoms and B atoms with B atoms, i.e. the liquid is on the verge of immiscibility. This may account for the inflected liquidus curves observed in a large number of systems (Section 3). As more B is added, the structure may either split into two liquids, or be energetically unable to maintain its near-immiscible state; more A–B bonds may thus be formed, and the viscosity will begin to fall with increasing B concentration. At some compositions the viscosity must begin to rise again as the number of B atoms increases. Thus, the viscosity will reach a minimum value at a composition at which the number of A–B bonds reaches a maximum. It will be argued later (Section 9), with the aid of further evidence, that this composition is identical with that of the eutectic, at which the liquid structure is therefore relatively random. A simple analysis of this sort can, of course be confused by any composition-dependence of the three interatomic potentials. This, and the effect of size and other factors, may explain the wide variety of viscosity isotherms that have been reported for metallic systems. It is very difficult to judge the reliability of such work without a clearer understanding of the controlling factors involved. This understanding may eventually be achieved through direct structural measurements on liquid alloys (Section 2), from which interatomic potentials and hence viscosities may in principle be calculated.[18]

4.2.4. *Diffusivities in Alloys*

There are insufficient data (Table XXV) for a systematic investigation of dependence upon thermodynamic characteristics, and as a result of extreme experimental difficulty the available data are of very low quality; errors may be as high as 100%. Both the diffusivity and the activation energy are composition-dependent, although the total variation across a system may be less than the total error in the observations. The only reliable detailed investigations appear to be of the Hg–Zn system[230] (up to only 4·5 at.-% zinc), which shows that diffusion coefficients of mercury or zinc are little affected by composition; of the Hg–Tl system,[231, 232] which indicate that the diffusivity reaches a minimum value at a composition corresponding to the solid-state compound Hg_5Tl_2; and of two compositions in the In–Pb system.[233] Cordes and Döge[237] studied diffusivities of lead and antimony in the Pb–Sb system.

Generally, the diffusion constants behave in a similar way to those for viscosity, showing a smooth variation with composition in solid-solution systems, and possibly anomalous behaviour in some alloys of eutectic composition. Diffusivities are low and activation energies high in systems such as the Hg–Tl system, which contain compounds because, like η and E_η, D and E_D are closely related to the interatomic potential.

4.2.5. *Thermal Diffusion*

Winter and Drickamer[211] have measured thermal diffusivities (diffusion of the components along a temperature gradient—the so-called Soret effect) in a number of liquid alloys based on tin. Their values of α (equation 4.11) are given in Table XXIX. Earlier, and apparently less precise, measurements have been made by Kawakami[234] (again on tin-based systems) and by Ballay.[235] The technique of measurement is extremely difficult, and it is doubtful whether the data are quantitatively valid. The rate of thermal diffusion and hence the Soret coefficient appear to be strongly composition- and temperature-dependent. Thermal-diffusion measurements are also reported in liquid lithium.[236]

5. DENSITY: VOLUMES OF MIXING

5.1. PRINCIPLES

Densities, coefficients of thermal expansion, and compressibilities are discussed in this section. The thermodynamic significance of the change in volume of an alloy on mixing has been reviewed in Section 3.

Various, mainly empirical, expressions have been used to define the density of a mixture in terms of composition. There seems little justification for the use of any other than Vegard's law:

$$d_{ij} = d_i x_i + d_j x_j \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.1)$$

Most liquid alloys show small (1–5%) deviations from this.

The temperature-dependence of the volume of a liquid may be expressed in the usual way as:

$$V_t = V_0(1 + \alpha T), \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.2)$$

where α = bulk coefficient of thermal expansion.

Alternatives, claimed to be a better representation of the facts, have been proposed,[98] but for liquid metals the accuracy of the experimental data hardly justifies the search for an alternative to equation (5.2).

Compressibilities are usually determined by measurement of the velocity of ultrasound, u. Then the adiabatic compressibility is given by:

$$\beta_A = \frac{1}{u^2 d} \quad (d = \text{density}) \quad . \quad . \quad . \quad . \quad . \quad (5.3)$$

and the isothermal compressibility, β_I, by:

$$\beta_I = \gamma \beta_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.4)$$

where

$$\gamma = C_p/C_v = \frac{u^2 \alpha^2 T}{C_v} + 1 \quad (T = \text{temperature, degK}) \quad (5.5)$$

The adiabatic compressibilities of a few liquid metals have been determined (Table XXX).

5.2. Results

Experimental techniques are reviewed in ref. (594).

5.2.1. *Pure Metals*

Atomic volumes at the melting point, changes in volume on fusion (discussed in more detail in Section 8.3), and coefficients of thermal expansion and compressibility are indicated in Table XXX. The anomalous temperature-dependence of density in some metals at temperatures just above and below the melting point is discussed in Section 8.

Within the limits of the data, the values of V_A (the atomic volume), α, and β_A vary with atomic number exactly as in the solid state.[45] This is usually interpreted in terms of the high bond strengths (low V_A, α, β_A) resulting from the considerable interaction between d-shell electrons in the ion-cores of the transition and Group IB metals, compared with the bonding in the alkali metals (high V_A, α, β_A) in which the ion cores are well separated and in which only s-type valence electrons are involved. Because many other properties of liquid metals are also periodic functions of the atomic number (e.g. viscosity, surface energy), density correlates well with these.

5.2.2. *Alloys*

Very few systems have been systematically investigated over the entire composition range. The data for those that have are listed, partly in Tables XVIII–XXIII and partly here, taken from the work of Sauerwald *et al.* (Al–Cu,[238] Cu–Sn,[238] Cu–Sb,[239] Cu–Zn,[239] Al–Zn,[239] Bi–Sn,[240] Sb–Zn,[239], Al–Sb,[239] Cd–Pb,[241] Cd–Sn,[241] Sn–Zn,[241] Au–Cu,[242] Ag–Cu,[242] Al–Mg,[243] Mg–Zn,[243] Mg–Pb,[244] Mg–Sn,[244] Hg–K,[245] Ag–Sn;[246] some of this work has been summarized in Ref. 136); Kleppa *et al.* (Hg–In,[247] Cd–In, Sn, Tl, Pb, Bi,[248] Hg–Cd, Sn, Tl, Sn, Pb, Bi,[249] Zn–Cd, In,Sn, [249] Pb–Bi,[249]) and others (Al–Si, Pb–Sn;[251] Al–Cu, Al–Ni, Be–Ni;[252] Sn–Zn;[253] Cu–Pb;[254] Cu–Pb, Cu–Bi, Ni–Bi (all dilute solutions of high-m.p. metal);[255] Hg–K, Hg–Na;[256] Fe, Co, Ni–Si;[257] Ba–Na,[258] Mn–Fe, Si, C;[259] Bi–S;[260] Hg–Tl;[261] Cd–Sb, Pb–Sn.[264] Earlier work will be found in the assessments of Frost,[8] of Kubaschewski and Catterall,[129] and in Ref. (299). The work of Matuyama[250] appears to be extremely unreliable, and disagrees considerably with more recent measurements.

The data are dependent upon the type of alloy system; eutectic systems, which exhibit a positive enthalpy of mixing, also have a small positive volume of mixing, i.e. they expand on mixing with respect to a rectilinear mixing law, as is to be expected if mixing is difficult. Mercury-based systems are anomalous : in alloys with Zn, Cd, Tl, Sn, Pb, Bi, there is no correlation with enthalpy or entropy of mixing.[249] The volumes of mixing in these systems are *all* negative, while enthalpies are positive in alloys with Zn, Pb, Sn, and Bi. Mercury may be incompletely ionized in the pure state, but may lose electrons on alloying (Section 6) and the resultant decrease in size of the mercury cation may lead to the observed negative volumes of mixing.

In compound-containing systems in which the enthalpy of mixing is negative, volumes of mixing are generally also negative. Exceptions are the Bi–Pb system ($H^{M}_{\mathrm{max.}} - 250$ cal, $V^{M} + 0{\cdot}25\%$) and the Bi–Mg and Sn–Zn systems, which are discussed later. In all cases the composition of the maximum negative volume of mixing coincides approximately with the composition of the main compound; this suggests that the contraction is caused by the high total bond energy at these compositions. Contractions may be very high indeed. Gel'd and Gertman[257] report values for alloys of iron, cobalt, and nickel with silicon of -36, -30, and -23%, at the compositions FeSi, CoSi, and Ni_2Si.

Enthalpies of mixing in the liquid state are reported to be −9, −11, and −16 kcal.mole^{-1}, respectively (Table XXIII). The transition metals have negligible solid solubility in silicon, as a result of the stability of these compounds, but dissolve easily in the liquid state, suggesting that the sp^3 hybrid bond in silicon is largely destroyed on fusion. The large contraction on mixing may result partly from a destruction of the remaining directional bonding in silicon, leading to a more closely packed structure, and partly from the very high attractive forces between silicon and transition-metal atoms.

Volumes of mixing of intermetallic compounds may differ widely between solid and liquid states. For example, the relatively open 'ionic' structures of Mg_2Sn, Mg_2Pb, Sb_2Zn_3, and, possibly, Cd_3Sb_2 lead to positive volumes of mixing in the solid state. A contraction occurs on fusion, partly because bonding characteristics in the liquid are more metallic (i.e. more free electrons, with fewer associated with specific ions; the electrical behaviour in the liquid state is characteristic of a metal), leading to closer packing, and partly because, even without the change in bond character, the removal of any necessity to pack in the form of an 'open' long-range lattice allows greater freedom to select a more efficient packing arrangement. Volumes of mixing in the solid state have not been recorded for the Hg–K and Hg–Na systems, which also have 'ionic' solid-state structures, but there will probably be a further contraction on fusion. Similar behaviour is reported for 'Cu_3Al', and for Fe_3C (solid −4%; liquid −5·4%),[136] probably for the same reason. In some cases, volumes of mixing are also positive in the liquid alloys (CdSb + 3%, Sb_2Zn_3 + 0·4%), which suggests that directionality of binding persists after fusion, leading to a structure that is 'open' relative to those of the components.

The high negative volumes of mixing in some compound systems have been attributed above to highly attractive, partially non-metallic bonds between unlike atoms and to the relatively open structure of at least one component. (It is important to remember that the volume of mixing is a *relative* thermodynamic quantity.) It is known that materials which do not behave in a predominantly metallic fashion in the solid state become more metallic on fusion (for example, Se, Si, Bi, Sb) as a result of the destruction of homopolar bonding (see Section 6) and that this process often continues upon heating in the liquid state. If this is true for molten intermetallic compounds, liquid-state volumes of mixing should decrease as bonding becomes more metallic. Such behaviour has been observed in Mg_2Pb liquids,[262] in which V^M decreases from −8% at the melting point (550°C) to $\sim -1{\cdot}5\%$ at 800°C.

The case of the compound Mg_3Bi_2 appears to be anomalous. In this case, V^M is −2·1% at 20°C, becoming +2·0% on fusion, and invariant with temperature up to 872°C.[243] Mg_3Bi_2 crystallizes in the La_2O_3 structure, and is normally considered to be intermediate between the purely metallic structures and the ionic inorganic salt structures.[154] The negative volume of mixing in the solid may result from the open structure of solid bismuth (with homopolar bonding), which itself contracts on fusion. In the liquid, there is evidence that a high degree of non-metallic bonding leads to a low electrical conductivity[167] (Section 6), and it is possible that sufficient heteropolar bonding is present in the liquid to preserve an open structure of low coordination relative to *liquid* bismuth. If this is the case, the structure is remarkably stable.

Toye and Jones[263] claim to find maxima in molar volumes at compositions corresponding to solid-solubility limits, and at eutectic compositions. Data are given, over limited composition ranges, for Sn–Cu, Sn–Ni, and over the entire system for Sn–Pb alloys. The rather scattered data suggest minimum rather than maximum molar volumes at eutectics, but the data make a decision impossible. Eutectic density minima have been reported in a few systems;[251] more work is needed to establish the validity of these density anomalies.

5.2.3. *Coefficients of Expansion: Compressibilities: Velocities of Sound*

Data for pure liquid metals are listed in Table XXX. Apart from the value for mercury, measured directly by Bridgman,[265] the compressibilities have been obtained by ultrasonic techniques.[266–268] The values of α and β_A follow exactly the pattern observed in the solid state,[45] i.e. the highest expansivities and compressibilities are observed in the alkali metals where the free volume is large, and the lowest in the transition and IB metals, where there is little free volume, and compression is therefore difficult. The low free volume is associated with the strong bonding that results from interactions between electrons in *d*-shells and prevents easy thermal disordering of the lattice.

For most metals, $\alpha_{\text{solid}}/\alpha_{\text{liquid}}$ is $\sim 0{\cdot}75$–$1{\cdot}0$. In Bi, Sb, Ge, Si, Se, Te, and similar materials it is much smaller at $\sim 0{\cdot}3$–$0{\cdot}4$, corresponding to the high entropy of fusion and negative volume change on fusion of these elements.[269] The relatively greater expansivity in the liquid state of these elements results from the breakdown of thermally stable (both in direction and length) homopolar bonds on fusion. No coefficients of expansion of molten alloys appear to have been measured. They will probably be small and temperature-dependent in systems containing intermetallic compounds with homopolar bonding which breaks down with increasing temperature.

Velocities of ultrasound, and thus adiabatic compressibilities, have been measured for a few alloy systems. Composition-dependence is smooth in a number of eutectic systems (Pb–Sn, Bi–Sn, Cd–Sn, Bi–Pb, Cd–Pb, Cd–Bi) with slight negative deviations from 'linear mixing'.[270–272] Anomalously low compressibilities at the eutectic composition have been claimed in Pb–Sn alloys but too few results are reported to justify this conclusion.[272]

The attenuation of ultrasonic-wave amplitude (i.e. ultrasonic absorption) is much more difficult to measure than the velocity of sound.[273, 276] Jarzynski[274] and Hunter *et al.*[275] have made measurements on liquid mercury, gallium, and bismuth. Jarzynski suggests that two structures may exist in equilibrium in gallium and bismuth, one more ordered than the other; the evidence is not conclusive. No such situation was detected in mercury, but Abowitz and Gordon[282] conclude that two such structures are in equilibrium in Hg–Tl alloys. Possibly the equilibrium here is between a more ordered structure corresponding to the compound 'Hg_5Tl_2' and the relatively disordered 'matrix'. The ordered structure may perhaps consist of clusters, or at least groups, of atoms of relatively complete short-range order. A similar suggestion has been made on the basis of thermodynamic measurements.[69] Velocity and attenuation measurements are also reported for Na,[276–278], K,[277–278] Bi, Co, Pb, Sn, Zn,[279] Cd and Zn amalgams,[280] and Sb–Zn alloys.[281] More work of this nature is clearly needed, especially in compound-containing systems, but extreme experimental difficulty is experienced at higher temperatures; even at room temperature, attenuations probably cannot at present be measured to better than ±15%.

6. ELECTRONIC PROPERTIES

6.1. Principles

The electronic properties of pure liquid metals have recently been the subject of a comprehensive review by Cusack,[283] who dealt with the theoretical background to these properties and discussed the available experimental data on pure liquid metals.* In the last two years, considerable advances have been made, particularly in the determination of electronic properties of pure metals and alloys; the discussion that follows summarizes, for the sake of completeness, the situation that was reviewed by Cusack, presents the recent work on pure metals, and reviews in detail the properties of liquid alloys and intermetallic compounds.

6.1.1. *Theories of Electron Transport in Liquid Metals*

The theory of electron transport in liquid metals is as yet very much in its infancy; there is still considerable disagreement about the validity

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* See also N. F. Mott, Ref. 596, p. 152.

of the fundamental assumptions that must be made in order to achieve progress. All the early approaches to the subject treated the liquid as a perturbed form of the solid and used what was basically solid-state theory. Only very recently have treatments that do not invoke this basic and faulty assumption been produced; these treatments have already made very considerable progress, but there is still a long way to go before they can be said to offer even a qualitative understanding of the factors that govern the behaviour of current carriers in liquid conductors or semiconductors.

The resistivity at constant pressure of most solid metals and alloys at room temperature and above may be represented approximately by

$$\varrho_S = \alpha_S T + \beta_S \quad . \quad . \quad . \quad . \quad . \quad (6.1)$$

where β_S represents a 'residual' or 'impurity' component of the resistivity and $\alpha_S T$ an 'ideal' or thermal component. Many liquid metals are also found to obey this approximate rule. Until recently, most theories have concerned themselves only with the effect of melting on the mean free path of the electron through one or other of the terms in equation (6.1).

According to elementary Bloch theory for solids, the thermal-scattering term is proportional to the mean square displacement of an ion from its equilibrium position, and thus to $T/M\theta_E^2$, where θ_E is the Einstein[94] characteristic temperature, and M the mass of an atom. Mott[284] extended this treatment to the liquid state, ignoring any effect due to increased atom mobility, so that ϱ_L/ϱ_S, the ratio of resistivities in the solid and liquid states, could be taken as proportional to θ_S^2/θ_L^2. The values of ϱ_L/ϱ_S may be estimated from the enthalpy of fusion, H^F, assuming that the Einstein model may be applied to the liquid as well as the solid state (but see Section 3). From this, assuming that the entropy of fusion arises only from an increase in oscillatory motion, it may be shown that:

$$\varrho_L/\varrho_S = \exp{(80H^F/T^F)} \quad (H^F \text{ in kjoule.mole}^{-1}) \quad . \quad (6.2)$$

where T^F is the melting point (see Refs. 285–287). For metals, ϱ_L/ϱ_S is normally greater than unity (Table XXX and Section 6.2.1). An exactly similar expression may be used for κ_S/κ_L, the ratio of thermal conductivities.

Mott's theory gives good values for ϱ_L/ϱ_S for many metals, but also predicts that the liquid resistivity should be proportional to T (at constant volume) for all metals, which is contrary to what is generally observed. Clearly, more than just thermal scattering is involved, and a complete theory must take into account the contribution to the resistivity made by the disorder introduced at the melting point; that Mott's theory gives reasonable agreement suggests that this contribution is surprisingly small. The first attempt in this direction was made by Shubin,[288, 289] followed after a long interval by Gubanov,[290–295] and by Ziman and his co-workers.[296–299]

Gubanov's theory consists of calculating, by means of a free-electron treatment, the perturbation of the electron caused by a distortion and disordering of the solid lattice. No attempt is made to introduce any parameter which is a direct measure of the actual structure of the liquid. The total scattering is considered as three separate contributions: 'thermal scattering', which may be dealt with along the lines of Mott's theory; 'liquid scattering', which is a direct result of the structural disorder; and 'defect scattering', which results from sharply localized departures from order—'holes' in the liquid perhaps, or local density fluctuations. Gubanov's theory, which has the disadvantage of great mathematical complexity, reduces to that of Mott as a special case. The degree to which a free-electron treatment is acceptable for liquid metals is discussed later.

Gubanov's theory had the built-in weakness of using a 'crystalline' model of the liquid, but more recent theories[296, 301, 302] have incorporated, through the radial distribution function, a measure of the actual structure of the liquid. The aim in every case has been to calculate ϱ_L (and, in the case of Ziman,[296] the temperature-dependence of ϱ_L and the thermoelectric power) from the so-called structure factor, $a(K)$, using a free-electron approach. $a(K)$ is the Fourier transform of the radial distribution function (Section 1), expressed in terms of the wave-number of the free conduction electrons being 'diffracted' by the screened ion fields in the liquid:[300]

$$a(K) = 1 + \varrho_0 \int_0^\infty \left[g(r) - 1 \right] \frac{\sin Kr}{Kr} . 4\pi r^2 \, dr \qquad . \quad (6.3)$$

where $g(r)$ is the radial distribution function as defined on p. 390, and $K = 2k_F \sin(\theta/2)$. θ is, of course, the scattering angle, k_F is the radius of the Fermi sphere and ϱ_0 the average density of atoms in the liquid. Fig. 12 shows a plot of $a(K)$ as a function of K, together with values of $2k_F$ for metals of valence 1, 2, 3, &c.[283] It is important to note that for monovalent metals, $2k_F$ lies below the main peak in $a(K)$, while for divalent and higher-valent metals, it lies above it.

The difficulty of calculating $g(r)$, and therefore $a(K)$, has already been emphasized; for the present both must be obtained from X-ray or other diffraction studies. Gerstenkorn[301] was the first to do this, although it was necessary to extrapolate $a(K)$ to $K = 0$ using a rather dubious microcrystalline model of the liquid, since measurements are not usually reported at angles lower than those corresponding to K-values of about

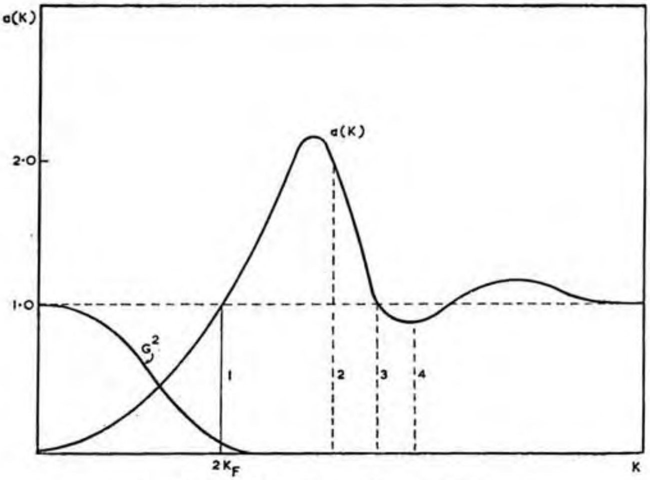

FIG. 12.—$a(K)$ vs. K. (From Ref. 283).

half those at the first peak in $a(K)$. The resistivity was calculated from an expression of the form:

$$\varrho_L = P \int_0^\pi I(\theta).a(K).(1 - \cos\theta).\sin\theta.d\theta \qquad . \quad (6.4)$$

where $P = \dfrac{2\pi m}{ne^2}\dfrac{N}{V}.V_F$, and V_F is the Fermi velocity. The other quantities have their usual meaning. The theory was applied only to the alkali metals, using an exponentially screened form of the scattering potential.* This presented some difficulty in estimating the screening radius, but nevertheless calculated values of ϱ_L are of the right order of magnitude.

Ziman[296] used the pseudopotential,[303] instead of Gerstenkorn's exponentially screened potential, in a form of equation (6.4) in which $a(K) = 1$ for all θ (which means that all the atoms in the liquid metal are scattering independently, and the assembly is therefore equivalent to a gas). The pseudopotential varies considerably from one metal to another and thus allows the theory to distinguish clearly between them. Values of the pseudopotential may be estimated, albeit not very accurately, from the energy gaps between states on the Brillouin zone face in the crystalline state, which may be obtained from band-structure

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* For a recent discussion of *pair* potentials in liquid metals, see Ref. (18).

calculations. These have been performed for the alkali and noble metals.[45] The use of the pseudopotential in this context has been criticized.[304]

The scattering calculated in this way is usually too great (except for liquid sodium), and may be corrected by restoring the form of $a(K)$ to that in equation (6.4) (for which $a(K) \neq 1$). This reduces the calculated resistivities by 60%, but the values are still too large, possibly as the result of ignoring any dependence of $a(K)$ upon K (Fig. 12). Agreement for sodium, however, is made worse, and it appears that there is an additional scattering mechanism, at least in liquid sodium and probably in all liquid metals, which is possibly caused by local, thermally induced fluctuations in the density of positive ions (cf. Gubanov's theory). This second contribution to the scattering of conduction electrons has been termed 'plasma scattering', and is of greatest importance at low K-values. It has been estimated by Ziman,[296] who calculates that sodium has plasma resistance only (see also Ref. (305)).

Even when plasma scattering is taken into account, agreement between observed and calculated resistivities is poor for most metals. The separation of the resistance into two components does allow, however, an interpretation of the temperature-dependence of resistivity, and the change in resistance on fusion.

Temperature-Dependence of Resistivity

In liquid sodium the pseudopotential is small; the mean free path of the electrons, and thus the resistivity, are determined by the region of K near $K = 0$, where the plasma term is large.[169] It may be shown that $a(K)$ at $K = 0$ depends upon thermal motion only, and is given by the mean square density fluctuation:[300]

$$a(K)_{K=0} = \frac{NkT\beta_A}{V} = \varrho_0 kT\beta_A \quad . \quad . \quad . \quad (6.5)$$

where β_A = compressibility; $N/V = \varrho_0$ = number of identical scattering centres/unit volume. Thus, ϱ_L is predicted to be proportional to T, which is observed. In cæsium, on the other hand, the pseudopotential is strong, and the mean free path is largely determined by K near $K = 2k_F$. In this region, $a(K)$ is much less temperature-sensitive, so that about one-third of the resistivity of cæsium is temperature-insensitive—and β_S in equation (6.1) is thus qualitatively justified. An exact knowledge of equation (6.1) requires information on the variation of $a(K)$ with T.

The Ratio ϱ_L/ϱ_S (Table XXXII)

In sodium, where plasma scattering predominates, ϱ_L/ϱ_S is determined by $[a(K)]_L/[a(K)]_S$ at $K \simeq 0$. Thus, from equation (6.5) at $K = 0$:

$$\varrho_L/\varrho_S = \frac{\beta_L}{\beta_S} = 1{\cdot}3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.6)$$

This is a minimum value of ϱ_L/ϱ_S, since as K increases, so does the ratio $[a(K)]_L/[a(K)]_S$. In fact ϱ_L/ϱ_S is 1·45 for sodium. In the other alkali metals, the larger values of ϱ_L/ϱ_S may be explained qualitatively by the higher values of $[a(K)]_L/[a(K)]_S$ as K increases, since for these, values of $a(K)$ at $K \gg 0$ are important. The larger the pseudopotential, the higher is the significant value of $a(K)$, and the higher is ϱ_L/ϱ_S, which therefore provides a useful qualitative guide to the size of the pseudopotential.

The theory so far has met with real success only for the univalent A-Group metals. In a more recent paper, Bradley *et al.*[297] have attempted an extension to polyvalent metals. In this case, the diameter of the Fermi sphere extends beyond the first peak in $a(K)$, and thus the integration in equation (6.4) (and its modification when $a(K) \neq 1$) now includes this first maximum.

One of the characteristics of the Group IIB metals is the unusual temperature-dependence of resistivity $\partial\varrho/\partial T$ is negative just after fusion, becoming positive with increasing temperature for zinc and cadmium). Since the plasma term is negligible in these metals,[297] $\partial\varrho/\partial T$ must be explained through the temperature-dependence of $a(K)$, or more precisely of the function

$$g(K) = \frac{1}{4k_F^4} \int_0^{2k_F} .a(K).K^3\,dK. \quad . \quad . \quad . \quad . \quad (6.7)$$

Actual values of the integral have been calculated by Bradley *et al.*, from X-ray diffraction data and are shown in Table XXXI.[297] For complete disorder the value of the integral is unity, and for some metals it is already nearly at this value at the melting point. In zinc and cadmium, there is room for a decrease as T rises, and this must be invoked to explain the initially negative $d\varrho/dT$ in these metals. The subsequent rise in plasma scattering eventually brings about a positive $d\varrho/dT$. It is not clear why mercury, gallium, and tin do not behave in the same way, since in every case the integral is greater than unity.

The properties of mercury are somewhat anomalous. It has an abnormally high value of ϱ_L/ϱ_S, a negative pressure-dependence of resistivity, and alloying elements of valence 2 or greater decrease, rather than increase, its resistivity, possibly as a result of the negative

V^M. Sodium and potassium, but not lithium, increase the resistivity, however.[307] Alloying with higher-valent elements may decrease the resistivity through a variation in $a(K)$. It will be suggested later (p. 489) that mercury may be incompletely ionized when pure, and ionized when alloyed. The high value of ϱ_L/ϱ_S may be due to a very high $a(K)$ value in the liquid, possibly because $K = 2k_F$ falls on the main peak of the $a(K)$ curve. The position of mercury, as well as of all higher-valent metals, is so far not satisfactorily resolved in terms of the Ziman theory (or, indeed, any other).

The overlap of $K = 2k_F$, and the first diffraction peak, in liquid divalent and higher metals leads to the obvious suggestion that zone-boundary effects may occur in liquids, although in a much less marked fashion than in the solid, at Fermi-sphere diameters corresponding to the first main peak in $a(K)$—i.e. at $\sim 1{\cdot}6$ electrons/atom. There is no evidence of this (but see the work of Roll *et al.*, reported below).

The Ziman theory may be used to calculate resistivities of pure liquid metals from experimental diffraction data. This calculation has been performed for a number of metals.[308, 309] Agreement is only fair in most cases, but it is impossible to tell whether the theory or the diffraction data is the source of the discrepancies. The assumptions involved in the Ziman theory are considerable, the most fundamental being the use of the nearly-free-electron model. The use of this for liquid metals has been criticized.[304, 310] Experimental evidence to be described below suggests that the nearly-free-electron model may apply for the alkali metals and perhaps a few metals of higher valence but, in general, electron mean free paths determined experimentally are shorter than those predicted on the basis of the free-electron model. This is especially true in the structurally complex liquid metals such as gallium,[311] although tin, surprisingly, appears to exhibit free-electron behaviour.[311] The use of the Ziman theory is therefore questionable for at least some metals; this limitation will be discussed in more detail later. The theory, with the same basic assumptions, has been applied to alloys.[299] Strictly, the model is applicable only to free-electron alloys whose components have the same atomic volume and valence; a size difference is approximately allowed for by a modification of the pseudopotential of the solute[312, 315]—in principle, a similar technique may be used in statistical theories of non-metallic liquid mixtures.[14, 102] More detailed diffraction data than are at present available for alloys are required for the quantitative application of the theory, but the model does allow a discussion of the qualitative differences that are observed between the electrical properties of liquid and solid alloys (see below). There is no evidence that the nearly-free-electron model *does* apply to liquid alloys; in at least one alloy (Hg–In) it apparently does not.[313] The general validity of the nearly-free-electron approach has also been discussed by Watabe and Tanaka,[314] who suggest that the density of states at the Fermi surface in the alkali metals is nearly-free-electron, while in higher-valent metals it is not. The matter will receive further consideration below.

An alternative approach to the calculation of electronic transport properties in liquid metals is the calculation of electronic states, i.e. the band structure for a disordered system. While considerable advances have been made in this field in recent years, the theory is still a long way from comparison with experimental results, and will only be reviewed very briefly here. A more detailed account has been given by Cusack.[283] Much of the work reported has been for a one-dimensional chain model of the liquid in which disorder is introduced only by variation of the atom spacing. Such models, while not able to give any useful results for comparison with a real liquid, have served to establish the methods of calculation for use in more refined approaches.[290–291, 316, 317] The results of Makinson and Roberts[317] show that an energy gap may occur even with some long- or short-range disorder, but that it closes rapidly as the degree of disorder is increased.

Three-dimensional models of the liquid will ultimately provide more satisfactory results, but have so far proved to be much more difficult to handle. The first attempt was made by Gubanov[293–295] using a distorted-solid-lattice model to calculate transport properties. Much more significant is the work of Edwards,[318–321] in which the motion of electrons in a disordered system is treated by the weak-binding approximation. Edwards shows that for the completely disordered liquid, a parabolic E/K plot is obtained which is very similar to the free-electron parabola, and which contains no indication of band gaps. If, however, a certain amount of order is introduced, a disordered version of this parabola is obtained, with inflections in the curve instead of band gaps, and with a continuous density of states. The situation is illustrated schematically in two dimensions in Fig. 13, and suggests that zone effects may be observed in alloys of electron:atom ratios > 1. This is in qualitative agreement with Ziman's theory; the next stage is to calculate the way in which the properties of the liquid might be affected.[322]

To sum up, there is no fundamental approach to the calculation of the electronic states in liquid metals that has reached the stage of predicting properties for direct comparison with experiment, although qualitatively the slightly-ordered-liquid model has had some success. At present, better results may be achieved by taking the experimentally determined radial distribution function, and considering how changes in temperature or composition will affect the electronic properties through their effect on the RDF. Some quantitative progress has already been made in applying this technique to the structurally simple (Section 2) liquid metals from Group IA.

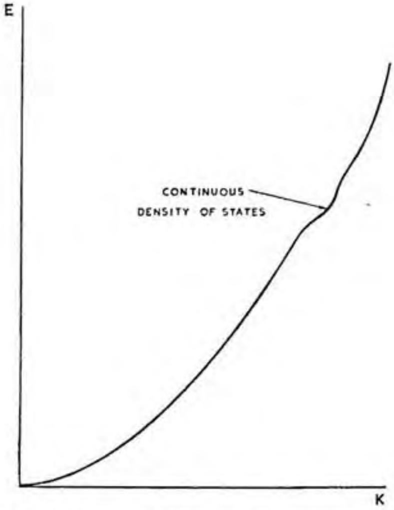

FIG. 13.—Schematic E/K curve for a liquid metal.

6.1.2. *Optical Properties*

There are two fundamental optical constants: $\bar{n}$, the complex refractive index, and k, the extinction coefficient, related by

$$E = E_0 \exp\left(i\omega\left\{\frac{\bar{n}x}{(c - t)}\right\}\right) \quad . \quad . \quad . \quad (6.8)$$

where E_0, E are the incident and reflected energies, and $\bar{n}$ is defined by $\bar{n} = n + ik$. From these may be obtained, using classical free-electron theory:

$$\bar{n}^2 - k^2 = 1 - \frac{4\pi\bar{N}e^2}{m}\left(\omega^2 + \frac{1}{\tau^2}\right)^{-1} \quad . \quad . \quad (6.9)$$

and

$$2\bar{n}k = \frac{4\pi\bar{N}e^2}{m}\cdot\frac{1}{\omega}\left(\omega^2 + \frac{1}{\tau^2}\right)^{-1} \quad . \quad . \quad (6.10)$$

where $\bar{N}$ = number of conduction electrons/unit volume.

e, m are the charge and mass of the electron.

ω is defined by considering a plane-polarized wave, and denoting its electric vector by

$$E = E_0 \exp(-i\omega\tau).$$

τ is the relaxation time; $\tau = m\sigma_0/\bar{N}e^2$, where σ_0 is the d.c. conductivity.

For pure solid metals, E/E_0 varies sinusoidally with incident wavelength as a result of sudden changes in k with wavelength ('absorption edges' in X-ray work). In liquid metals the dependence of the real and imaginary parts on frequency is usually of the form given by equations (6.9) and (6.10), which allows experimental values to be obtained for σ_0, and for $\bar{N}/m$. These can be compared with the directly measured conductivity and with the full value of $\bar{N}/m$.

6.1.3. *The Hall Effect and Thermoelectric Power*

If a magnetic field of strength H is exerted at right angles to a current I_x^0 flowing parallel to the x-axis in a conducting plate lying in the z-plane of three rectangular axes, x, y, z, then the paths of the flowing electrons become curved between collisions. This gives rise to a transverse electric field, E_y, measured in the y-direction; this is the Hall effect. In addition the current I_x^0 is reduced to I_x, so that the conductivity:

$$\sigma = \frac{I_x}{E_x}$$

is a function of H; this is the transverse magnetoresistance effect. The Hall coefficient, R, is defined by

$$R = \frac{E_y}{I_x . H}$$

Free-electron theory shows that the Hall coefficient may be given by

$$\bar{N} . |e| . R = -1 \qquad . \quad . \quad . \quad . \quad . \quad (6.11)$$

where $\bar{N}$ is again the number of conduction electrons per unit volume. More detailed calculations are given elsewhere.[306, 323] The free-electron value of R in solids should be obtained if the Fermi surface is spherical, and the relaxation time isotropic. Neither of these is achieved in the solid, but it is possible that they may be achieved in the liquid, as the structure is now isotropic, and deformation of the Fermi sphere by juxtaposition to Brillouin-zone faces can no longer occur.

The absolute thermoelectric power may be defined by:

$$S(T) = \int_0^T \frac{C_T}{T} . dT \qquad . \quad . \quad . \quad . \quad . \quad (6.12)$$

where C_T is the Thomson coefficient. If a thermocouple of metals A and B has its cold junction at T, and the hot junction at $T + dT$, and if the open-circuit Seeback electromotive force be counted as positive if current flows across the hot junction from $A \rightarrow B$, then

$$\frac{dE_{AB}}{dT} = P_{AB} = S_B - S_A \qquad . \quad . \quad . \quad (6.13)$$

Normally, P_{AB} is measured for a liquid and a solid, with the absolute thermoelectric power for the solid determined separately. Considerable experimental difficulties are involved.[325]

We may now write

$$S(T) = \frac{-\pi^2 k^2 T}{3 . |e| . E_F} . x \qquad . \quad . \quad . \quad . \quad (6.14)$$

where k is Boltzmann's constant, and E_F is the Fermi energy. It is easy to show that

$$x = E_F \left[\frac{\partial}{\partial E} \ln \sigma(E) \right]_{E=E_F} \qquad . \quad . \quad . \quad . \quad (6.15)$$

where $\sigma(E)$ is the conductivity of the metal with the Fermi surface at energy E. Values of x and dx/dT may easily be obtained from experimental values of $S(T)$ by using an approximate value of E_F.

6.1.4. *Magnetic Susceptibility: The Knight Shift*

The metallic elements fall into three classes according to the sign and magnitude of their magnetic susceptibility: diamagnetic (Cu, Ag, Au, χ weakly negative); paramagnetic (most other metals, χ weakly positive); and ferromagnetic (χ strongly positive). No ferromagnetic liquid metals or alloys are known. The total susceptibility of the liquid χ_L, may be expressed as the sum of that for the ion cores (diamagnetic) and for the electrons (paramagnetic):

$$\chi_L = \chi_I + \chi_E \qquad . \quad . \quad . \quad . \quad . \quad (6.16)$$

χ_I should be little affected by melting, so that χ^F, the change in χ on fusion, may be given by:

$$\chi^F = \chi^F_E; \qquad . \quad . \quad . \quad . \quad . \quad . \quad (6.17)$$

χ_L apparently changes extensively on fusion.

The Knight Shift, S_K, is caused by the conduction electrons only, and is expressed as the fractional difference between the values of the magnetic resonance frequency of a nucleus in a metal and in a non-conducting salt. The local magnetic field at the nucleus is strengthened by the conduction electrons, and S_K depends upon both the paramagnetic susceptibility of the electrons and upon the value of the electron-wave functions at the nucleus:

$$S_K = \frac{8\pi}{3}\chi_P . mP_F \quad . \quad . \quad . \quad . \quad (6.18)$$

where χ_P = paramagnetic susceptibility/unit mass of electrons.

m = mass of one atom.

P_F = average probability density at the nucleus for electrons at the Fermi surface.

Thus, the Knight Shift should reflect any change in electronic states on melting, since both χ_E and P_F should be susceptible to the removal of any zone-boundary effects during fusion.[326, 327]

6.1.5. *Electrotransport in Liquid Metals*

When an electric field is applied to an alloy, solid or liquid, a small amount of mass transport, or separation of the species, takes place. The process has also been termed electromigration, or electrodiffusion,* and has been the subject of a number of reviews.[328–332]

Two effects can be distinguished which lead to ion transport. These are the 'field force' exerted upon the ions by the electric field, and an opposing 'drag force' from ion/electron collisions. The resultant force may be expressed as:

$$F \doteq \Sigma_i n_i e Z_i E - n_e e E \quad . \quad . \quad . \quad . \quad (6.19)$$

where all the ions are assumed to be positively charged, the 'electron valence' is taken as -1, and

n_i = number of ions of component i per unit volume.

n_e = number of electrons per unit volume.

E = applied electric field.

Z_i = valence of component i.

By using the modified Einstein equation[335] for the absolute mobility:

$$B_i = \frac{D_i}{fkT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.20)$$

(f is a correlation coefficient and is unity for liquids), the 'electric mobility', U_i, may be shown to be:

$$U_i = B_i e\left(Z_i - \frac{\delta_{ei}}{e}\right) = \frac{D_i e}{fkT}\left(Z_i - \frac{\delta_{ei}}{e}\right) \quad . \quad (6.21)$$

where δ_{ei} is a friction coefficient relating the electric field strength to

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* In isotope separation studies, it is known as the Haeffner effect.[332–334].

the drag force of the electrons upon the component i:

$$\delta_{ei} = \frac{f_{ei}}{E} \qquad \text{(6.22)}$$

The bracketed term in equation (6.21) is usually termed the 'effective valence' Z'_i. Only U_i and D_i may be determined from direct transport measurements, and Z_i cannot normally be calculated. The sign of Z'_i indicates the direction of transport in the alloy; a negative sign indicates that drag forces predominate, and a positive sign that the field force predominates, transport being towards the anode and cathode, respectively.

Several theoretical attempts have been made, with little success, to develop an expression for δ_{ei}, which would then allow calculation of Z_i.[336–353] These have been reviewed in detail by Verhoeven.[332] A new approach by Hurle *et al.*, dealing specifically with the application of this phenomenon to the motion of liquid-alloy zones along a bar under the influence of an electric current, has greater prospects of success.[354]

6.2. Results

6.2.1. *Pure Metals*

Data for the resistivity and the change in resistivity on fusion for pure liquid metals are shown in Table XXXII, together with values of α_L and β_L (equation 6.1). Some of these values have already been quoted elsewhere.[283, 286]

It is possible to classify the molten elements according to the values of ϱ_L/ϱ_S, α_L, α_S. Almost all possible combinations are known:

Class	α_S	α_L	$\frac{\varrho_L}{\varrho_S}$	*Elements*
1	+	+	>1	Most metals; this is the 'norm'
2	+	−	>1	Zn, Cd (α_L becomes + at higher T's)
3	−	+	>1	No example known
4	−	−	>1	Se? (ϱ_L/ϱ_S is very dependent upon purity[355])
5	+	+	<1	Bi, Sb
6	+	−	<1	HgTe; no pure metals
7	−	+	<1	Ge, Si
8	−	−	<1	Te, Sb_2S_3

A value of $\varrho_L/\varrho_S < 1$ is usually thought to indicate an increase in the concentration of negative carriers on fusion, through the destruction of non-metallic bonds. Lithium is exceptional in having a value of α_L that decreases with increasing temperature. This and the special case of zinc and cadmium have been discussed above in terms of Ziman's nearly-free-electron theory (p. 460). A negative value of α_L or α_S

(Classes 2–4, 6–8) is normally thought to be associated with semiconducting properties, i.e. it is supposed to arise from thermal excitation of electrons across what in most cases must be a very small energy gap (intrinsic semiconduction). It has often been proposed that the homopolar, or in some cases heteropolar, bonds in semiconducting liquids (and solids) gradually break down with increasing temperature, the resulting delocalization of electrons previously tied up in bound states thus providing more carriers for normal metallic conduction. In some cases this model is apparently valid—for example, in the 'true' liquid semiconductors Se, Tl_2Se_3, Tl_2S_3, amongst others—but in other cases it will be argued below that a negative temperature coefficient of resistivity does not necessarily indicate the destruction of covalent bonding. This mechanism was first proposed to explain the initially negative temperature coefficient in zinc, cadmium, and perhaps mercury,[356] but extensive covalent bonding in these liquids seems highly improbable, particularly since $\varrho_L/\varrho_S > 1$. Ziman's explanation[297] based upon the temperature-dependence of $a(K)$, is much more acceptable and may be used qualitatively to explain the properties of a number of intermetallic compounds in the liquid state. However, for a number of pure metals which exhibit a negative α_L there is clear direct evidence of an anomalous liquid-state structure (Section 2); these are commonly those metals in which homopolar bonding is present in the solid state, so that it is tempting to suggest that at least a contribution to the negative α_L may arise from the destruction of covalent bonding with increasing temperature in the liquid. (It may be significant that liquid mercury has an anomalous structure at low temperatures.[41]) In such cases the value of α_L should eventually become positive as soon as all the homopolar bonds are destroyed (this has not been observed) and the increase in negative carrier concentration should be evident in a decrease with increasing temperature of the Hall coefficient, the thermoelectric power, and other properties. Unfortunately, the evidence from these measurements is at present by no means conclusive (see below). In cases where α_S is negative and α_L positive (Classes 3 and 7) it may be argued that conversion to metallic from homopolar bonding is completed by fusion. Bismuth and antimony already exhibit metallic behaviour in the solid state but have a high resistivity. The homopolar contribution to bonding in these materials is small in the solid state but is sufficient to provide a value of ϱ_L/ϱ_S that is less than unity. Materials in Classes 4 and 6 are anomalous. Selenium is reported to exhibit a sharp increase in resistivity on fusion which is extremely sensitive to the degree of purity of the material[355] and which varies from × 30,000 for 'commercial' selenium to × 1 for the very pure material. The latter value has been selected (Table XXXII). Selenium is anomalous in other respects; it shows a decrease in density on fusion (Table XXX), as do 'normal' metals, yet the liquid is by no means a metallic conductor. The viscosity at temperatures just above the melting point is reported to be anomalously high;[357] diffraction and magnetic studies suggest that at this temperature its structure, like that of tellurium and sulphur,[364] is complex and contains long chains of selenium atoms.[358, 359] Further work may place selenium in Class 8.

The data in Table XXXII have been measured under conditions of constant pressure. The resistivity at constant volume may be determined from information on the compressibility, thermal expansion, and pressure-dependence of resistivity in the liquid state, or by direct measurement.[361–363] In sodium, $\varrho_L \propto T(°\mathrm{K})$ at constant volume, and this has been interpreted[296] in terms of the negligible pseudopotential scattering in liquid sodium. The pseudopotential (structure-scattering) term becomes larger for the alkali metals of higher atomic number.[362] Values of ϱ_L at constant volume for the alkali metals are given in Table XXXIII. For the alkali metals the restivity at constant volume is a linear function of the absolute temperature:

$$(\varrho_L)_V = (\varrho_0)_V + (\alpha_L)_V \cdot T \qquad . \quad . \quad . \quad (6.23)$$

(compare equation 6.1).

The value of the 'residual resistance' at constant volume, ϱ_0, is a measure of the 'structural' scattering by individual ion cores—i.e. by the pseudopotential—and is relatively unimportant in sodium whose resistivity arises mostly from the plasma term (p. 459), but highly significant in rubidium and cæsium. Measurements of the relative resistivity at constant volume have also been made on mercury and gallium,[363] together with measurements of the thermoelectric power (see below). Bradley[363] concludes that in mercury the pseudopotential, which is the major scattering term in the higher-valent metals, is strongly dependent upon the electron momentum, and hence upon the Fermi energy. The Fermi energy may change extensively on alloying in mercury, as is suggested by the decrease in the resistivity of the metal that is produced by most solutes. It follows that the pseudopotential may also change extensively, and hence affect other properties—e.g. the temperature-dependence of the resistivity—that depend upon it.

6.2.2. *Alloys*

A. *General: Dilute Solutions*

Two well-established rules govern the composition-dependence of the resistivity of solid alloys. The Nordheim rule states that the resistivity of an alloy should approximately be proportional to the product of the mole fractions of the two components; while the Linde rule states that the rate of increase in resistance with increasing concentration in *dilute* alloys should be proportional to the square of the difference in valence of the components. Thus:

$$\varrho_S = \text{const. } N_1N_2 \quad . \quad . \quad . \quad (6.24)$$

and

$$d\varrho_S/dN_2 = \text{const. } (Z_1 - Z_2)^2 \quad . \quad . \quad . \quad (6.25)$$

where component 2 is the solute.

These rules are not observed to apply generally to liquid alloys; in many cases the slope of the resistivity/composition isotherm at infinite dilution is of the wrong sign, and the isotherm itself may be linear, asymmetric, or otherwise of a more complex shape than predicted by the Nordheim rule. In an investigation aimed at determining the applicability of the Linde rule to liquid alloys, Scala and Robertson[365] observed that in liquid *copper* as solvent the resistivity is increased by small solute additions according to the Linde rule. In zinc, however, small additions of Cu, Cd, Al, and Bi have no significant effect, while additions of Sn and Sb increase the resistivity to about the same extent in each case. The different effects of bismuth and antimony may arise from the difference between the Bi–Zn and Sb–Zn structures (miscibility gap and heteropolar-bonded compound, respectively). In the Zn–Sb alloys electrons may be localized in interatomic bonds—even in the dilute alloys—leading to a resistance increase, since they are not available for conduction; while in the Zn–Bi alloys the large size factor prohibits the packing arrangements necessary for the formation of such bonds. The same may apply in the Zn–Al alloys. Kleppa has suggested (p. 429) that the positive enthalpy of mixing in the zinc-rich alloys with metals from groups III, IV, and V may arise from an abnormal composition-dependence of the Fermi energy, E_F. The resistivity is roughly inversely proportional to this and thus there will be a decrease in ϱ_L upon alloying to balance the increase due to ion scattering. This is in agreement with the observed small change of ϱ_L with composition.[263] The Linde rule also appears to be obeyed approximately in dilute solutions in molten aluminium.[366] Copper is reported to produce a very sharp decrease in the resistivity of tin, as does tin in nickel, and in lead.[263] (For reservations about this work, see later. These results are not confirmed by Roll *et al.*[367–374]) Some of these sharp decreases appear to be associated with the resistance minima reported at eutectic and solid-solubility-limit compositions,[263] and suggest modification of the electronic structure of the solvent. In tin, addition of copper may cause a modification of the proposed dual structure of liquid tin (Section 2), perhaps by substitution in the homopolar-bonded part of the structure.

A theoretical justification for the non-compliance of liquid alloys with the Nordheim and Linde rules has been attempted by Faber and Ziman.[299]

B. *Solid-Solution Systems*

A number of systems have been investigated by Roll and Motz[369] using the rotating-magnetic-field method.[367] The results are summarized in Fig. 14, and Table XXXIV. Anomalies in the resistivity isotherm consisting of two small maxima separated by a minimum are observed in ϱ_L and α_L at roughly constant composition in all three systems. There is little doubt that these anomalies are experimentally significant, since they are also observed at atom ratios of 1:2 in the eutectic Ag–Cu[370] and Pb–Sn[372] systems, and in the more complex Cd–Hg, Cd–Zn, and perhaps Ga–In,* systems.[373] They have also been

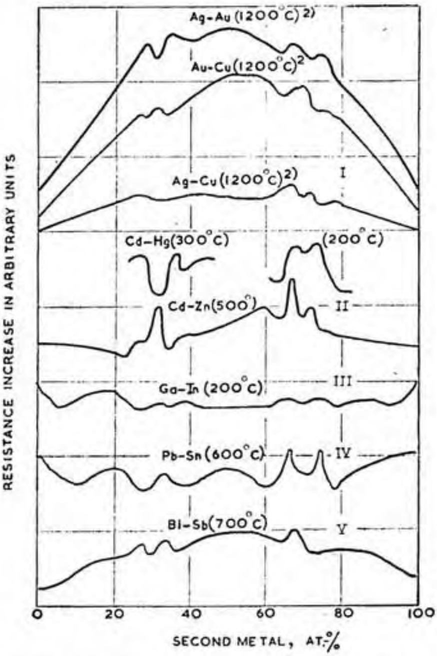

FIG. 14.—Relative resistivities for components of equal valence. (See Table XXXIV)

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* This anomaly is very slight in the Ga–In system.

observed independently in the Pb–Sn system.[375, 376] Since these phenomena are clearly not associated with the *type* of system involved, they are discussed in Section C (below). These anomalies have not generally been reported by other workers, but neither are they refuted by the inadequately detailed results that are almost universally presented. The composition-dependence of almost all physical properties of liquid alloys needs far more detailed investigation than it is usually given.

An unconfirmed discontinuity, which could be the result of the experimental technique, has been reported in α_L in the Bi–Sb system at $\sim$ 675°C.[373] Similar phenomena are observed in other liquid alloys (see below), and these may be due to a discontinuous change in structure of the alloy to one with more metallic characteristics. It may be significant that bismuth and antimony exhibit some 'non-metallic' tendencies.

C. *Eutectic Systems*

(i) *Components of Equal Valence*

The results of work on these systems, again mainly by Roll and his co-workers, are detailed in Fig. 14 and Table XXXIV. In every case there is evidence of an anomaly in the resistivity isotherms, and in most cases in the isotherm of $\alpha_L = (d\varrho_L)/(dT)$, at $\sim$ 33 and 66 at.-% of one component.

Roll *et al.* offer no interpretation of these phenomena, and it is difficult to construct a convincing explanation. It may be noteworthy that the size factor is low in all these systems except Ga–In, which does not exhibit a significant anomaly. The largest effect appears to be shown by the systems with the smaller size factors. This scanty evidence suggests that the anomalies might arise from a packing phenomenon. It is possible that with size factors of $< \sim 14\%$, packing becomes relatively easy, or relatively difficult, at atom ratios of 1:2 and 2:1, leading to slightly increased disorder and a resultant slight increase in resistivity. This explanation does not account for the *two* maxima observed, nor is it at present justifiable on any theoretical grounds known to the writer.

In the Cd–Zn system, α_L is reported to be negative at all temperatures for compositions between 10 and 100 at.-% zinc, with the exception of alloys in the range 80–95 at.-%.[373] For the latter alloys, and perhaps for pure cadmium, α_L is positive. This may indicate, on the basis of the Ziman theory[296] (p. 460), anomalous composition-dependence of the structure factor, $a(K)$, which should be detectable by X-ray diffraction measurements.

(ii) *Components of Different Valence*

Similar anomalies are observed in systems with a composition-dependent valence-electron concentration, but the central minimum now falls at a roughly constant e/a ratio of 2·3. The results reported by Roll and his co-workers are detailed in Fig. 15 and summarized in Table XXXV. If the reasoning used above for the solid-solution systems is correct, those systems with a size factor of $< \sim 14\%$ should also show an anomaly at ~ 44 and 66 at.-% of one component. Of the systems investigated, only the Hg–In, Al–Zn, and Sn–Zn have size factors of the right magnitude and unfortunately the data are in every case insufficient to permit any conclusion.

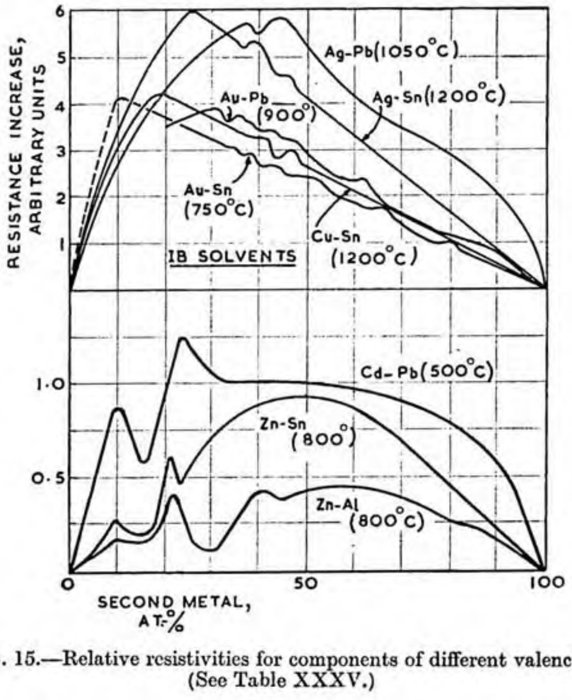

FIG. 15.—Relative resistivities for components of different valence. (See Table XXXV.)

In none of the systems investigated was any anomalous composition-dependence of ϱ_L or α_L observed at eutectic compositions, with the possible exception of the Cd–Zn system (minimum in ϱ_L), and the Cd–Pb system (maximum in α_L), although in most cases the data are not detailed enough at the relevant compositions to allow any firm conclusion to be reached. Minima in the resistivity at eutectic compositions have been reported for Sn–Cu, Sn–Ni, Sn–Pb alloys[263] (resistivity minima are also claimed at solid-solubility limits in the Sn–Cu and Sn–Pb alloys) and a number of aluminium-based liquids,[263] but the results are scattered, and more evidence is required before this can be accepted as a general phenomenon. Similar results have been reported by Korol'kov,[378] but again the results are not convincing.

No explanation has been suggested for the anomalies at constant valence-electron concentration. The shape of the anomaly is approximately that which would be predicted from an E/K curve with a sharp inflection, instead of the gap characteristic of the solid state, since ϱ_L is a function of the Fermi energy. This inflected curve is that proposed by Edwards[320] on theoretical grounds (Fig. 13). Such variations in dE/dK would correspond to a density-of-states curve which exhibited one minimum and two maximum E-values; these would presumably occur at an E-value corresponding to ~ 2 electrons per atom, by analogy with the solid state. An $N(E)$ curve of this sort has been calculated by Watabe and Tanaka[314] for liquid zinc from E/K curves obtained from a nearly-free-electron approach modelled on that of Edwards.[320] The density-of-states curve for the liquid does not, of course, return to $N(E) = 0$ at higher E-values but is continuous with that for the second energy band, i.e. the curve approximates to the free-electron parabola. The anomaly in ϱ_L may occur at 2·3 rather than 2 electrons per atom because of a reduction in the sharpness of definition of both the Fermi surface and the 'edges' of the energy bands in the liquid state.

Recently, Roll *et al.* have observed similar anomalies in liquid alloys at $e/a = 4{\cdot}2$;[379, 380] perhaps this corresponds to the second energy gap in the solid state at ~ 4 electrons per atom, which will also appear as an inflection in the E/K curve for the liquid. More detailed and careful measurements are required to establish these anomalies with complete certainty; some work is in progress at Birmingham University. The work of Roll and Swamy[374] on ternary alloys suggested that addition of a third component might move the anomaly to higher e/a values; this should be pursued. Meanwhile, a more elaborate interpretation must await further developments in the theory of Edwards and others. If the anomalies are indeed real, it follows that a strictly or even nearly free-electron treatment may not suffice, at least for liquid alloys; the exact degree of freedom that one should be allowed in a theoretical treatment is likely to remain a matter of opinion for some time!

Finally, an investigation of alloys with valence-electron concentration varying between 1 and 2, and 1 and 3, may be of value, with particular attention paid to the range of valence-electron concentrations from 1·3 to 1·4 electrons/atom, in which Ziman's theory suggests that the Fermi surface should make contact with any 'zone' surface resulting from the first peak in $a(K)$. The temperature-dependence of the resistivity is most likely to be affected in this range.

A number of other solid-solution and eutectic systems have been investigated; the results in all cases are less detailed than is desirable but the sources are given in Tables XXXIV and XXXV.

D. *Compound-Containing Systems*

Here the information is even more confused, and unreliable. Very few systems have been investigated over a wide composition range. The information on those studied is summarized in Tables XXXVI and XXXVII. A few selected groups of well-documented similar systems are discussed below.

The IB–Sn Group of Systems

The maximum and minimum values of ϱ_L and α_L in these systems are summarized below, *excluding* the anomalies at valence-electron concentrations of $\sim 2{\cdot}3$.

	(ϱ_L)max., microhm-cm	(α_L)min., microhm-cm.deg^{-1}
Cu–Sn	75 at 25–30 at.-% Sn	$-1{\cdot}5$ at 20 at.-% Sn
Ag–Sn	93 at 27 at.-% Sn	0 at 20 at.-% Sn
Au–Sn	80* at 22 at.-% Sn	0 at 20–40 at.-% Sn

* Approximate.[371]

X-ray diffraction work on these systems (Section 2) indicates that there is a tendency to form what are probably IB–Sn complexes at $\sim$ 25 at.-% tin. Similar conclusions may be reached from the viscosity measurements[377] on the Cu–Sn system. The maximum negative enthalpies of mixing in the Ag–Sn and Cu–Sn systems all fall at compositions towards the IB-rich end of the system. In Au–Sn, the maximum falls at higher tin compositions as a result of the tin-rich compounds:

	$H^M_{\text{max.}}$, kcal. mole^{-1}	Electronegativity Factor
Cu–Sn	$-1{\cdot}2$ at 22 at.-% Sn	0·39
Ag–Sn	$-0{\cdot}75$ at 20 at.-% Sn	0·29
Au–Sn	$-2{\cdot}6$ at 47 at.-% Sn	0·69

The values of $H^M_{\text{max.}}$ are clearly influenced by the electronegativity factor. Finally, the value of the magnetic susceptibility in Cu–Sn liquids reaches a minimum value of 25 at.-% tin,[381] which may be interpreted as a minimum in the electronic susceptibility, χ_E (since the ionic term χ_I is probably not much affected by composition), and suggests non-freedom of electrons (see below). The magnetic susceptibility for the solid alloys also reaches a minimum in the ε phase field.[382] It is possible that in all these alloys intermetallic bonding in the liquid is particularly strong at ~ 25 at.-% tin, and involves a fairly high degree of electron localization (relatively high ϱ_L; low α_L and χ_L) which is progressively destroyed over a considerable temperature range above the melting point ($\alpha_L = 0$, or negative). In both the Cu–Sn and Ag–Sn systems, a phase of ε structure (7/4 electrons per atom) is observed at this composition. The high electronegativity factor in the Au–Sn system prevents an ε structure in the solid state,[45] (the size factor is favourable), but the factors which attempt to bring about the formation of 7 : 4 compound in this system must operate in the liquid in favour of this rather than any other structure. The ε structures are essentially electronic in origin, as far as they are understood,[45] and their range of existence is determined primarily by Fermi-surface/Brillouin-zone interactions, which cannot occur in the liquid at the same composition. The structure must therefore be stabilized, at least in the liquid, by some other factor; the low α_L and χ_L, and fairly high ϱ_L suggest that either polar or homopolar bonding is involved. It has been suggested (Section 2) that liquid tin has some of the homopolar bonding characteristics of grey tin, which may result in a stable M_3Sn complex (where M is the IB metal), possibly consisting of tetrahedral configuration of four atoms or a multiple of this unit with directional homopolar or heteropolar bonding.[37] The resulting clustered structure and high bond energies (high H^M) would account for the high viscosities observed, and the homopolar or heteropolar bond for the apparent lack of free electrons, and, because its gradual destruction with increasing temperature provides more free electrons by releasing them from bound states, for the low or negative values of α_L. The effect of the IB–Sn association is enhanced in the Au–Sn system, where α_L is very small over a wide composition range, by the high electronegativity factor, which gives a wider composition spread of non-metallic bonding (probably partly heteropolar bonding in this case, in view of the NiAs structure of AuSn).

Of course, it may also be possible to explain the properties of these alloys in terms of the composition- and temperature-dependence of $a(K)$ through the Ziman,[296] March,[18] and similar theories, but many more diffraction data are required before this approach becomes feasible, even if a satisfactory (non-free electron?) theory can be developed.[199, 383] This approach and that used here are not incompatible; given a satisfactory explanation of the properties through $g(r)$, and hence $a(K)$, one still has to explain, in terms of the nature and properties of the interatomic bond, why $g(r)$ varies with temperature and composition in the way that it does. Meanwhile, Hall-effect or other measurements sensitive to the state of the electrons in the liquid would be of value. Almost certainly the Hall effect will exhibit typically metallic behaviour (R negative, independent of temperature), because this quantity is apparently not a very sensitive measure of small departures from truly metallic behaviour in liquid alloys (see below).

It is clear that evidence of strong bonding in the liquid state may not necessarily be found at a composition corresponding to a solid-state compound. If, as in the case of the ε structure in the Au–Sn system, a phase cannot exist in the solid state, the removal by fusion of the need to form a structure capable of long-range packing may allow the factors leading to compound formation a much greater freedom of choice of an optimum composition for satisfying all energetic requirements. This may lead to unlike-atom associations in the liquid at a composition quite different from that of any solid compound.

The Mg–Pb and Mg–Sn Systems

In each case the resistivity increases rapidly with increasing content of the Group IV element to a maximum at Mg_2Pb or Mg_2Sn, and then remains approximately constant. Mg_2Pb and, especially, Mg_2Sn are poor conductors in the solid state ($\varrho_S = 223$ and 42,000 microhm-cm, respectively), in both cases improved by fusion to ~ 100 microhm-cm. In the solid state the resistivity of Mg_2Sn is an exponential function of temperature, indicating semiconducting properties, while Mg_2Pb behaves as a metallic conductor (ϱ_S linear with T, $\alpha_S = 0{\cdot}0018$ microhm-cm.deg^{-1}).[384] Band gaps in the Mg–IVB compounds have been estimated to be:[385, 386]

	eV		eV
Mg_2Si	0·77	Mg_2Sn	0·36
Mg_2Ge	0·74	Mg_2Pb	0·0

Viscosity measurements[387, 388] indicate that the viscosity, and therefore the structure, of Mg_2Pb liquids is much more temperature-dependent than that of Mg_2Sn, while the resistivity of both shows little change with temperature. The probable partially heteropolar structure of these liquids at the Mg_2X composition, and the effect of this upon the shape of the resistivity isotherm and the partial molar enthalpy of solution of magnesium, has been discussed earlier (p. 433). The viscosity is sensitive only to the 'molecular' structure of the liquid. At lower temperatures, magnesium and lead or tin 'ions' probably associate to form ion clusters, as in molten salts, leading to a relatively high viscosity. Increasing temperature will destroy these clusters; this will occur more easily in Mg_2Pb, for which the enthalpy of formation is lower than

Mg_2Sn, leading to greater temperature-dependence of viscosity. The resistivity in each case is primarily a function of the heteropolar bond, which is little affected by heating in this temperature range.

Both Mg_2Pb and Mg_2Sn show a contraction on fusion resulting from the open CaF_2 structure in the solid. The volumes of mixing in solid and liquid are:[262]

	V_S^M	V_L^M
Mg_2Pb	+3·4%	−6·5%
Mg_2Sn	+6·7%	−4·1%

the lower V_L^M value in Mg_2Sn being commensurate with a greater retention and stability of an open ionic structure. Possibly Mg_2Si and Mg_2Ge, where the electronegativity factor is much greater, might exhibit positive volumes of mixing in the liquid, as do Sb_2Zn_3 and Mg_3Bi_2[262] (p. 454).

The Mg–Bi system may also exhibit heteropolar bonding in the liquid (Table XXXVI). The very sharp maximum resistivity at 'Mg_3Bi_2' in the liquid correlates well with the very strong short-range order deduced from e.m.f. measurements.[389] The properties of the liquid at the stoichiometric composition may approach those of an intrinsic semiconductor;[167] addition of magnesium may then lead to degenerate electron conduction, while addition of bismuth may contribute a small degree of positive-hole conduction, replaced at higher bismuth concentrations by electron conduction by bismuth valence electrons. The Mg–Pb and Mg–Sn systems may be considered as an intermediate system type between Mg–Bi and truly metallic systems.

The III–V, II–VI, and Similar Systems

The results for these systems are summarized in Table XXXVI; in some cases they may be invalidated by lack of knowledge of the exact composition of the melt, or by a lack of measurements in the temperature range just above the melting point. For some of the intermetallic compounds in these systems[221, 390–395] the change in resistance on fusion has been reported by Glazov *et al.* to be small and to be followed by a steep decrease in the resistivity for ∼ 40 degC above the melting point. This heating curve is not reproduced on cooling, and in some cases the increase in resistivity is reported to be time-dependent at a constant temperature. Supercooling is said to be possible only after considerable superheating. The kinematic viscosity is very high at temperatures just above the melting point and this, too, reaches normal values at ∼ 40 deg above the melting point. These phenomena are interpreted in terms of incomplete destruction of the solid structure until a superheat of ∼ 40 degC has been achieved. Recent work has not been able to repeat the resistivity measurements in InSb or in germanium,[396] or to indicate such 'structural' phenomena in any other way.[463, 464] However, these two materials have relatively simple solid-state structures; in materials of more complex structure, such as some of the selenides and tellurides, there may be a rather sluggish change in structure during the fusion process but it is doubtful whether Glazov's results are more than qualitatively correct; his melts were probably impure or non-stoichiometric. The situation needs further investigation. Supercooling phenomena in metallic liquids similar to those reported by Glazov have received an alternative explanation involving heterogeneous nucleation which could also apply here;[397] the suggestion that superheating is necessary to destroy all signs of the solid structure, and thus to prevent nucleation of the bulk solid on cooling, is probably incorrect.

The III–V Systems

The arsenides and antimonides of aluminium, gallium, and indium are the important intermetallic compounds in this group. The alloys containing thallium and bismuth do not, in general, form intermetallic compounds because of the large atomic size factors involved. Several arsenides and antimonides have been investigated in the liquid state; the data are summarized in Tables XXXVI and XXXVII. In all cases, the resistance decreases by a factor of between 2 and 10 on fusion, and the resistivity of the liquid is characteristic of a metal (∼ 100 microhm-cm) and increases with temperature. The Hall effect of InSb is negative in the liquid, positive in the solid.[400] Any non-metallic bonding in these materials appears to be largely destroyed on fusion; this is confirmed by the large reduction in the enthalpy of mixing. The resistivity/composition isotherm reaches a maximum at the stoichiometric composition, as does the viscosity, while the magnetic susceptibility reaches an equally sharp minimum.[394–395] These results suggest that some would-be conduction electrons are still involved in bound states, so that a proportion of non-metallic bonding, sufficient to produce these results, may be retained after fusion. The viscosity and susceptibility are strongly temperature-dependent and α_L for the stoichiometric composition, while positive, is smaller than that for the non-stoichiometric alloys. This suggests that electrons are being delocalized by increasing the temperature, but it is possible only to speculate on the exact process by which this 'unbinding' of electrons occurs. Bonding in the liquid may even be described as partially heteropolar. In these liquids there can be no clearly defined bond mechanism in the sense that the position and function of the valence electrons is known precisely. It is probably incorrect to use the terms 'homopolar' or 'heteropolar' in this context because they suggest too precise a model of bonding. Perhaps the general term 'non-free electron' or 'non-metallic' is preferable to indicate that some degree of electron localization is involved. Electrotransport measurements are being performed on these alloys at Birmingham University with the intention of shedding some light on the bonding situation.

The II–VI Systems

These are rather less well documented than the III–V compounds. Liquid-state resistivities are apparently much higher than for the antimonides and arsenides, although there is still a decrease in resistivity by a factor of ~ 10 on fusion. In addition, the temperature coefficients of resistivity of the liquids are negative. Localization of electrons in bound states seems to be much more complete in these systems. The viscosities and resistivities again reach a sharp maximum at the stoichiometric composition and the viscosities are again strongly temperature-dependent, suggesting a change in bond mechanism with increasing temperature. The liquids may perhaps be classified as very bad intrinsic semiconductors.

The III–VI Systems

It is rather more difficult to generalize about this group. Indium and gallium tellurides melt with little or no change in resistivity and have negative temperature coefficients of resistivity in the solid and liquid states; their liquid-state resistivities are high. Similar behaviour is exhibited by the tellurides and selenides of thallium; liquid resistivities range from 3×10^3 to 10^6 microhm-cm. The sulphides have similar or higher liquid resistivities. These liquids, in common with a number of other sulphides, apparently behave as intrinsic semiconductors in the liquid state and become degenerate as soon as the composition becomes slightly non-stoichiometric. This semiconducting behaviour is surprising when considered in terms of the conventional solid-state model of semiconduction, which requires a long-range solid-state lattice. It appears that the form of conduction exhibited by the liquid is determined by short- rather than long-range order; the next stage is the development of a theory to take account of this. A start in this direction has, of course, been made by Edwards. The problem has also been discussed by Knight *et al.*[327] and by Ioffe and Regel.[398, 399]

Other Systems

A number of other tellurides and selenides have been investigated at the stoichiometric composition (a study of the composition-dependence of the properties is much more valuable; it also avoids the problem of having to ensure stoichiometry, since data at the stoichiometric composition can be obtained by a small interpolation), although the results are usually of poor quality. Temperature coefficients are generally negative in the liquid state and there is a decrease in resistivity on fusion, but liquid-state conductivities are fairly high. Similar results are obtained for transition-metal silicides, which have liquid-state resistivities of $\sim 3 \times 10^3$ microhm-cm.

A number of investigators have reported a discontinuity in the temperature coefficient of resistivity, α_L, at temperatures well up into the liquid phase for several liquid alloys.[69, 368, 369] While it is clear that more investigation is needed, these observations do suggest the possibility of discontinuous structural changes in liquid alloys, perhaps in the form of 'phase changes'. There seems to be no fundamental objection to the possibility of one liquid 'structure' becoming unstable relative to another at a critical temperature, although at the high temperatures involved (and hence high atom-vibration amplitudes) the structures would have to be very stable. The phenomena could also be associated with the variation of $a(K)$ with temperature, since this controls the temperature coefficient of resistivity. Direct structural investigation would be of interest.

It is not possible to classify exactly any of the intermediate compounds so far investigated. None behave as pure salts (the temperature coefficients of resistivity are too high) or as pure semiconductors (the Hall effect is often negative, as is the thermoelectric power). A great deal more information is required before any clear picture of bonding or conduction mechanisms can be drawn. Meanwhile it is possible, as for pure metals, to classify behaviour according to the values of α_L, α_S, and ϱ_L/ϱ_S.

Class	α_S	α_L	ϱ_L/ϱ_S	
	near melting point			
1	+	+	> 1	Electron compounds: $MgZn_2$ and probably most Laves phases, depending on electronegativity factor
2	+	−		HgSe (VF +ve);
3	−	+		$NiTe_2$?, $CoTe_2$?
4	−	−		V_2O_5; CuTe?; $FeTe_2$?
5	+	+	< 1	Mg_2Pb? ($\alpha_L = 0$)
6	+	−		Mg_2Pb? ($\alpha_L = 0$); HgTe, Bi_2Se_3
7	−	+		MgSn? ($\alpha_L = 0$); InSb, GaSb, AlSb, GaAs, InAs
8	−	−		Mg_2Sn? ($\alpha_L = 0$); Sb_2S_3; Tl_2S; Bi_2O_3; Bi_2Te_3; Sb_2Zn_3; PbSe?; PbTe

It should be remembered that much of this work needs independent substantiation. Only in the case of the III–V compounds are the results in little doubt.

6.2.3. *Thermal Conductivity*

The available information is listed in Table XXXVIII, taken from the review by Powell,[401] with additions from more recent work; there is considerable disagreement between individual authors. The empirical Lorenz number, L, connects the thermal and electrical conductivity according to the Wiedemann–Franz–Lorenz law:

$$L = \frac{\kappa_L}{\sigma_L . T} \quad . \quad . \quad . \quad . \quad . \quad (6.26)$$

and its theoretical value for metallic (i.e. electronic) conduction is $2{\cdot}45 \times 10^{-8}\ V^2\ \text{deg}^{-2}$.[402] It will be seen that there is good agreement with this value for most liquid metals. κ_L varies in an approximately linear manner with temperature for potassium $\left(\frac{d\kappa_L}{dT}\ -\text{ve}\right)$, and mercury $\left(\frac{d\kappa_L}{dT}\ +\text{ve}\right)$, while for sodium $\frac{d\kappa_L}{dT}$ is negative at the melting point and becomes less negative with increasing temperature.[403] As a result, for these and some other metals, L is temperature-dependent. The data available provide no clue to the change in L on fusion: the values of κ_S/κ_L are very similar to those of ϱ_L/ϱ_S.

Single compositions in the Na–Hg, Na–K, and Pb–Bi,[404] Cd–Sn and Bi–Sn[405] systems have been investigated. The Wiedemann–Franz–Lorenz law is obeyed. Only the Te–Tl and Se–Te systems have been systematically studied for the composition-dependence of the thermal conductivity.[406, 417] From these (rather scattered) measurements and those of the thermoelectric power of these Te–Tl solutions, Cutler and Mallon[407] have suggested that the thallium-rich liquids are n-type semiconductors and that a transition to p-type conduction occurs at $\sim 34\%$ tellurium. It is also suggested that there may be a contribution from ambipolar diffusion (the generation of electron/hole pairs in hotter regions followed by their diffusion as a pair to cooler regions where they recombine[408]) to the thermal conductivity. The Wiedemann–Franz–Lorenz law is only partly obeyed. More work of this kind may be of some value but it appears that it may eventually be possible, at least for pure metals and 'simple' alloys, to obtain an estimate of thermal conductivity from the more easily measured electrical conductivities and an assumed Lorenz number. Certainly, the information available at present provides no conclusive information regarding electronic states in liquid metals.

Because of their much greater thermal conductivity, liquid metals used as heat-transfer media do not obey the usual equations[409–411] resulting from the analogy between heat and mass transfer, since these process are no longer mechanically similar.[412]

6.2.4. *Thermoelectric Power*

We turn now to measurements which can provide direct evidence of the state of the electrons in the liquid metal.

Values of $S_L - S_S$ (defined as in equation (6.14)) are given in Table XXXIX, together with values of x calculated from (6.15). There is frequently a considerable discrepancy between values of $(S_L - S_S)$, and therefore of x, in the literature. Values of x are also subject to the error introduced by the assumed values of E_F (eqn. 6.15) which have been taken from Cusack's review.[283]

In cases where plasma scattering is predominant, $x = 3$, in agreement with the observed value for sodium. It is doubtful whether the accuracy of the experimental values of x justifies detailed analysis for those metals in which pseudopotential scattering predominates. The negative values of x in many of these metals arises because $\sigma(E)$ (equation 6.15) falls as E rises, as a result of the increase in $a(K)$. The alkali metals fit into this pattern, but the Group IB metals appear to be anomalous; the investigation of these would be worth repeating in view of the difficulty of measurement at such high temperatures. (The divalent metals have been discussed in the light of Ziman's theory by Bradley *et al.*;[297] a number of rather dubious assumptions are required in their interpretation, which, together with the inaccuracy of the x-values, probably invalidate any possible conclusions.)

Seebeck potentials have been measured for a number of liquid alloys. Dutchak has investigated composition-dependence in the Bi–Sb,[413] Pb–Sn,[414] and Bi–Sn[415] systems. Linear dependence upon composition is observed in the Bi–Sb system, but the shape of the isotherms for the other systems is complex; too few experimental points are given for these anomalies to be certain. Dutchak has also measured Seebeck potentials between molten couples.[416] The work of Cutler and Mallon on Te–Tl alloys has been referred to.[407] These workers also investigated the Se–Te system;[417] their results are in agreement with the earlier work of Mokrovsky and Regel.[398] Selenium increases the already large and positive Seebeck potential of tellurium. Dancy has investigated alloys of tellurium with tin, silver, and copper,[418] finding that the composition coefficient of the potentials in all cases changes sign from positive to negative in the region of the stoichiometric compositions of the compounds in these systems, as the metal concentration is increased; she concludes that conduction is intrinsic at the stoichiometric composition with degenerate electron and hole conduction in metal- and tellurium-rich solutions, respectively. This argument has also been used above, and is essentially the same as that of Mallon and Cutler for Te–Tl liquids. It is supported by resistivity measurements on these and similar liquids[418, 419] which behave as liquid semiconductors.

6.2.5. *The Hall Coefficient*

More can be determined by measurements of Hall coefficients. Values gathered from the literature are shown in Table XL, from which it will be seen that a surprisingly close approximation to apparently free-electron behaviour ($\overline{N}/e/R = -1$) is achieved by many liquid metals.[420] In view of the extreme difficulty in performing accurate measurements, agreement between different sources is very good. The apparent nearly-free-electron behaviour of metals such as gallium, germanium, and tin is surprising, considering the diffraction evidence of possible homopolar bonding in the melts (Section 2), and will be referred to later. Until more reliable information is available, it is difficult to assess the significance of the apparent deviations from free-electron behaviour shown by lead, bismuth, and rubidium. The temperature-dependence of the Hall effect is an important quantity, because it provides an indication of the way in which the negative or positive carrier concentration in the material varies with temperature. Thus, if an increase in temperature results in the release of electrons from localized states in non-metallic interatomic bonds, the Hall coefficient should become more negative with increasing temperature. The free-electron value of the Hall coefficient increases slightly with temperature through the temperature-dependence of the atomic volume.

The temperature-dependence of R has been determined frequently in the solid state, but more rarely in the liquid. R exhibits slight temperature-dependence in the liquid state in zinc,[421] mercury,[422, 423] and apparently varies considerably in tellurium[424, 427] but not in InSb[425] or in CdSb, ZnSb, and Bi_2Te_3.[428] R nearly always changes on fusion, often by a very large amount (e.g. Ge, InSb[426]) indicating a significant change in electronic states. With Ge, Bi, Sb, InSb, this presumably occurs as the result of the freeing of electrons by destruction of *sp*-hybrid homopolar bonds. Enderby and Walsh[428] have investigated molten CdSb, ZnSb, and Bi_2Te_3, finding temperature-independent Hall coefficients more negative than the free-electron values and typically metallic resistivities. It would be interesting to have similar results for the typically non-metallic liquids such as the sulphides and selenides of thallium.

Hall effect and thermoelectric-power measurements on Hg–In alloys indicate considerable departures from apparent free-electron behaviour,[429, 430] which is surprising in view of the apparent free-electron behaviour of the components. Similar conclusions are reached from optical measurements[431] (see below). This system contains two compounds which melt congruently at a very low temperature; measurements were made at room temperature and above, so that little unlike-atom association in the liquid seems probable. The results can probably be explained in terms of the anomalous electronic behaviour of mercury. Lower-temperature measurements may provide more information.

Bückel[432] has reported that very thin films of gallium and bismuth with a highly disordered structure also have approximately free-electron Hall coefficients; heating, which produces a change of structure to that of the normal solid, also produces a marked change in R to values normal for the crystalline solid. It seems that free-electron behaviour is a characteristic of a random assembly of like atoms, and may not be sensitive to a small degree, at least, of short-range order and non-free-electron bonding.

6.2.6. *Optical Properties*

The information in Table XLI is taken mainly from the work of Hodgson and of Schulz.[431] The only other work known to the writer is some incomplete work on Hg–Tl alloys.[433, 434] The results are expressed as $N_{\text{obs}}/N_{\text{val}}$, (which should equal unity for free-electron behaviour, with N_{obs} calculated from equations (6.9) and (6.10)), and as $\sigma_{\text{opt}}/\sigma_{\text{elec}}$, with σ_{opt} calculated using $\tau = m\sigma_{\text{obs}}/\overline{N}e^2$, from equation (6.10), and σ_{elec} from Table XXXII. Generally, behaviour is not far removed from that predicted by the Drude theory, although discrepancies in some cases are quite large, and agreement can therefore be achieved only by totally unrealistic assumptions about the number of valence electrons per atom. Thus, optical measurements generally agree with those of the Hall coefficient in suggesting free-electron behaviour for the 'simple' liquid metals. However, it is clear that, as expected, the solid metals investigated do not obey free-electron theory. It has been argued that compliance with the Drude theory is not a sensitive measure of free-electron behaviour, at least in the wavelength range commonly used for optical measurements.[438]* Schulz[431] has also investigated alloys in the Hg–In system, and finds that they do not obey the Drude theory, in agreement with the Hall coefficient measurements[429,430] referred to earlier. However this worker's results for mercury appear to be incorrect, and this creates some doubt about his other work.

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* See also Ref. 596, p. 166.

6.2.7. *Magnetic Susceptibility: Pure Metals*

This field has recently been extensively reviewed by Busch and Yuan,[435] and Table XLII consists mainly of information taken from this paper. Since χ_E is arrived at by the rather unjustifiable subtraction of χ_I;[436] and since both χ_L and χ_I may be in error, the tabulated value should not be considered as more than an estimate of the true electronic susceptibility. It is doubtful whether any useful purpose is served by a further comparison of χ_E with $\frac{2}{3}\chi_P$, the Pauli–Landau value of χ_E for free electrons.[435] Certainly to express $(\chi_L - \chi_S)$ as a percentage of χ_E must be meaningless.

The values obtained from χ_E are always positive, but may differ appreciably from $\frac{2}{3}\chi_P$. The information available thus provides no clue to the state of the electrons in liquid metals. Certainly no support is provided for the possibly free state of the electron suggested by thermoelectric power and Hall coefficient measurements.

More positive evidence may be obtained from Knight shift measurements, which are expressed in terms of equation (6.18). If, as would appear to be the case for a number of metals from Hall coefficient and thermoelectric power measurements, there is a considerable change in electronic states on fusion (as indeed there must be if a free-electron model is to be acceptable for liquid metals), there should be an appreciable change in the Knight shift on fusion. That there is *not*, is clearly shown in Table XLIII.[327] Some small change in K on fusion may be accounted for by volume changes[437] but this amounts to $< 1\%$, Clearly, no significant change in band structure is indicated by these figures; Knight *et al.*[327] argue that this may be because the band structure is determined by short- rather than long-range order, and is therefore (Section 2) not far different from that of solids, a view that is supported to some extent by the theoretical work of Edwards (above). However, K_L values are known for only a few metals, and a wide investigation is required before any conclusion can be reached, at least from this work.

6.2.8. *The Free-Electron Model for Liquid Metals*

There has recently been considerable interest and speculation as to the degree to which the conduction electrons in liquid metals may be considered to be free. Some discussion of the use of this concept as a basis for theoretical calculations has been given above. It is appropriate at this stage to summarize the evidence for and against.

Measurements of the Hall coefficient and optical reflectivity apparently provide evidence that the electrons are free, or at least approximately obey the Drude theory, even in those liquid metals (Bi, Sb, Ga, Ge, &c.) for which diffraction studies have suggested a proportion of non-metallic, and therefore non-free-electron, bonding (Section 2). For most metals there are, however, small deviations from true free-electron behaviour; at present it is not possible to decide whether these arise from errors in measurements, errors in the atomic volumes used to calculate free-electron values, insensitivity of the theory, or true departures from free-electron behaviour. Other evidence must therefore be sought. The limited number of Knight shift measurements available indicate, indirectly, non-free-electron behaviour by showing no change in shift, and hence in electronic states, on fusion. Measurements of magnetic susceptibility are unable, for various reasons, to provide support either way, but, in common with electrical resistivities and the Hall effect, show a substantial change on fusion, always towards a free-electron value. This suggests qualitatively, and in disagreement with the Knight shift data, that there is a considerable change in the density of states on fusion, although not necessarily to a free-electron situation. A number of other measurements are reported, mainly for gallium, which add useful evidence. Faber[439] has observed nuclear quadrupole interactions in gallium during nuclear magnetic resonance measurements and interprets this, in agreement with diffraction studies, as an indication of an anomalous structure, and therefore non-freedom of electrons, in this liquid. Positron annihilation measurements are reported for gallium[440, 441] and for sodium, indium, and tin.[441] Calculated electron mean free paths, *l*, for sodium, indium, and perhaps tin, agree approximately with the free-electron values calculated from conductivity measurements:[283]

$$l = \frac{mV_F\sigma}{\bar{\mathrm{N}}e^2} \text{ where } V_F \text{ is the Fermi velocity} \quad . \quad (6.27)$$

For gallium there is a considerable discrepancy, and it is concluded that this metal does not exhibit free-electron behaviour. No change in electron-spin resonance upon melting is reported for lithium, but this metal approaches free-electron behaviour in the solid state, and only a small change of states would be expected on fusion.[442] Apparent non-free-electron behaviour in liquid aluminium is indicated by Catterall's measurements of soft X-ray spectra[48] (and by its behaviour in some of its alloys, Section 3), although Watabe and Tanaka[314] have argued that this result is not incompatible with a *nearly*-free-electron model for liquid aluminium. The possible indication of non-free-electron bonding from diffraction data on metals in higher groups and lower periods of the Periodic Table has already been referred to.

Most of the experimental evidence, and the success of nearly-free-electron theories, suggest that a free-electron model is correct for the liquid alkali metals—this is to be expected, for the solids exhibit near-free-electron behaviour.[45] For other metals the evidence is less conclusive. It seems probable that more precise measurements of electronic properties will indicate that the free-electron model is by no means adequate for metals in Groups higher than IA in the Periodic Table, and that it becomes less adequate as the group number increases and the period number decreases. It is probable that the apparent agreement with the elementary free-electron theory is misleading for these elements; it has already been shown to be so in the case of optical measurements.[438] Small deviations from free-electron behaviour may, in any case, not be detectable by measurements of the precision possible at present.

There is too little evidence to allow of any conclusion regarding the state of the electrons in liquid alloys. Hg–In alloys may be unique in not obeying the Drude theory; certainly much other evidence suggests that mercury-based alloys are not typically metallic. Much more experimental effort is necessary in this direction. Again, care must be taken to ensure that the measurements made really *are* a sensitive measure of free-electron behaviour; the fact that a number of liquid intermetallic compounds approximately obey free-electron rules may not be very significant. More direct measurements would be of even greater value for alloys—especially those which diffraction studies have suggested may, like the non-free-electron pure liquid metals, be structurally anomalous.

6.2.9. *Magnetic Susceptibility: Alloys*

The results of investigations on alloy systems are summarized in Table XLIV. In no cases are any variations in susceptibility observed to correspond with solid-state eutectics or solid-solubility limits. The anomalous change in χ_L in the Fe–Co system has been attributed[443–445] to a change from the 'close-packed' structure of cobalt to the 'more open' iron structure; no such anomaly is observed in the Co–Ni system where the structures of the components are closely similar. χ_L for iron shows an abnormal temperature-dependence in the liquid state for ~ 200 degC above the melting point,[443–445] which has been interpreted[444] as a gradual change in the structure of the liquid, possibly to one more close-packed. Similar conclusions may be reached from viscosity measurements[446] but this interpretation seems unreasonable at such high temperatures. Systems containing intermetallic compounds almost universally exhibit a minimum in χ_L at the compound composition, which may result from the localization of electrons involved in the formation of hybrid orbital bonds, and their resulting non-contribution to the electronic susceptibility χ_E. However, χ_E is very small in all but the alkali metals, which suggests that the main effect may occur through the ionic susceptibility. There is at present no way of resolving this problem. The system is always divided into two halves by the susceptibility isotherm, which usually shows smooth composition-dependence for the two pseudo-binaries.

The liquid-state behaviour of the ε-brass structures (Cu–Sn, Cu–Zn systems) has already been interpreted (p. 476) in terms of a proportion of non-metallic, non-free-electron bonding in both solid and liquid states. In both cases, the susceptibility of the solid reaches a minimum at the same composition.

Bates has reported susceptibility measurements on a wide range of amalgams[447, 448] (some of his data are apparently invalidated by the non-homogeneous state of the amalgam) and concludes that the solutes form cations (+ve charge) in mercury. This, and the increase in the conductivity of mercury when alloyed with at least the higher-valent metals, suggests that mercury is incompletely ionized, i.e. behaves with an effective valence of < 2 (possibly < 1) in qualitative agreement with the theory (p. 460). The possible partially ionic nature of amalgam has also been discussed by Wagner[449] and is supported by surface tension (p. 494),[450] and electrotransport measurements (see below), which show that the solute usually moves toward the cathode. Friedman and Schug,[451] as a result of thermodynamic equilibrium measurements in dilute alkali-metal amalgams, suggest ionic-type clustering of small negatively charged mercury ions around the large positively charged alkali-metal ions. Clearly the liquids are not completely ionic, since the resistivities have metallic values, but some maldistribution of charge seems to exist. In this respect the amalgams may be unique and care must be taken when considering them in comparison with 'metallic' solutions.

Finally, Knight shift measurements have been made on several liquid *alloys*.[452, 453] The results have been discussed by Oriani,[454] but do not appear to lend themselves to easy interpretation.

6.2.10. *Electrotransport*

The results for liquid alloys have been adequately summarized elsewhere,[332] and are only briefly repeated here. Quantitatively, much of the earlier work is in some doubt, but in most cases the direction of migration of the solute is probably reported correctly. The information is summarized in Table XLV.

Transport in amalgams has been investigated by several workers.[329, 343] Angus and Hücke[455] also investigated the temperature-dependence of electrotransport in dilute Hg–Na liquids. They find a reversal of migration direction at $\sim 0{\cdot}5$ at.-% sodium at low temperatures which no longer occurs at the higher temperatures and which is interpreted in terms of associations in the melt that disperse at higher temperatures. The resistivity isotherm of these alloys has a maximum at about this composition at room temperature,[456] suggesting association of unlike atoms in the melt. The reversal of migration may result from a decrease in the drag component (p. 466) as the size of the 'clusters' is reduced. Disagreement between authors may in some cases be due to a reversal of migration with composition. The direction and rate of solute migration is little affected by the group of the solvent, but is consistently affected by its Period Number,[457, 458] indicating that, as might be expected, electrotransport is sensitive to the type of interatomic bond in the liquid. There has been no systematic investigation of the composition-dependence of electrotransport in any type of system.

Studies of dilute solutions of various metals in sodium and potassium[459] have shown that a eutectic alloy may be separated into its components by electrotransport; if the temperature is close to the liquidus, the first concentration changes will initiate solidification at the electrodes. The two solidifying fronts will then grow towards one another. Thus, in addition to its fundamental significance, electrotransport may be of help in controlling the growth of crystals from alloy or 'doped' melts, in single-crystal work and in regulating the movement of the molten zone along a solid bar in zone refining. In both cases a current passed between solid and liquid can control the concentration of impurities, provided that these are transported.[354, 460] This aspect of the work is under investigation in several laboratories, including that at Birmingham University.[461, 462]

7. SURFACE PROPERTIES

7.1. PRINCIPLES

The very many theoretical attempts to account for the surface energies of metals and alloys, both in terms of the fundamental properties of the atom,[465–479] and in terms of bulk thermodynamic properties,[480, 481, 483] have been reviewed in some detail by Semenchenko,[450, 473] and will not be discussed in detail here. None have been conspicuously successful.

The Gibbs Absorption Isotherm[482]

$$\Gamma_i = -\frac{1}{RT}\left(\frac{d\gamma}{d\log a_i}\right)_T = -\frac{1}{RT}\cdot a_i\cdot\frac{d\gamma}{da_i} \quad . \quad (7.1)$$

where Γ_i is the surface excess of component i—i.e. the difference between the actual amount of i present in a given volume, including the interface, and that which would be present if the whole system were homogeneous —and γ is the surface energy. Thus, if $d\gamma/d \log a_i$ is positive, Γ_i is negative, and vice versa, i.e. a substance which lowers γ is present in excess at the interface, and is said to be 'surface-active'. For dilute solutions, approximately,

$$\Gamma_i = -\frac{1}{RT} C_i \frac{d\gamma}{dc_i}, \quad . \quad . \quad . \quad . \quad . \quad (7.2)$$

where c_i = concentration of component i. Neither equation (7.1) nor (7.2) predicts the effect of the bulk thermodynamic properties upon the surface excess.

Temperature-Dependence

Eötvös[484] suggested empirically that for pure liquids

$$\gamma V^{2/3} = K_E(T_C - T) \quad . \quad . \quad . \quad (7.3)$$

where V = atomic volume

T = temperature

T_C = constant

K_E = Eötvös constant, and is equal to 2·12 for an unassociated liquid, becoming less on association. For metals, $K_E = 0{\cdot}6 - 0{\cdot}8$.

Various modifications of this have been proposed, of which the most useful is that of Katayama:[485]

$$\gamma \left(\frac{M}{d_L - d_V} \right)^{2/3} = K_E(T_C - T) \quad . \quad . \quad . \quad (7.4)$$

where d_L, d_V are the densities of liquid and vapour, respectively, T_C is the critical temperature,[486] and M the molecular weight of the liquid. All the alternatives to equation (7.3) indicate that the surface tension should be a linear function of temperature.[450, 472, 473] This is true for most pure metals over a limited temperature range. In common with the Arrhenius equations for viscous flow and diffusion, equation (7.3) has no fundamental significance.

Semenchenko[450, 487] has suggested that the effect of a solute upon the surface tension of a solvent is determined by the difference in the 'generalized moments' of the solvent and solute:

$$m = \frac{Ze}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.5)$$

where $e = 4{\cdot}80 \times 10^{-10}$ e.s.u.

Z = ion valence.

r = ion radius.

Equation (7.5) appears to hold quite well for amalgams, and for ionic melts (further indirect evidence of the apparently ionic nature of amalgams), but not so well for other solvents. The solubility of a given solute in various solvents is also a function of the difference in generalized moments.[488] There is still no adequate theoretical explanation of this quantity.

Connection with Bulk Properties of Solutions

Butler[489] makes the questionable assumption that the surface may be considered as only the first layer of molecules, and derives:

$$\gamma_m = \gamma_i + \frac{RT}{A_i} \ln \frac{a_i'}{a_i} = \gamma_j + \frac{RT}{A_j} \ln \frac{a_j'}{a_j} \quad . \quad . \quad (7.6)$$

where γ_m is the surface tension of the mixture; the prime quantities refer to the monomolecular surface layer, and A_i, A_j are the molar surface areas of components i, j.* For the ideal solutions in both surface and bulk, $a_i' \rightarrow x_i'$ and $a_i \rightarrow x_i$.

Modifications of equation (7.6) have been suggested, using a quasi-lattice model,[490, 491] for regular solutions for which $A_i = A_j$. Hoar and Melford[492] have removed the restriction to equal area fractions of the components, and find that, where the $\bar{A}_{i,j}$ are the partial molar surface areas of the components, the surface tension of the mixture may be given by:

$$\begin{aligned} \gamma_m &= \frac{A_i}{\bar{A}_i}\gamma_i + \frac{RT}{\bar{A}_i} \ln \frac{a_i'}{a_i} \\ &= \frac{A_j}{\bar{A}_j}\gamma_j + \frac{RT}{\bar{A}_j} \ln \frac{a_j'}{a_j} \end{aligned} \quad . \quad . \quad . \quad . \quad (7.7)$$

where $x_i'\bar{A}_i + x_j'\bar{A}_j = A_m$ and $\bar{A}_{i,j}$, $A_{i,j}$ are not necessarily equal. For regular solutions, equations (7.7) reduce approximately to those of Guggenheim. The authors compare surface energies calculated from known thermodynamic properties with experimental curves for liquid Pb–Sn and Pb–In alloys, and find excellent agreement. Taylor[493] achieved quite reasonable agreement for such simple systems by using less refined theories, but obtained much less satisfactory agreement for systems containing compounds. A more rigorous test of Hoar and Melford's approach should involve similar comparisons. Taylor has suggested that an assumption that the surface layer is *more* ideal than the bulk can account for some of the discrepancies between measured and calculated values, but this is effective only in a limited number of

* i.e. the area occupied by 1 mole spread out as a layer one molecule thick.

cases, usually those tending toward immiscibility. None of the theories so far available allows an easy understanding of the relationship between bulk and surface properties, since the unknown thermodynamic parameters of the surface are involved, and it is not yet possible to predict satisfactorily whether positive or negative deviations from additivity will be observed in a given system. It is probable that some progress will eventually be made using statistical–mechanical treatments,[14,18,102] at least for simple liquids.

7.2. Results

Experimental techniques have been reviewed by a number of authors.[450,533,534,594]

7.2.1. *Pure Metals*

Data available for the pure liquid metals will be found in Table XLVI, together with, in parentheses, values estimated by the methods outlined below. It will be noted that very high values are observed for the transition metals, and very low ones for the alkali and alkaline-earth metals. Surface energy is, in fact, a periodic function of atomic number (predictably, since it is a function of surface bond strength) and thus correlates well with a number of similarly dependent quantities—the atomic volume, heat of sublimation, &c.[497,498] Using these correlations, it is possible to predict with reasonable accuracy (perhaps ± 10%) values of the surface energies of those metals for which determinations have not been made. These are included in Table XLVI. Some of the individual values quoted may be subject to considerable error, since surface energies are extremely sensitive to the slightest degree of contamination.

The surface tensions of liquid metals are very much higher than those of non-metallic non-electrolytes or of molten salts. A number of theories have attempted to account for this in terms of the theory of metals[494–496] with little apparent success. Some of this lack of success may result from the very scanty and contradictory nature of the evidence available. The main contribution of this work lies in its emphasis on the importance of the 'atomic surface tension' of liquids—the product of the surface tension, and the area occupied by a gram-atom or gram-molecule spread out as a monatomic layer. On this basis, the atomic surface energy of metals is more nearly equal to that of dielectric liquids. However, some of the discrepancies in this work undoubtedly arise from the assumptions[494] that interaction energies, and therefore distances between atoms in the surface, are the same as those in the bulk liquid.[495] It is because they are not, that it is unlikely that much can be deduced about the bulk properties of the liquid from the measurement of surface energies.

The exact nature of the temperature-dependence of the surface tension of liquid metals requires more investigation; $d\gamma/dT$ is negative for most metals. In many cases (e.g. mercury, bismuth), there is clearly not a linear dependence upon temperature.

7.2.2. *Alloys*

Here the information is even less reliable, and is contradictory. Experimental effort has been concentrated on amalgams, and to a lesser extent on the low-melting-point alloys of tin, lead, bismuth, and similar metals, with a few unreliable measurements on transition metals and their alloys. In all cases, either through difficulty of interpretation, or inadequate information, no conclusion regarding the structure of the bulk liquid may be reached from the results. The data are often interpreted in terms of an empirical theory, developed for the occasion and seldom applicable to more than a very limited number of alloys.

Dilute Solutions

Very many investigations have been carried out on amalgams, almost all at very low concentrations, by Semenchenko[450, 499] and others, who find that the degree of surface activity of each solute is dependent upon the difference between its 'generalized moment' (equation 7.5) and that of mercury; the less positive, or the more negative the value of $(m_{Hg} - m_M)$, the less surface active is the solute. The surface-active solutes (especially the alkali metals) produce a very sharp initial fall in γ_{Hg}, followed by a much smaller composition-dependence, thus suggesting surface saturation by the solute.

The surface tensions of mercury and of other liquid metals, and the effect upon them of small concentrations of contaminant, have recently become of some technical importance with the increasing use of these liquids in heat-exchange and boiler circuits. To obtain good liquid/solid heat transfer, efficient wetting is necessary, and some knowledge of suitable alloying elements for use in achieving this may be obtained from fundamental studies. The known data for mercury are summarized in Table XLVII. Dilute solutions in tin and bismuth obey only very approximately the 'law of generalized moments' proposed by Semenchenko,[450] and it seems that the applicability of this is limited to amalgams. Since the law also applies to ionic melts,[500] this may prove to be indirect support for the proposed ionicity of amalgams (pp. 460 and 489).

The Sn–Te alloys are of particular interest in fairly extensive Russian work on dilute tin- and bismuth-based alloys.[501, 502] These have initially positive temperature coefficients of surface tension, becoming negative (as in cadmium, bismuth, mercury, and perhaps copper) at higher temperatures. As in the pure metals, this phenomenon, which may be due to contamination of the materials used, remains unexplained. Dilute solutions in iron have also been investigated.[503–506]

The available data for the effects of various solutes in dilute solution are summarized qualitatively in Table XLVII. A more quantitative account is not justified by the accuracy of the data.

Concentrated Solutions

In addition to these dilute solutions, a number of complete binary systems have been investigated.[450, 492, 493] Because, as has been shown earlier, the bulk thermodynamic properties are affected by the type of interaction existing between unlike atoms, and hence the type of solid-state system observed, some effect may be expected, through equations (7.7) for example, upon the surface properties. At present, too few reliable data have been presented to allow any clear conclusions to be reached. Both solid-solution and eutectic systems appear to give smooth composition-dependence of surface tension, often linear within the limits of accuracy of the data, or showing slight negative deviations from additivity. The sources of available data are listed without comment in Table XLVIII according to the type of solid-state system involved. It is probable that only the work of Hoar and Melford is quantitatively reliable.[492] In most cases, too few compositions have been investigated to establish the composition-dependence with any confidence.

Klyachko and Kunin[509] report a minimum at the eutectic composition in the surface-tension isotherms for Pb–Sn,[510] Bi–Pb, and Bi–Sn alloys at temperatures very close to the liquidus; this minimum is not observed at higher (e.g. liquidus + 20–40 degC) temperatures. The effect is small, but significant, and results in a positive $d\gamma/dT$ over a short temperature interval above the eutectic. It has not been confirmed for Bi–Sn alloys by more recent, but inadequately detailed, work in the same temperature range,[516] or for any other eutectic system.[512–514] However, Toye[515] finds a eutectic minimum in the work function of Cu–Sn alloys which is of interest in view of the suggestion by Zadumkin and others[478, 517] that the free electrons at the surface of a metal make a large contribution to metallic surface tensions, and the observation that the resistivity isotherm, also a function of the freedom of electrons, may reach a minimum at the eutectic (Section 6).

Systems containing intermetallic compounds apparently give even stronger negative deviations from additivity, but without more information this cannot be predicted from equations (7.6). The point of maximum deviation from additivity may occur at about the compound composition, but the evidence for this comes from one possibly unreliable* source for the Al–Mg and Mg–Zn systems.[513] This is not confirmed as a general phenomenon.[507–509, 522] Eremenko *et al.*[518–520] report a maximum on a generally negative deviating isotherm for the Ni–Al and Ni–Be systems at about the compound composition. There is an extensive literature on the specific problem of the ability of liquid metals to wet various refractory materials.[521–527] This is usually connected with compatibility or contaminant problems, or with phase relationships. Systems investigated include alkali metal/oxide,[521, 522] transition metal/oxide,[523, 526] transition metal/carbide,[524] and lead/uranium dioxide;[525] some of the practical problems have been reviewed by Taylor.[527]†

Finally, Spinedi[528–532] has studied the oxidation of *liquid* alloys. Some of the (unconfirmed) results indicate a relatively low rate of oxidation at, or near, the eutectic composition, but the usefulness of the work is limited by the inadequate ranges of composition and temperature investigated.

It is evident that it is not yet possible to draw any conclusions about the structure of liquid metals or alloys from surface tension measurements. To allow this, measurements of considerably greater accuracy are required, together with a better fundamental understanding of the exact origin of the surface energy of metals.

8. MELTING, SOLIDIFICATION, AND SUPERCOOLING

8.1. Introduction

In this section, the changes in physical properties that occur during melting or solidification are briefly reviewed, together with the properties of supercooled liquids, and reports of changes in physical properties that 'foreshadow' melting or solidification. No attempt is made to discuss the mechanics of solidification, already reviewed by Winegard.[535]

8.2. Melting Models

Models of melting usually start from the Boltzmann expression for the entropy of fusion:

$$S = R \ln \frac{W_L}{W_S} \qquad \ldots \ldots \qquad (8.1)$$

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* The very few results reported are widely scattered.

† See also Ref. 596, pp. 243, 281 and 285.

where W_L and W_S represent the different degrees of order in liquid and solid, respectively. Some models have suggested that there is not a discontinuous change in entropy on fusion, but these are not supported by the observation of a positive entropy of fusion for every known case. There is evidence, however, that fusion may not be completed at a unique temperature in some materials (see below). Equation (8.1) accounts only for the change in configurational entropy on fusion; in general, there is also a vibrational contribution to the entropy of fusion of simple solids and, for more complex structures, a rotational contribution. The vibration spectrum of metals changes only to a small extent on fusion (Section 3) and its contribution to the entropy of fusion may probably be ignored. Only complex structures, such as those of tellurium or selenium, which persist in the liquid state are likely to contain a rotational contribution in the entropy of fusion. Most thermodynamic models of fusion take account only of the configurational entropy term.

Theories of fusion have been reviewed in detail by Temperley.[74] His classification is used in the brief account that follows. As Temperley points out, the ideal theory of fusion should not make any *a priori* assumptions about the mechanism by which fusion takes place, but should show only that such a process arises as a natural consequence of the mathematics of a more general theory which should also be capable of predicting the thermodynamic and physical properties of the solid and liquid and, of course, the related phenomenon of liquid/gas equilibrium. So far, there is no successful theory that does this, although such a result is, in principle, obtainable from the distribution-function theories of Born and Green[12(a)] and Kirkwood *et al.*[12(b), 536–538] Other theories describe only the liquid–solid transition; sometimes in terms of the instability of the solid at the melting point, sometimes in terms of similar or different models for the two phases in equilibrium at the melting temperature.

Models Considering Only the Instability of the Solid

The original Lindemann theory,[539] which postulated that fusion took place when the amplitude of atomic vibration exceeded a critical fraction of the interatomic spacing, has formed the basis of several more recent attempts to predict melting temperatures from 'first principles'. The Lindemann theory does not prove that melting occurs; it makes the prior assumption that it does so. Attempts have been made on the basis of similar models to show that fusion is a result of a crystal instability which arises naturally from the model.[89, 540, 541] Other similar approaches have used the Grüneisen[542] equation connecting the lattice potential energy with the distances between the atoms, and have attempted to show that this also predicts lattice instability when the vibration amplitude exceeds a critical value.[543-545] These theories all have the common fault that they predict an *absolute* instability for the solid and not an instability relative to a specified liquid phase. As a result, the quantitative results have been poor.

One Model Describing Solid and Liquid

The now-classic theory of Lennard-Jones and Devonshire[547] falls within this category, and was the first of its kind, although an earlier theory of Braunbek had used a highly artificial model of the liquid.[546] The Lennard-Jones theory, which is based on the Bragg–Williams[107, 548] order–disorder theory, predicts that melting will take place when the concentration of vacancies and interstitials reaches a critical level; a concentration of $\sim 50\%$ of atoms away from their lattice sites is required for melting. This figure is much greater than that normally predicted by 'hole' theories of liquids, and is certainly very much greater than the vacancy concentrations that have been determined for solid metals at temperatures just below the melting point.[287, 549] The theory takes no account of the progressive change in vibrational modes which must take place just before and during fusion. Agreement of predicted melting points with experiment is only fair.

Different Models for Solid and Liquid

This approach is further removed from the 'ideal' theory than is the Lennard-Jones and Devonshire approach, but has had some success. Fowler and Guggenheim[548] have used two similar models for liquid and solid—an harmonic oscillator model for the liquid and the Einstein single-frequency model for the solid. Agreement with experiment is satisfactory. The cybotactic model of liquids of Stewart and Benz,[72] referred to earlier, may also be used in a melting model.[73]

8.3. PRE- AND POST-MELTING AND PRE-FREEZING EFFECTS

Most melting theories suggest that superheating of the solid state and supercooling of the liquid should be possible, whereas in practice supercooling only is found. The problem has been discussed in terms of the theory by a number of writers;[74, 87] it is probable that superheating of solids will not be observed, even if it is thermodynamically possible, because the relatively disordered regions in solids caused by dislocations and other defects act as nuclei for the liquid state (dislocation models of melting have been proposed[555, 556]). Supercooled liquids, of course, occur much more frequently, the commonest examples being the glasses; supercooling results from the very sluggish crystallization processes in these liquids, which universally have highly complex three-dimensional liquid structures. As soon as this structure is destroyed, for example, by the introduction of alkali-metal oxides, supercooling to the glassy state is no longer possible.

The supercooling of normal liquids cannot be explained on this basis. Borelius[550–552] concludes that fusion is only part of a process which begins below and ends above the melting point. The theory predicts both supercooling of the liquid and superheating of the solid to about the same extent (most theories predict rather less superheating); the available data on supercooling[553] agree quantitatively with the theory. The lack of observed superheating may again be explained in terms of the greater possibility of the existence of liquid nuclei in the solid than of solid nuclei in the liquid. The main interest in the Borelius theory lies in its prediction of the pre- and post-melting and solidification phenomena that have been reported in a number of materials. Unfortunately, similar phenomena are easily produced by impurities, particularly those which form a low-melting-point second phase at very low concentrations, or by less than meticulous experimental technique, so that in many cases there is considerable doubt about the validity of the reported phenomena. The data for metals are probably less reliable than the considerably greater bulk of information on the melting of organic and inorganic compounds, which are more easily purified,[220, 566] but the conclusions reached from a study of these relatively complex materials may not apply to the simpler metallic structures.

The premelting predicted by Borelius is reliably reported in a number of organic materials and some thiocyanates, where a premelting disruption of the structure takes place.[554] In metals the increase in vacancy concentration below the melting point in the alkali metals has been referred to. Carpenter[557, 558] reports anomalous behaviour in the specific heats of Li, K, and Na over a range 50–100 degC below the melting point, probably due to the formation of vacancies. Similar singularities are reported in a variety of physical properties of Bi, Zn, Cd;[559] Sn, Cd;[560] Mg;[560, 561] In and Ga;[562] and Al, Au, and Ag.[563] Undoubtedly, some of these are due to local melting induced by impurities[567]—nucleation of the liquid presents no problem, since its formation provides an increase in entropy—which tend to congregate at already partly disordered lattice sites (dislocations and stacking faults, for example). In other cases, particularly in the alkali metals, which have a very 'open' structure, there may be an abnormal increase in the vacancy concentration just before melting which could account for most of the effects observed. Similar phenomena may be observed in ionic-type intermetallic compounds.[579, 580] In many cases, careful work has disproved previously reported anomalies. In tin, for example, Boyle *et al.*[564]

claimed that an enhanced rate of self-diffusion produced the anomalous Mossbauer effect observed by them at near-melting temperatures; the tin used contained no less than 2% of impurities, and more recent work on pure materials has shown that their effect was spurious.[565] Great care to ensure high purity is essential in such work. It seems probable that many of the anomalies reported above will in due course also prove to be scientific red herrings. In organic materials of complex structure, however, premelting effects may result from disorientation of molecular axes.[220, 566]

The Borelius model also predicts that the melting process may continue beyond the melting point and thus affect the structure and properties of the liquid, a phenomenon which is of more interest than premelting in the context of this review. Once again, the purity of the material investigated is of paramount importance. Reference has already been made to anomalous physical properties[221, 390–395, 572–574] reported at temperatures just above the melting point in a number of metals and alloys, some of which have almost certainly been due to suspended solid or (in intermetallic compounds) non-stoichiometry. Recently, post-melting phenomena extending over a very small temperature range above the melting point have been reported by Predel for Al, Bi, Cd, Ge, In, Pb, Sb, Sn, and Tl.[583] Effects of impurities were specifically sought and eliminated; the effects observed were greatest in bismuth and antimony—which structurally are relatively complex, and change their structure extensively on fusion ($\varrho_L/\varrho_S < 1$, V^F −ve) and least in cadmium and indium which have a simple structure and are "more metallic" in their behaviour. The anomalies may result from a post-melting structural rearrangement over a very small temperature range. Similar phenomena observed in liquid Hg–Zn alloys at temperatures just above the liquidus have been interpreted in the same way.[584] In some structures of great complexity the structure *may* break down progressively with temperature to give a non-Arrhenius temperature-dependence of the viscosity during heating. In such cases is seems possible that on cooling the structure may not re-form until the melting point is reached, because of the small energy difference between the structural and non-structural liquid; this may account for the 'hysteresis' effects reported for a number of intermetallic compounds (e.g. Ga_2Te_3), but the work needs confirmation. A number of organic and inorganic solids such as o-terphenyl seem to melt in the same way to produce, for various reasons, a clustered liquid,[568, 569] although in these materials no hysteresis of the physical properties is reported. The clustering in such cases is due to the enmeshing of molecules and can be detected by viscosity measurements,[220, 566, 568] which are sensitive to the presence of molecular associations. Similar phenomena may occur in ionic melts with complex anions—nitrates or silicates, for example. It does not follow that this is correctly described as a foreshadowing of freezing, since the cluster structure need not occur in the solid state. This situation, which has been referred to previously, may arise in the Au–Sn system, and in some binary molten salt mixtures such as KBr–TlBr.[570] Ubbelohde[566] has described such melts as 'anticrystalline', as opposed to the 'quasicrystalline', more random melt. It appears that similar phenomena may occur in the Cd–Sb system, which merits more careful examination.[571]

The anomalous structures reported for some pure liquid metals from diffraction studies (Section 2) may also, perhaps, be classified as 'anticrystalline', since, because supercooling is still possible, the structure of these liquids is clearly not capable of nucleating the solid and therefore must be structurally quite different from it. This 'anticrystallinity' is probably most extensive in liquid selenium, tellurium, and sulphur,[358–360, 364, 575–577] which are structurally similar to the polymer liquidus.

To summarize, it appears that in some materials the process of melting may begin as structural disordering below the melting point, and continue as a thermally induced modification of the liquid structure above the melting point. It seems that the phenomena reported as occurring below the melting point in solids with a simple structure are probably non-existent in high-purity materials. There may be exceptions for some of the 'open-structured' pure metals and intermetallic compounds, and these effects are certainly observed in some structurally complex inorganic salts. Post-melting or pre-freezing phenomena are more common, although here too, some results are due to the impurity content of the melt. For certain complex intermetallic compounds, the structure may not be dispersed until temperatures well above the melting point are achieved. Associations, perhaps in the form of discrete clusters, are observed in some metallic and non-metallic liquids at temperatures above the melting point, and result in anomalous physical properties, but this phenomenon is not correctly described as a 'foreshadowing' of solidification.

In some metallic liquids (e.g. Bi–Sb,[373] Cu–Sn, Mg–Pb,[370] Cd–Sb,[571] Hg–Tl[69]) the temperature derivative of the resistivity (and possibly other properties) shows a discontinuity at temperatures well above the melting point, perhaps as the result of a discontinuous breakdown of the liquid structure. Similar results may be observed in complex ionic and non-metallic liquids, apparently for the same reason.[220]

Kubaschewski[269] has classified the metallic elements, according to the value of S^F/V^F at the melting point, into true metals (Li, K, Na, Cu, Ag, Au, Mg, Ca, Al, Co, Ni, Ti), meta-metals (Zn, Cd, Hg, In, Pb), and semi-metals (Si, Ge, Sn, Sb, Bi, Te, Se, Ga). Klemm[578] suggested a similar classification based on the chemical properties of the solids. The semi-metals often show a negative volume change on fusion, and an abnormally high entropy of fusion, and are those which contain a high proportion of non-metallic, probably homopolar, bonding, at least in the solid state (in tin, only at lower temperatures, in grey tin). Once again, it is significant that these metals have been reported from diffraction studies to have an anomalous structure (Section 2). A similar classification (Table XXX) may be made on the basis of the ratios of the expansivities of solid and liquid (α_S is low in the semi-metals because of the strong homopolar bonds which are destroyed on fusion). α_S/α_L lies between 0·75 and 1·05 for the 'true metals', but is only 0·3–0·45 for the 'semi-metals'. In many of the non-metallic elements where bonding in solid and liquid is similar, α_S/α_L is again high. Similarly, (Section 6) ϱ_L/ϱ_S is < 1 for the semi-metals, and usually ~ 2 for the true metals, and this again may be explained by the partially homopolar bonding of the solid being destroyed, albeit incompletely, on fusion, thus providing more 'metallic' electrons for conduction.

Attempts have been made to extend Kubaschewski's classification to intermediate phases of the NaTl (B32) type, with little success.[579–580] These compounds show an anomalous expansion from ~ 100 degC below the melting point, interpreted as a partial conversion from homopolar to metallic bonding which is completed on fusion. Similar pre-fusion phenomena are reported in Mg_2Pb,[581] HgTe, and some other semi-conducting compounds[398] and, as in the pure elements, may be due to impurities or to a deviation from stoichiometry at high temperatures as a result of the volatilization of one component. Some attempt has been made in Section 6 to classify intermetallic compounds according to their electrical behaviour in the solid and liquid state.

The structures of all liquids are roughly similar, with a few exceptions, and may be described as moderately close-packed. Thus the structural change on fusion of some metals is greater than others, since solid-state structures differ widely. It follows that, at least in those cases where the solid and liquid structures are quite different, a transition region of finite thickness must exist between solid and liquid during fusion, in which solid-state structure rearranges to that of the liquid (and vice versa on solidification). Such a three-dimensional transition layer has been suggested on the basis of measurements of solid/liquid interfacial energies in copper and silver;[582(a) and (b)] this, however, cannot be considered conclusive. It is possible that the initial process of *fusion* is the breakdown of the solid structure into clusters having the solid-state structure. These clusters could then transform, perhaps through an intermediate random arrangement, to the structure characteristic of the liquid. Since this involves a reduction in configurational energy, and an increase in entropy, this process should be much easier than the reverse, viz. solidification. In addition, it is almost certain that growth from the liquid occurs laterally across the solid/liquid interface by the attachment of single atoms at 'active' sites, rather than by attachment of clusters of atoms already having the solid structure.[582(b), 585] Hence, on this model, melting and solidification are not structurally reversible, and this would partially explain the ease of supercooling compared with superheating. (This is additionally a problem of comparative ease of nucleation of the liquid structure, discussed above.)

Since diffusion is much easier in the liquid, fusion and solidification are essentially liquid-controlled operations, i.e. nearly all atomic movements take place on the liquid side of the solid/liquid interface; this is of some importance in alloy solidification, not considered here.[535]

8.4. SUPERCOOLING

The difficulty of producing nuclei of the right structure in a liquid leads to supercooling. The extent to which this is possible depends upon experimental conditions and upon the liquid concerned.[552, 553] We consider here only the properties of the supercooled liquids, and the way in which they differ from normal liquids.

This viscosity of supercooled liquids shows no change at the melting point. The activation energy for viscous flow, however, is slightly higher in some supercooled liquids.[574, 586–588] Since it is dependent upon the shear viscosity,[273] the ultrasonic attenuation (not the velocity) also changes slightly. The temperature coefficient of velocity is slightly increased.[589, 590] Liquid metals have not been adequately investigated, but appear to obey these general rules, although there is some disagreement over gallium.[212, 586] No discontinuity in electrical resistance or in its temperature coefficient is observed; this behaviour contrasts with that of molten salts, where there is some effect, possibly as a result of the formation of larger ion clusters upon supercooling.[591] Finally, in dielectric liquids with polar molecules (salol, menthol, diphenyl ether), the dielectric constant shows a discontinuity at the melting point, [586] again possibly arising from a molecular aggregation.

It seems unlikely that a change in the nature of the interatomic potential will result from supercooling, so the phenomena observed may be due to small structural changes, which may take the form of associations or clusters of molecules. These would, in addition, produce a small reduction in the entropy of the liquid; specific-heat measurements on supercooled liquid metals would be of interest in this context.[588] The resulting associations (which may already exist to a lesser extent in the normal liquid) clearly cannot have the solid-state structure, or they would act as nuclei for solidification.

9. GENERAL CONCLUSIONS

9.1. Introduction

This section attempts to:

(1) Summarize the conclusions that may be reached from the information now available on liquid metals and alloys.

(2) Suggest interpretations for some of the evidence, particularly that on eutectic systems.

(3) Indicate the value of the various experimental approaches that are possible, and hence

(4) Suggest fruitful lines of research for the future.

9.2. Pure Liquid Metals

Diffraction studies (Section 2) suggest that many liquid metals are structurally simple and similar to the liquid rare gases. Exceptions are the 'semi-metals' and 'meta-metals' (p. 501) which occur in the higher groups and lower periods of the Periodic Table; in these metals a degree of non-metallic bonding apparently exists in the liquid state and results in two distances of closest approach between atoms in the liquid. These distances often correspond closely with similar distances in the solid state. The anomalous nature of the bond in the 'semi-metals' is also shown by the negative volume change and the decrease in resistance on fusion, together with a low ratio of the thermal expansivities of solid and liquid, although these observations tell us nothing about the structure of the resulting liquid. No structural conclusions can be reached from the generally inaccurate data on atomic transport (Section 4) and surface energies (Section 5) of liquid metals, although there is no contradiction of the conclusions reached above.

The non-metallic contribution to the bonding must also result in partial localization of conduction electrons in bound states around the metal atoms. A number of properties supposedly sensitive to the state of the electrons in metals (e.g. Hall effect, optical reflectivity) indicate that the conduction electrons are nearly or completely free in the alkali metals, metals from B-Groups I–V of the Periodic Table, and even in those metals for which partially non-metallic bonding is indicated by other measurements (e.g. Ga, Ge, Sn, Bi, Sb). It now seems likely that these supposedly sensitive measurements are not in fact a very good measure of the true degree of freedom of electrons in liquid metals. It is very doubtful whether the electrons in any but the liquid alkali metals (which approximately obey a free-electron model in the solid state) may justifiably be considered to be free for theoretical or other purposes.

A more exact structural understanding of liquid metals must await detailed investigation, perhaps by a combination of direct diffraction techniques, but it seems possible that the homopolar bonded structure may exist as small clusters or 'islands' of a structure, probably different from that of the solid, in dynamic equilibrium with a more randomly structured 'metallic' matrix. These clusters will undoubtedly have a short lifetime, say 10^{-9}–10^{-10} sec, compared with the liquid relaxation time for diffusive motion of $\sim 10^{-12}$ sec, but each atom will spend a time in any one of these clusters that is long compared with the time spent in any other configuration. Supercooling of the liquid will still be possible because the proposed liquid structure is essentially 'anticrystalline' and the clusters will not be capable of nucleating the solid structure. The tendency to cluster is apparently a function of position in the Periodic Table and hence of the degree of non-metallic bonding in the liquid. It seems likely that a number of metals so far incompletely investigated will exhibit such behaviour—notably liquid silicon, which must, like germanium, contain a proportion of homopolar bonding, and perhaps liquid aluminium, zinc, indium, and thallium.

Very few properties of pure liquid metals can provide unambiguous structural information. The most promising area for future experimental work is undoubtedly that of direct X-ray or neutron diffraction but much more care than usual is needed in the determination of radial distribution curves. These, of course, are fundamental to several current theoretical approaches to the electronic properties and the interatomic bond in liquid metals, which at present can make only limited quantitative progress because of the lack of accurate direct structural data. Measurements of viscosity, density, surface tension, and other 'non-electronic' parameters are not able to provide direct structural evidence, although in principle it is possible to determine interatomic bond strengths from the data through one of the radial-distribution-function theories of liquids. Thermodynamic and physical measurements on high-purity materials may provide information on pre- and post-melting phenomena; specific heat measurements on many liquid metals are required, particularly over wide temperature ranges, to investigate the apparent temperature-dependence of the vibrational spectrum in these materials, and its change on fusion. Direct electronic measurements, particularly of the Hall effect, thermoelectric power, and magnetic properties are greatly needed to establish precisely the degree to which a free-electron model may be applicable to liquid metals. There is considerable scope for work on the higher-melting-point metals, although here, of course, the experimental problems are considerable. It seems probable that much direct evidence could be obtained from some of the so far less common measurements—for example, of positron annihilation and hence electron mean free paths, or of soft X-ray spectra. Nuclear magnetic and electron spin resonance measurements also seem to be able to provide useful results. Clearly, a very large amount of experimental information is required before the structure of liquid metals can be resolved, and particularly before any theoretical treatment can be tested rigorously by comparison with experiment. Much greater precision of measurement is necessary; it is unfortunately true that an exact quantitative interpretation of much of the diffraction and electronic data, at least, places considerable weight upon the accuracy of the fine detail in the experimental results.

9.3. SOLID-SOLUTION SYSTEMS

The small positive or negative enthalpies of mixing, and the near-zero excess free energies and entropies of mixing in these systems, suggest almost-random mixing of the components and interatomic forces which are nearly equal. This is confirmed by the limited number of measurements of physical properties made on this group of systems; these properties almost always obey an 'ideal mixing' law (p. 446). Thus, the liquid-alloy structure is probably similar to that of the components, which are nearly always near neighbours in the Periodic Table (e.g. Bi–Sb, Cd–Mg, Cu–Ni) and are therefore structurally similar. Systems of this type are apparently not formed by elements which form structurally different liquids. However, the factor that prevents the formation of a solid-solution system may not be solely structural; structurally similar elements may fail to form a solid-solution system because of differences in size (see below) or electronegativity.

The liquid alloys in these systems may therefore behave in a similar manner to the pure components; if the latter exhibit an anomalous structure (e.g. Bi–Sb), so will the alloys, while the extent of the deviation of the alloys from, for example, free-electron behaviour should be similar to that of the pure components. More direct structural investigation of these systems would be welcome; it is unlikely that much structural information will be obtained from physical measurements. Further study of their electronic properties is necessary, both to establish the reliability of the observations that the resistivity isotherms may exhibit anomalies at atom ratios of 2:1 or 1:2, and to determine the extent to which the free-electron model may be used to describe these properties. The size factor may influence the composition-dependence of a number of electronic properties by creating compositions of relatively efficient or inefficient packing of atoms, and hence modifying the composition-dependence of $g(r)$ and $a(K)$. This effect should also be detectable in diffraction studies and perhaps in precise and detailed measurements of densities, viscosities, or even thermodynamic properties. The anomalous composition-dependence of the susceptibilities in the iron–cobalt system may be spurious, as may the discontinuity in the temperature coefficient of the resistivity in the bismuth–antimony system. The apparent simplicity of these systems has led investigators to ignore them; it is likely that from a theoretical point of view they may be more easily handleable than more complex alloys, so that in the immediate future precise measurements of physical properties may prove of more value for these materials than for any others.

9.4. EUTECTIC SYSTEMS

Direct structural evidence is available in considerable quantity on this group of systems but there is still doubt about its reliability. It is claimed that at lower temperatures the liquid structure indicates a tendency to separation into the two components—incipient immiscibility—while at higher temperatures the liquid structure is random. The isotherms of several physical properties have been reported to exhibit a relative maximum or minimum at the eutectic composition, and usually at temperatures fairly close to the eutectic temperature, which indicates that the liquids of this composition are in some way unique. Thermodynamic evidence and the inflected type of liquidus common in this group of systems both indicate a tendency toward liquid immiscibility (Section 3), which may be accentuated at temperatures very close to the liquidus. It is interesting to speculate on the structure of these liquids; a possible interpretation is that the point of inflection of the liquidus corresponds to a point of maximum difficulty in mixing of two liquid structures, one characteristic of the pure component on that side of the system, and one characteristic of the eutectic; the latter may be a *relatively* disordered (i.e. more randomly mixed) liquid. In systems where these two structures are similar and miscible —'compatible'—the liquidus will not show a point of inflection (the NI systems). The relatively randomly mixed liquid at the exact eutectic composition will ideally show no tendency to separate into clusters of two different structures and will therefore result in minima in viscosity and perhaps, at low temperatures, resistivity, and possibly in some anomaly in the density isotherm. At compositions slightly removed from that of the eutectic the structure of the 'pure' liquid on that side of the system will appear, and may account for the two-structure liquids sometimes observed in diffraction studies. It is also possible that, at temperatures only just above the eutectic temperature, the eutectic liquid also exhibits incipient immiscibility because it is about to solidify as two immiscible solids, although this suggestion is not compatible with the extensive supercooling possible in such liquids. The situation just above the critical curve in the liquid/liquid mixtures is not analogous, because no rearrangement of the structure is necessary in this case for separation to occur. It follows that the maximum tendency to separate into two *liquids* will occur at the point(s) of inflection in the liquidus, and that detailed thermodynamic and physical measurements at near-liquidus temperatures about the point of inflection in the liquidus may indicate clustering, through an anomalous variation in S_i^M, a less positive H^M, or a relative maximum in the viscosity. Diffraction studies should indicate similar conclusions. It is possible that the structure of the pure liquid may be able to accommodate a limited amount of solute before becoming unstable: this may account for reports of anomalies in physical properties at compositions corresponding roughly with solid-solubility measurements.

The ease of mixing of the components at the exact eutectic composition will clearly depend upon temperature. Just above the eutectic temperature there may be a tendency to separation into two structures corresponding to the pure components (a 'foreshadowing' of solidification?). At higher temperatures (e.g. corresponding to the temperature of the inflection in the liquidus), the liquid should become random. The effect of temperature upon the composition isotherms of the physical properties will depend upon the relative ease of breakdown of the three liquid structures. In cases where the liquidus shows no inflection, and hence little evidence of "unmixing," no anomaly may be observed at the eutectic, except possibly at temperatures very near the eutectic temperature.

Thus, the structural model proposed for liquid eutectic alloys, at least at temperatures close to the liquidus, is that of two structures corresponding to the two component liquids, and one, partially incompatible with either of these and of relatively easy packing of the two components, corresponding to the eutectic. The latter may account for the observation by Hume-Rothery and Anderson that eutectics tend to fall at certain preferred compositions. These may be positions of *relatively* easy packing of the liquids although, thermodynamically, the liquid still tends towards immiscibility, i.e. has a positive enthalpy of mixing. It would be of interest to analyse each group of systems according to size factor to determine whether the latter dictated the composition of optimum packing, since the size factor is of major importance (see Section 3) in determining whether or not two components form a eutectic. It may be significant that the 2:1 and 1:2 atom ratio at which resistivity anomalies are observed is also one that is 'popular' for eutectics, and is possibly affected by the size factor (Section 6).

Clearly, very much additional information is required before a more detailed eutectic model can be suggested. It is probable that direct structural measurements, unless they are of extreme precision, will be relatively unproductive. Electronic measurements are not likely to be sufficiently sensitive to the very slight changes in structure with composition and temperature that are apparently involved. The viscosity is possibly the most sensitive property, together with direct thermodynamic measurements if they can be made with sufficient precision. The greatest effect, if the model suggested here is correct, should be observed in DI eutectic systems; it will therefore be of greatest interest to carry out detailed investigations of the chosen property at very closely spaced composition and temperature intervals, especially at temperatures and compositions well down into the eutectic valley. Apart from this, eutectic systems in general need, in common with all liquid-metal systems, much more detailed general investigation of all physical properties. The remarks made concerning the need to establish the degree of electron freedom in solid-solution systems also apply here; in addition, eutectic systems seem to provide a convenient means of investigating in detail the effect of the size factor upon the thermodynamic and other properties of metallic solutions. If the size factor does result in 'optimum-packing' compositions, the effect upon the composition-dependence of most physical properties is likely to be small; once again, much more careful and detailed study is necessary than is usually the case. It is probable that investigations at composition and temperature intervals > 2 at.-% and 10 deg, respectively, are not adequately detailed.

9.5. MISCIBILITY-GAP SYSTEMS: THE SIZE FACTOR IN LIQUID ALLOYS

These represent the limiting case of the general group of systems with inflected liquidus curves. There is little direct experimental evidence of any sort on metallic miscibility-gap systems but some structural conclusions may be reached from information on non-metallic systems. Positive clustering should be detectable in the single-phase liquids at just above the critical temperature and perhaps at temperatures along the critical curve. The gap is usually bordered by two eutectics, the structures of which, if the model suggested in Section 9.4 is correct, must be those in equilibrium at the miscibility gap. Further investigation of almost all aspects of these liquids would be of value. In the structurally anomalous liquid elements Ga, Ge, Si, &c., the bond is to some extent homopolar, and apparently not capable of being broken at all by certain solute elements (e.g. Cd in Ga) and only with great difficulty by others (Al–Ge, Zn–Ge, &c.). In such cases a moderate size factor may help to tip the balance in favour of immiscibility. The tendency towards immiscibility produced by aluminium (e.g. Al–Sn, Al–Cd, Al–In) seems to have no logical explanation at present since this liquid appears to be structurally normal; possibly *s–p* hybrid bonds are formed in liquid aluminium. The miscibility gaps in uranium systems may be due to *d*-electron bonding in the liquid, and the same may apply to the transition metals, which apparently mix only with great difficulty with the IB metals despite a low size factor. The difficulty in mixing may also result from the reluctance of the IB metals to lose the stable *d*-shell of ten electrons, as would be necessary on alloying. Thus, immiscibility appears to arise from a total incompatibility of the two types of bond—just as oil and water are immiscible for this reason. In the eutectic and miscibility-gap systems considered here (Sections 1 and 2), the tendency toward immiscibility increases as the size factor, with the exception of systems containing Al, Ga, Ge, Si, Sn, Sb, and Bi and those between the IB and transition metals. In the 'pure size-factor' systems—i.e. those in which the electronegativity factor is low—the difficulty in mixing must result from the change in coordination that occurs when an atom of different size is introduced into an assembly of atoms; this results in a change in the interionic potential, and hence in the internal energy of the liquid. In a sense, the energy change arising from the mixing process represents a strain energy in the liquid solution,[105, 592] since the source of the energy change is the displacement of atoms from their equilibrium positions. The modification of the inter-ionic potential should be detectable by electron-transport measurements—resistivity, Hall effect, for example.

Little more than the obvious result is likely to be achieved by a search for clustering in these liquids along the critical curve; it will almost certainly be detected by careful measurements of viscosity or thermodynamic parameters. Much more important are the reasons for immiscibility, and it is difficult to suggest a profitable line of research in this case because, in practice, it is not easy to distinguish between the contributions made by the several factors that control alloying behaviour. There appear to be two main reasons—the size factor generally and in some cases a fundamental incompatibility between the two liquids, perhaps because of a considerable difference in their bond mechanisms, and hence structure. The effect of the size factor may perhaps be detectable in composition-dependence of the radial distribution function for these liquids; from the latter it may eventually be possible to calculate the composition- and hence the size-factor-dependence of the interatomic potential. It may also be possible to determine this from other properties—viscosity, for example. It is probable that further progress will require a clearer theoretical understanding of the effect of the size factor upon bonding in liquid alloys; clearly, a large size factor dictates that there should be a considerable absorption of energy upon mixing which should be calculable from a suitable structural model. Similarly, a fundamental understanding of the nature of the interatomic bond in the transition metals and IB metals is required before the precise reasons for the immiscible liquids commonly formed by elements from these two groups can be established.

9.6. COMPOUND-CONTAINING SYSTEMS

Thermodynamic evidence indicates that these liquid alloys should show a preference for unlike-atom associations. Direct evidence from diffraction studies suggests that in some cases the liquid consists of clusters of a structure formed by a strong association of the components; this clustering is most evident in the liquid at about the composition of the solid-state compound. These clusters may be structurally quite different from the corresponding solid while having similar bonding characteristics. The resulting localization of conduction electrons in bound states between the clustered atoms results in the observed maximum resistivity at the compound composition; the composition-dependence of resistivity can often be explained in terms of degenerate semiconduction in the liquid at non-stoichiometric compositions, while its temperature-dependence may be accounted for by the breakdown of the clustered structure and the resulting increase in the negative carrier concentration as electrons are released from bound states. The nearly-free-electron value for the Hall coefficient in some liquid intermetallic compounds is apparently not a very good measure of the real freedom of electrons. Some free electrons are always present in such liquids (only those with near-metallic liquid-state resistivities have so far been investigated) and it is apparently these that are 'seen' by the Hall effect and similar measurements. The composition-dependence of the Hall effect would be a valuable quantity for such liquids, in which the nature of the current carriers may vary with composition. In addition, Hall-effect measurements are needed on liquid intermetallic compounds such as the thallium tellurides and selenides, which have a very high resistivity. In these, it is likely that only a very small proportion of the conduction is electronic and the Hall coefficient should be less 'metallic' (more positive).

In all cases, the interpretation proposed here is that the factors that bring about the formation of a solid-state compound (or would do so if they were not overridden by factors peculiar to the solid state), also operate in the liquid (except in the case of 'pure' electron compounds) to form associations of atoms of a different structure and different bonding characteristics from those of the 'matrix' liquid. The cluster 'concentration' reaches a maximum at a composition which is dictated by these factors and which usually coincides with the solid-state stoichiometric composition. Because the interatomic distances in the cluster are different from those of the matrix liquid by virtue of the difference in bonding, the diffraction studies indicate two distances of closest approach, or even one, if the clustering is complete. Similarly, the degree of short-range order reaches a maximum at the stoichiometric composition and, as a result, the partial and integral thermodynamic parameters—in particular the entropies of solution—are inflected, with an axis of symmetry at this composition.

No indication of the exact nature of the associations in the liquid can be derived from the information at present available. More useful data may be obtainable from the three-pattern X-ray and neutron-diffraction experiment proposed by Keating,[70] although it seems likely that the mathematical problems involved in a rigorous analysis of the results may be insuperable, at least at present. Meanwhile, information of the nature of the bond in these materials may be obtained from almost any physical and 'electronic' property, although, again, a great deal of emphasis on precision and detail of measurement is necessary. Much more information is obtainable from the composition-dependence of properties in these systems than from the investigation of liquids of only the 'stoichiometric' composition. Of particular value would be measurements of the temperature- and composition-dependence of the resistivity, Hall effect, thermoelectric power, and related properties, combined with a direct structural investigation by neutron- or X-ray diffraction. Supporting measurements of viscosity would be of value in establishing any qualitative relationship between the temperature-dependence of the 'electronic' properties and that of the more directly structure-sensitive measurements.

The temperature-dependence of the physical and thermodynamic properties of molten intermetallic compounds requires further study. In some cases there appears to be a discontinuous change of structure at temperatures well above the melting point, while the available diffraction evidence suggests that structural breakdown is more gradual. In some of the more structurally complex compounds, as in some of the pure elements, a gradual destruction of the solid state seems to take place over some 50 degC above the observed melting point. In this instance, the first stage of fusion is probably the breaking of weak van der Waals forces, holding together more strongly bonded structural units, followed by more gradual breakdown of these units. In some cases these liquids may solidify to a glass-like structure. It appears that, at least in these systems, there is indisputable evidence of a relationship between the structures of the liquid and solid, not because one gives rise to the other but because both are brought about by factors which are at least qualitatively unchanged by fusion.

9.7. General Summary

It must be clear from the extent to which hypothesis rather than scientific deduction has been used to explain some of the results discussed in this review that disappointingly little is known about the structure of liquid metals and the relationship between properties and structure. A very much larger experimental and theoretical effort is necessary (and there are signs that it is forthcoming in a number of laboratories) before these materials are even qualitatively understood. The present level of comprehension is similar to that which had been reached for the solid state of metals some thirty-five years ago; this lack of progress has largely resulted from the understandable absence of practical interest in liquid metals and alloys. Even now, the future for liquid metals as commercially viable materials is by no means clear, and most financial support for research is not provided for the immediate commercial value of the results. It is to be hoped that those metallurgical industries for whom liquid metals are a basic raw material may be sufficiently farsighted to consider, in the not too distant future, the possibility that the financing of research in this field might bring valuable returns in the form of an improved understanding (and hence application) of liquid-alloy thermochemistry, slag/metal equilibria, liquid-metal fluidity, and liquid-metal/mould surface energies, to mention only a few commercially important factors. Perhaps this review, by emphasizing some of the areas in which experimental work is likely to be profitable, may help to promote this enlightenment in cases where it does not already exist.

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TABLE I.—*Solid-Solution Systems*

System	Size Factor, %	Electronegativity Factor (approx.)
Ag–Au	11·8	0·40
Ag–Pd	5·0	0·20
As–Sb	25·2	0·05
Au–Cu	11·8	0·30
Au–Ni	14·1	0·05
Au–Pd	5·0	0·20
Au–Pt	4·2	0·23
Bi–Sb	12·2	0·30
Cd–Mg	5·1	0·40
Co–Fe	0	0·05
Co–Ni	0	0·0
Cr–Fe	1·6	0·05
Cu–Ni	2·4	0·25
Fe–Mn	8·4	0·50
Fe–Ni	0·8	0·05
K–Rb	5·3	0·03
Mn–Ni	9·2	0·55
	Av. 6·1	Av. 0·21
	(excluding As–Sb)	

TABLE II.—*NI* Eutectic Systems*

System	Size Factor, %	Electronegativity Factor (approx.)
Ag–Cu	11·8	0·10
Al–Si	20·0	0·35
Al–Sn	4·3	0
Be–Si	3·5	0·40
Bi–Cd	18·0	0·25
Bi–Sn	14·1	0·20
Cd–In	3·2	0·05
Cd–Sn	3·9	0·05
	Av. 9·8	Av. 0·17

* Neither liquidus inflected

TABLE III.—*SI* Eutectic Systems*

System *A–B*	Axis of Symmetry Inflections, at.-% *B*	Size Factor, %	Electronegativity Factor (approx.)
Ag–Tl	50	17·7	0·45
Ag–Bi	65	23·3	0·10
Ag–Pb	55	19·4	0·35
Al–Be	55	23·4	0·05
Al–Ge	65 ?	2·8	0·30
Al–Sn	45	10·0	0·15
As–Pb	25 ?	33·3	0·05
Au–Co	55	14·1	0·05
Au–Tl	?	17·7	0·85
Cd–Pb	40	14·1	0·00
Cd–Tl	35	12·3	0·10
Cd–Zn	60	10·3	0·05
Cs–Na	20	9·5	0·15
Ga–In	50 ?	15·1	0·15
Ga–Sn	?	15·7	0·00
Ga–Zn	?	14·7	0·10
Ge–Zn	?	1·4	0·25
In–Zn	60	13·6	0·00
Na–Rb	?	26·6	0·12
Pb–Sb	?	8·3	0·55
Pb–Sn	60 ?	10·2	0·05
S–Te	50 ?	31·6	—
Sn–Tl	?	8·5	0·15
Sn–Zn	35	14·2	0·10
		Av. 16·5	Av. 0·18
		(excluding Al–Ge, Ge–Zn)	

* One liquidus inflected

TABLE IV.—*DI* Eutectic Systems*

System *A–B*	Axis of Symmetry Inflections, at.-% *B*		Size Factor, %	Electronegativity Factor (approx.)
Ag–As	?	50	14·1	0·15
Ag–Be	?	45	24·1	0·50
Ag–Ge	12	60	3·5	0·15
Ag–Si	?	60	20·7	0·10
Au–Ge	15	?	3·5	0·55
Au–Si	?	?	20·7	0·50
Ge–Sb	?	?	14·7	0·35
Na–Rb	25	?	26·6	0·10
			Av. 20·1	Av. 0·30
			(excluding Au–Ge, Ag–Ge)	

* Liquidus inflected in both cases

TABLE V.—0% *SI* Systems*

System	Size Factor, %	Electronegativity Factor (approx.)
Ag–Na	28·6	1·00
Al–Hg	8·0	0·30
As–Bi	37·1	0·25
Bi–Cu	23·2	0·20
Bi–Hg	16·0	0
Cu–Li	20·3	1·05
Ga–Ge	2·6	0·15
Ge–In	12·2	0·30
Ge–Pb	22·3	0·20
Ge–Sn	12·8	0·15
Ge–Tl	21·2	0·30
In–Si	29·2	0·35
Sb–Si	31·7	0·30
Si–Sn	29·8	0·20
	Av. 29·1	Av. 0·35
	(Excluding Al–Ag, Ga–Ge, Ge–In, Ge–Sn, average 8·9)	

* Liquidus inflected; eutectic near 0%
The axis of symmetry of the inflection in these systems falls at ~ 50 at.-%.

TABLE VI.—*Complex Eutectic Systems*

System	Nearest "Simple Type"	Size Factor, %	Electronegativity Factor
Au–Bi	DI	23·3	0·50
Au–Pb	NI	19·4	0·25
Au–Sb	NI	11·1	0·20
Bi–Ni	0% SI	22·2	0·55
Bi–Pb	NI	8·9	0·20
Cs–Na	SI	33·8	0·14
Hg–Pb	0% SI	12·1	0·25
Hg–Sn	0% SI	1·9	0·20
Hg–Zn	0% SI	12·3	0·30
In–Sn	SI	0·6	0·15
K–Na	NI	21·4	0·10
Sb–Tl	DI	6·6	0·64
		Av. 12·7	Av. 0·30

TABLE VII.—*Simple Peritectic Systems*

System	Size Factor, %	Electronegativity Factor
Cd–Hg	1·9	0·25
In–Pd	10·8	0·08
In–Tl (complex)	9·1	0·02
Sb–Sn	1·9	0·49
	Av. 5·9	Av. 0·21

TABLE VIII.—*Miscibility-Gap Systems (Non-Transition Metal)*

System	Composition of Maximum in Critical Curve	Size Factor, %	Electronegativity Factor (approx.)
Ag–Tl	Not established with sufficient accuracy (see Table XX)	17·7	0·45
Ag–U		4·2	0·60
Al–Bi		24·0	0·30
Al–Cd		6·1	0·05
Al–In		9·3	0·0
Al–K		24·9	0·65
Al–Na		29·2	0·60
Al–Pb		20·1	0·10
Al–Tl		18·4	0·00
As–Tl		31·6	0·60
Bi–Zn		28·2	0·30
Bi–Ga		29·6	0·15
Bi–Si		43·4	0·05
Ca–Cd		25·8	0·50
Cd–Ca		11·8	0·05
Cd–K		44·1	0·75
Cu–Pb		23·9	0·45
Cu–Tl		29·3	0·55
Cu–U		7·5	0·70
Ga–Pb		25·8	0·05
Ga–Tl		24·1	0·15
Ga–Hg		13·8	0·20
K–Zn		53·9	0·70
Li–Na		20·0	0·05
Mg–Na		18·2	0·25
Na–Zn		33·4	0·60
Pb–U		23·6	0·25
Pb–Zn		24·3	0·05
Tl–Zn		22·7	0·05
U–Zn		0·7	0·20
U–Th		26·4	0·05
		Av. 26·6	Av. 0·30
		(Excluding uranium systems and Al–Cd, Al–In)	

TABLE IX.—*Miscibility-Gap Systems (Transition Metal)*

System	Composition of Maximum in Critical Curve	Size Factor, %	Electronegativity Factor (approx.)	Notes
Cr–Ag	Not established with sufficient accuracy (see Table XX)	10·2	0·25	
Cr–Cu		1·6	0·15	
(Cr–Au)		14·1	0·05	Peritectic
Cr–Tl		30·5	0·70	
Cr–Pb		29·5	0·60	
Cr–Sn		19·4	0·55	
Cr–Bi		21·4	0·35	
Mn–Ag		5·0	0·20	
(Mn–Cu)		13·3	0·30	Solid soln.
(Mn–Au)		25·0	0·60	Compound
Mn–Tl		22·7	0·25	
Mn–Pb		24·3	0·15	
Mn–Bi		28·2	0·10	
Fe–Ag		12·5	0·30	
(Fe–Cu)		0·8	0·20	Near M.G.
(Fe–Au)		14·8	0·30	Peritectic
Fe–Tl		30·1	0·75	
Fe–Pb		31·8	0·65	
Fe–Bi		35·6	0·45	
Co–Ag		13·3	0·35	
(Co–Cu)		1·6	0·25	Near M.G.
(Co–Au)		14·1	0·05	
Co–Tl		30·9	0·60	
Co–Pb		32·6	0·70	
Co–Bi		36·4	0·50	
Ni–Ag		14·1	0·35	
(Ni–Cu)		2·4	0·25	Solid soln.
(Ni–Au)		14·1	0·05	Solid soln.
Ni–Tl		31·6	0·60	
Ni–Pb		33·3	0·70	
(Ni–Bi)		22·2	0·50	Complex

TABLE X.—*Electron-Compound Systems with No Maximum in Liquidus*

System	Size Factor, %	Electronegativity Factor (approx.)	Notes
Ag–Cd	5·4	0·35	
Ag–Zn	5·0	0·40	
Ag–Hg	7·3	0·10	
Ag–Al	0·7	0·40	
Ag–Ga	6·5	0·30	
Ag–In	8·6	0·40	
(Ag–Tl)	17·7	0·45	M.G. system
Ag–Sn	9·3	0·30	
(Ag–Pb)	19·4	0·35	SI eutectic
Ag–Sb	11·1	0·20	
(Ag–Bi)	23·3	0·10	SI eutectic
Cu–Zn	6·8	0·50	
(Cu–Cd)	17·1	0·45	E.C. max.
(Cu–Hg)	19·1	0·20	E.C. max.
Cu–Al	11·1	0·50	
Cu–Ga	5·3	0·40	
(Cu–In)	20·3	0·50	E.C. max.
(Cu–Tl)	29·3	0·55	M.G.
Cu–Sn	21·0	0·40	
(Cu–Bi)	30·0	0·20	M.G.
(Cu–Sb)	22·8	0·10	E.C. max.
(Cu–Bi)	34·8	0·20	0% SI eutectic
	Av. 8·2	Av. 0·35	

E.C. = electron compound. M.G. = miscibility gap.

TABLE XI.—*Electron-Compound Systems with Liquidus Maximum*

System	Size Factor, %	Electro-negativity Factor (approx.)	Compn. of Max.	T(°C) of Max.	Structural Notes
Cu–Cd	17·1	0·45	0·6 Cd	563	γ-brass
Cu–In	20·3	0·50	0·3 In	682	γ-brass
Cu–Sb	22·8	0·10	0·3 Sb	684	DO_3, between 'Cu_3Sb' and 'Cu_2Sb'
Au–Cd	5·4	0·65	AuCd	627	B2, 3:2 electron Also $AuCd_3$
Au–Zn	5·0	0·80	AuZn	725	B2, 3:2 electron Also complex
(Au–Hg)	4·1	0·50	—	—	Complex
Au–Al	0·7	0·80	$AuAg_2$	1060	C1
Au–Ga	6·5	0·70	$AuGa_2$	492	C1
Au–In	8·6	0·80	$AuIn_2$	544	C1
(Au–Tl)	17·7	0·85	—	—	SI eutectic
Au–Sn	9·3	0·70	AuSn	418	B8 (NiAs), also $AuSn_2$, $AuSn_4$. Complex NI eutectic
(Au–Sb)	11·1	0·20	—	—	Complex eutectic
(Au–Bi)	23·3	0·50	—	—	Complex eutectic
Ag–Mg	10·5	0·75	AgMg	820	B2, 3:2 electron
Au–Mg	10·5	1·15	AuMg	1150	B2, 3:2 electron Also $AuMg_3$, $AuMg_2$
	Av. 10·6	Av. 0·67			

TABLE XII.—*Non-Electron Compounds with Liquidus Maximum*

System	Size Factor, %	Electro-negativity Factor (approx.)	Compn. of Main Max.	T(°C) of Main Max.	Structural Notes
Hg–Tl	10·4	0·35	Hg_5Tl_2	14·4	A1
Au–Mn	5·0	0·60	AuMn	1260	A2
Al–Mg	11·2	0·30	0·59 Mg	462	A12
Sn–Te	10·0	0·45	SnTe	790	B1
Sn–Se	5·4	0·75	SnSe	860	Distorted B1 + M.G. and $SnSe_2$
Hg–Li	12·8	0·85	LiHg	595	B2
Al–Ni	13·4	0·75	AlNi	1638	B2
Al–Sb	11·8	0·60	AlSb	1065	B3
Ga–Sb	17·6	0·50	GaSb	706	B3
In–Sb	2·5	0·60	InSb	530	B3
Cd–Te	6·1	0·55	CdTe	1050	B3
Te–Zn	4·3	0·60	TeZn	1239	B3
Hg–Te	4·7	0·30	HgTe	Decomposed	B3
Hg–Se	25·5	0·55	HgSe	680	B3
Al–As	30·7	0·60	AlAs	1600	B3
Ga–As	2·4	0·40	GaAs	1238	B3
In–As	25·8	0·55	InAs	942	B3
Al–Se	20·8	0·85	Al_2Se_3	930	B4
Al–Te	0	0·60	Al_2Te_3	895	B4
Co–Sn	23·3	0·65	0·35 Sn	1170	B8 + CoSn, $CoSn_2$
Se–Sb	23·6	0·85	0·43 Sb	1020	B8
Ni–Sn	23·3	0·65	Ni_3Sn_2	1264	B8
Au–Sn	9·3	0·70	AuSn	418	B8 + $AuSn_2$, $AuSn_4$
Bi–In	14·7	0·30	InBi	1110	B10 + In_2Bi
Co–Si	6·6	0·45	CoSi	1460	B20
Fe–Si	8·2	0·40	FeSi	1410	B20
Na–Tl	11·0	0·55	NaTl	305	B32
In–Te	12·4	0·60	InTe	696	B37 (In_2Te_3, B3, m.p. 667°C)
Ga–Te	15·8	0·45	GaTe	824	B37 (Ga_2Te_3, B3, m.p. 790°C)
Mg–Si	31·0	0·65	Mg_2Si	1100	C1
Mg–Ge	26·9	0·60	Mg_2Ge	1115	C1
Mg–Sn	5·8	0·45	Mg_2Sn	778	C1
Mg–Pb	8·9	0·40	Mg_2Pb	550	C1
Mg–Zn	15·4	0·35	$MgZn_2$	590	C14 (Laves phase)
Al–Ca	31·8	0·45	$CaAl_2$	1079	C15
Cu–Mg	22·2	0·85	$MgCu_2$	819	C15 + Mg_2Cu
Fe–Te	14·2	0·05	$FeTe_2$	900	C18
Co–Te	13·4	0·20	$CoTe_2$	950	C18
Ni–Te	14·2	0·15	$NiTe_2$	850	C18
Hg–Na	213	0·90	$NaHg_2$	353	C32 + several others
Bi–Te	8·0	0·30	Bi_2Te_3	585	C33

TABLE XII—*continued*

System	Size Factor, %	Electro-negativity Factor (approx.)	Compn. of Main Max.	T(°C) of Main Max.	Structural Notes
Bi–Se	28·8	0·55	Bi_2Se_3	706	C33
Mn–Si	15·7	0·13	Mn_3Si_3	1285	D8 + MnSi (B20), 1275°C
Bi–Mg	12·9	0·60	Mg_3Bi_2	823	D52
Na–Bi	5·3	0·90	Na_3Bi	775	DO18
Na–Sb	17·6	1·20	Na_2Sb	856	DO18
Al–Fe	11·8	0·75	Al_5Fe_2	1165	OR + FeAl, $FeAl_3$
Cd–Sb	5·7	0·55	CdSb	456	OR + Cd_3Sb_2, metastable
Bi–Tl	5·6	0·30	0·625 Bi	213	Hex
Ni–Si	6·6	0·42	Ni_2Si	1318	Hex (OR at low T) + others
Cd–Na	23·2	0·65	$NaCd_2$	384	? + $NaCd_6$
Cs–Hg	52·9	1·05	$CsHg_2$	208	? + several others
Hg–K	42·2	1·00	KHg_2	270	OR
Ga–Na	34·9	0·70	Na_6Ga_8	556	?
K–Tl	32·2	0·65	KTl	335	?
Na–Se	49·4	1·45	Na_2Se	~900	?
Na–Pb	9·3	0·65	Na_5Pb_2	400	? + others
Na–Sn	19·4	0·70	NaSn	578	? + Na_2Sn and others
Pb–Tl	17·3	0·10	0·625 Tl	380	? max. in solid-soln. liquids
Sb–Zn	16·1	0·60	Zn_3Sb_2	566	? + ZnSb, Zn_4Sb_3
Al–Mn	4·3	0·20	0·74 Mn	1280	? + others
	Av. 16·6	Av. 0·54			

OR = orthorhombic

TABLE XIII.—*Systems Containing Compounds and Miscibility Gaps*

System	Size Factor, %	Energy Factor (approx).	Compn. of Main Max.	T(°C) of Main Max.	Compn. of Gaps, &c., %	T (°C) of Gap(s)	Structural Notes
Ag–S	32·2	?	Ag_2S	838	0·245 0·755	1120 ?	
Ag–Se	21·5	0·45	Ag_2Se	897	0·22 Se 0·70 Ce	? ?	C1
Ag–Te	0·7	0·45	Ag_2Te	959	0·20 Te Eutectic at 0·67 Te $T_E = 351$	?	Complex F.C.C.
Al–S	31·6	?	AlS	1200	0·30 S	1500	
Cd–Na	(Phase diagram uncertain: data in Table XII)						
Ce–Mn	28·2	0·50	No max.	—	0·25 Ce Eutectic at 86 Ce $T_E = 612$	?	
Co–Se	7·5	0·10	CoSe $CoSe_2$	1055	0·18 Se	?	B8 C2
Cu–Se	9·8	0·35	Cu_2Se	1110	0·18 Se	?	F.C.C. + Cu_3Se, CuSe
Cu–Te	11·1	0·10	Cu_2Te	1125	0·15 Te	?	F.C.C. + Cu_2Te, CuTe
Fe–Sn	21·8	0·60	No max.	—	0·55 Sn	?	Fe_3Sn, Fe_3Sn_2, FeSn, $FeSn_2$
Pb–Se	54·9	0·80	PbSe	1076	0·15 Se 0·92 Se	?	B1
Te–Tl	18·4	0·62	Tl_3Te_2	~440	0·80 Tl	?	

In many of the systems listed above, the phase diagrams are not well established, and the existence of a miscibility gap may be uncertain.

TABLE XIV.—*Structural Data for Pure Liquid Metals*

Element	T^F, °K	T (°K) of Measurement	r_1, Å	Z_1	r_2, Å	Method	Ref. (see p. 574)
Li	453·7	453·7	3·15	9·5	6·0	N	1
Na	371·0	373	3·83	9·5	7·0	X	4 (13)
		373	3·82	9·0	7·2	N	1
K	336·4	338	4·64	9·0	8·6	N	1
		343	4·64	8·0	8·7	X	2, 3 (13, 14)
Rb	312	313	4·97	9·5	9·6	N	1
Cs	301·8	303	5·31	9·0	9·8	N	1
Ag	1234	1273	2·86	10·0	5·6	X	10 (17, 18)
Au	1336	1350 ?	2·85	8·5	5·5	X	6, 10 (18)
Mg	923	933	3·35	10·0	6·0	X	15
Zn	692·7	733	2·94	10·8	5·2	X	5
Cd	594	623	3·06	8·3	5·7	X	5
Hg	234·3	296	3·10	8·3	6·0	N	11
		?	3·05	7·5	6·0	X	10, 16
Al	932	973	2·96	10·6	5·4	X	5
Ga	302·9	293	2·77	11·0	5·5	X	6
In	429·3	433	3·30	8·5	6·3	X	5
		438	3·17	8·0	6·0	X	6, (10)
Tl	577	648	3·30	8·0	6·1	X	6
Ge	1210	1273	2·70	8·0	5·8	X	6, (10)
Sn	505	505	3·26	8·2	6·5	X	12
Pb	600·6	604	3·39	12·1	6·8	X	9
		623	3·38	11·7	6·6	N	9
		623	3·40	9·4	6·6	N	(8)
Sb	903	938	3.12	6·1	6·3	X	7
Bi	544·5	558	3·35	7·6	6·4	X	9
		573	3·36	7·8	6·7	N	9
		573	3·40	8·0	6·8	N	(8)
Ni	1725	1750	Intensity curve only			X	17

N = neutron diffraction

X = X-ray diffraction

Z_1 = coordination number, first coordination shell

T^F = melting point

r_1 = nearest-neighbour distance

r_2 = next-nearest-neighbour distance

References in parentheses may be unreliable

NOTE ADDED IN PROOF: Data for Cu (1100°C), Ag (1050°C), Sn (335°C), and Hg (28°C) have recently been reported by Wagner.[19]

TABLE XV.—*Thermodynamic Properties of Solid and Liquid Metals*

Metal	H^F k cal	S^F cal.g-atom^{-1} deg^{-1}	H^S at 25°C, k cal. g-atom^{-1}	S^V at T^F cal. g-atom^{-1} deg^{-1}	$(C_p)^S$ at 25°C, cal. g-atom^{-1} deg^{-1}	$(C_p)^S$ at T^F cal. g-atom^{-1} deg^{-1}	Ref. $(C_p)^S$ (see p. 575)	$(C_p)^L$ at T^F cal. g-atom^{-1} deg^{-1}	Ref. $(C_p)^L$ (see p. 575)	ΔC_p, % at T^F	Ref. Vapour Pressure (see p. 575)
Li	0·717	1·58	38·6	21·8	5·78	7·06	29	7·26	29	+2·8	30, 1
Na	0·622	1·68	26·0	20·0	6·72	7·49	33	7·61	33	+1·6	1
K	0·562	1·67	21·5	18	7·07	7·75	28	7·68	28	−0·9	1
Rb	0·540	1·73	20·5	17	7·36	7·55	21	(7·5)	4	0	1
Cs	0·520	1·72	18·8	16·7	7·65	7·72	21	7·62	21	−1·3	1
Be	(2·8)	(1·8)	79·0	25·6	3·93	(7·8)	11, 1	(7·5)	12	(−3·8)	1
Mg	2·14	2·32	35·6	22·3	5·95	7·85	16, 31	7·80	31	−0·6	1
Ca	1·97	1·75	46·0	20·7	6·26	9·93	9(*b*)	7·4	9(*b*)	−23·4	1
Sr	(2·4)	(2·3)	(43)	20·15	(6·3)	(9·7)	1	(7·4)	1	(−23·7)	1
Ba	(2.3)	(2·33)	(46)	19·4	—	(17·5)	9	11·5	9	(−34)	10, 1
Al	2·57	2·75			5·82	7·70	4, 5	7·0	6	−9·0	7, 1
Se	(2·72)	(1·50)	(78·5)	(23·5)		—	—	—	—	—	—
Y	2·73	1·52	(105)	24·4	6·34	8·37	46	10·30	46	+23·0	1
Si	12·1	7·18	107·5	26·15	4·89	—	9(*c*)	—	—	—	48
P (Yellow)	0·151	0·48	14·05	22·4	4·56	4·64	48	5·88	48	+26·7	48
S	0·295	0·76	?	?	5·26	6·0	48	7·5	48	+23	48
Cu	3·12	2·30	81·5	25·5	5·86	7·47	1	(7·5)	3	0	1
Ag	2·855	2·31	65·6	24·9	6·07	7·70	1	7·3	3	−5·2	11
Au	2·955	2·21	90·5	26·0	6·06	7·31	8	7·0	3	−4·2	1
Zn	1·765	2·55	31·5	23·3	6·07	7·01	1	7·5	12	+7·0	1
Cd	1·46	2·46	26·8	22·9	6·21	(7·1)	16	7·1	15	0	1
Hg	0·549	2·34	—	22·5	6·69	6·81	26	6·81	26	0	26, 1

TABLE XV.—*continued*

Metal	H^F k cal	S^F cal.g-atom^{-1} deg^{-1}	H^S at 25°C, k cal. g-atom^{-1}	S^V at T^F cal. g-atom^{-1} deg^{-1}	$(C_p)_S$ at 25°C, cal. g-atom^{-1} deg^{-1}	$(C_p)_S$ at T^F cal. g-atom^{-1} deg^{-1}	Ref. $(C_p)_S$ (see p. 575)	$(C_p)_L$ at T^F cal. g-atom^{-1} deg^{-1}	Ref. $(C_p)_L$ (see p. 575)	ΔC_p % at T^F	Ref. Vapour Pressure (see p. 575)
Ga	1·335	4·41	66·5	24	6·18	6·20	24	6·65	24	+7·3	25
In	0·78	1·82	(60)	23·65	6·39	7·25	27	7·05	27	−2·8	1, 57
Tl	0·975	1·69	43·2	22·4	6·29	7·9	40	7·2	15	−6·3	1
Ge	7·7	6·36	91·7	26·3	(6·2)	(7·3)	9(*c*)	—	—	—	—
Sn	1·67	3·31	72·2	24·4	6·45	7·35	1	7·10	39	−3·4	1
Pb	1·14	1·89	46·9	21·0	6·32	7·02	36	7·32	36	+2·8	1
As	Sublimes		29·0 (As)	—	5·9	—	9(*c*)	—	—	—	—
Sb	4·69	5·19	(63)	23·4	6·03	7·30	1	7·50	5	+2·7	41
Bi	2·60	4·77	49·5	23·3	6·20	6·80	1, 13	7·6	9	+11·7	14, 1
Se	1·50	3·03	(25)	(23·7)	6·1	7·2	9	7·0	9	−2·8	43
Te	4·20	5·80	41·0 (Te_2)	20·3	6·0	8·4	9	9·0	9	+7·1	42
Ti	(4·46)	(2·3)	111·7	28·5	5·98	9·20	1	8·0	12	−13	1
V	(5·05)	(2·3)	121·9	39·9	5·90	10·62	41	9·5	4	−10·5	47
Cr	(5·00)	(2·3)	96·0	27·7	5·58	(12·45)	1	(9·4)	20	(−24)	1
Mn	3·50	2·30	67·5	22·7	6·29	(11·3)	1	(11·0)	4	(−2·7)	1
Fe	3·63	2·01	95·2	26·6	6·00	10·02	1	10·50	12, 22	+4·8	1, 23
Co	4·10	2·32	101·5	28·3	5·93	9·21	1	(9·0)	1	(−2·2)	1, 19
Ni	(4·21)	(2·44)	(107)	28·5	6·23	9·07	1	9·2	35	+1·4	1
Zr	(4·90)	(2·3)	141·6	29·5	6·01	(8·27)	1	(8·0)	1	(−3·3)	
Nb	(6·30)	(2·3)	188·0	32·6	5·58	8·30	1	8·0	12	−3·6	1
Mo	(6·65)	(2·3)	142	28·6	5·68	10·0	4	(10·0)	4	0	1, 32
Ru	(6·21)	(2·3)	(160)	32·3	5·75	(10·0)	1	(10·0)	1	0	1
Rh	(5·15)	(2·3)	(140)	29·6	5·97	(10·0)	1	(10·0)	1	0	1
Pd	(4120)	(2.3)	(90)	26·3	6·21	8·30	1	(8·3)	1	0	1, 55–56
Hf											

Os	(7·6)	(2·3)	(195)	(33)	5·90	(8·63)	1	(8·3)	1	(−3·8)	1
Ir	(6·3)	(2·3)	(165)	31·4	6·00	(9·35)	1	(9·35)	1	0	1
Pt	(4·7)	(2·3)	(140)	29·7	6·18	8·42	37	8·3	12	−1·4	1, 38
La	(1·29)	(1·08)	(105)	26·4	6·65	(8·1)	1	(8·3)	1	(+2·4)	1
Ce	1·24	1·15	(95)	24·8	6·44	9·05	17	9·35	17	+3·3	1, 18
Pr	(2·7)	1·83	(80)	23·9	(6·59)	—	1	0	1	—	49
Nd	1·70	1·32	(80)	18·65	6·55	10·65	17	11·66	17	+9·5	1
Sm	2·13	1·58	(53)	18·97	7·06	11·22	44	12·57	44	+12·0	1, 45
Eu	(2·3)	(1·5)	(45)	24·16	—	—	—	—	—	—	1, 50
Gd	(2·4)	(1·5)	(75)	(23·7)	8·86	—	1	—	—	—	—
Tb	(2·4)	(1·5)	(70)	(23·7)	6·91	—	1	—	—	—	1, 51
Dy	(2·7)	(1·5)	(64)	19·16	6·73	—	1	—	—	—	1, 51
Ho	(2·7)	(1·5)	(70)	(22·8)	6·49	—	1	—	—	—	1, 51
Er	(2·7)	(1·5)	(70)	(24·1)	6·72	—	1	—	—	—	1, 51
Tm	(2·8)	(1·5)	(50)	28·81	—	—	1	—	—	—	1, 52
Yb	(1·6)	(1·5)	(40)	(20)	—	—	1	—	—	—	1
Lu	(2·9)	(1·5)	(60)	(25)	—	—	1	—	—	—	—
Th	(4·5)	(2·3)	(140)	23·8	6·53	(11·0)	1	(11·0)	1	0	1
U	(3·09)	(2·2)	(135)	26·8	6·61	9·15	1	(9·15)	1	0	54
Pu	0·94	1·03	(80)	22·9	7·65	9·70	1	(9·7)	1	0	53

Data in parentheses are estimated or otherwise unreliable.

TABLE XVI.—*Melting and Boiling Points of the Elements*

Element	M.P.	B.P.	Liquid Range	Liquid Fraction
	T (°K) at 760 mm			
Li	453·7	1597	1143	0·716
Na	371·0	1156	785	0·679
K	336·4	1031	695	0·674
Rb	312	975	665	0·682
Cs	301·8	963	661	0·686
Be	1556	2756	1200	0·425
Mg	923	1376	453	0·329
Ca	1123	1756	633	0·360
Sr	1043	1648	605	0·367
Ba	983	1895	912	0·481
Ra	1233	1415	180	0·127
B	(2573)	(2823)	(150)	(0·088)
Al	932	2714	1782	0·656
Sc	1812	3218	1406	0·437
Y	1803	3577	1774	0·495
Si	1685	3513	1328	0·520
P	317·1	553	236	0·427
S	386	717	331	0·462
Cu	1357	2846	1489	0·523
Ag	1234	2437	1203	0·493
Au	1336	3081	1745	0·566
Zn	692·7	1184	491	0·415
Cd	594	1040	446	0·428
Hg	234·3	629·7	395·4	0·628
Ga	302·9	2520	2217	0·880
In	429·3	2343	1914	0·817
Tl	577	1760	1183	0·672
Ge	1210	1973	1763	0·593
Sn	505	2896	2391	0·825
Pb	600·6	2016	1415	0·701
As	Sublimes			
Sb	903	1908	1005	0·527
Bi	544·5	1936	1391	0·718
Se	493·5	958	465	0·485
Te	722·8	1263	540	0·427

Data from Hultgren (General Ref. 130).
Data in parentheses are estimated or otherwise unreliable.

TABLE XVI.—*Melting and Boiling Points of the Elements—continued*

Element	M.P.	B.P.	Liquid Range	Liquid Fraction
	T (°K) at 760 mm			
Ti	1940	3575	1635	0·457
V	2190	3652	1462	0·400
Cr	2176	2938	762	0·259
Mn	1517	2324	807	0·347
Fe	1809	3148	1339	0·425
Co	1768	3174	1306	0·411
Ni	1725	3160	1435	0·454
Zr	2125	4688	2563	0·546
Nb	2740	5007	2267	0·453
Mo	2890	4924	2034	0·413
Ru	2700	4392	1692	0·385
Rh	2239	4000	1761	0·440
Pd	1823	3020	1197	0·396
Hf	2500	—	—	—
Ta	3269	5513	2244	0·407
W	3650	5808	2158	0·371
Re	3453	5960	2507	0·420
Os	3300	(4500)	(1200)	(0·266)
Ir	2727	4662	1935	0·415
Pt	2043	4097	2054	0·501
La	1193	3634	2441	0·672
Ce	1077	3742	2665	0·712
Pr	1200	3295	2095	0·636
Nd	1297	3335	2038	0·611
Pm	(1320)	(2700)	(1380)	(0·511)
Sm	1345	2076	631	0·352
Eu	1099	1764	665	0·376
Gd	1623	(3273)	(1650)	(0·504)
Tb	1638	(2800)	(1162)	0·415
Dy	1773	2905	1132	0·390
Ho	1773	2973	1200	0·404
Er	1798	2900	1102	0·380
Tm	1873	(2005)	(132)	(0·066)
Yb	1097	(1900)	(803)	(0·422)
Lu	1973	(2200)	(327)	(0·108)
Th	1968	5120	3152	0·615
U	1405	4473	3068	0·686
Pu	913	3508	2595	0·740

TABLE XVII.—*Specific Heats of Liquid Alloys*

System	Observed ΔC_p (max.), cal. g-atom^{-1} deg^{-1}	Ref. (see p. 576)	System	Observed ΔC_p (max.) cal. g-atom^{-1} deg^{-1}	Ref. (see p. 576)
Au–Bi	(+0·5)	2	Cd–Sn	−0·34 at 0·4 Sn	5
Au–Sn	+0·6 at 0·5 Sn	1	In–Sn	±0	6
Au–Tl	large, +ve	2	Hg–Tl	+0·7 at 0·5 Tl	7
Au–Zn	+1·0	1	Sn–Zn	−0·95 at 0·5 Zn	5
Bi–Pb	±0	3	Na–Tl	+2·1	8
Bi–Sb	large, +ve?	4			

TABLE XVIII.—*Liquid-State Thermodynamic Data: Solid-Solution Systems*

System *A–B*	Ref. (see p. 577)	*GE*max. k cal. g-atom^{-1}	N_B at *GE*max.	*SE*max e.u.	N_B at *SE*max.	*HM*max. k cal. g-atom^{-1}	N_B at *HM*max.	*T*(°K) at which data quoted	*HM*max. (solid) k cal g-atom^{-1}	*VM* %
Ag–Au		−0·60	0·48	−0·34	0·50	−1·10	0·50	1350	−1·10	+ve, very small
Au–Cu		−1·69	0·58	0	—	(−1·10)	(0·60)	1300	−1·25	−0·5 at 0·5 Cu
Au–Ni		+ve	—	+ve	—	0·6	0·5	1369	+1·8	—
Bi–Sb		—	—	—	—	0·3	0·5	1073	0·0	+0·8 at 'Bi$_3$Sb' −0·5 at 'BiSb$_3$'
Cd–Mg	1, 2	−1·15	0·48	−0·24	0·50	−1·25	0·45	923	−1·3	—
Co–Ni		—	—	—	—	+ve	—	—	—	±0
Cu–Ni	3, 5	+ve	—	(−ve)	—	(+0·5)	—	—	+0·45	±0
Fe–Mn		+0·3	0·5	0	—	0	—	1863	—	—
Fe–Ni		−0·72	0·63	—	—	−ve	—	1873	—	—
K–Rb	4	—	—	—	—	0·03	0·5	384	—	—

e.u. = entropy unit = cal g-atom^{-1} deg^{-1}.

Standard reference states for the solid-state and liquid-state thermodynamic quantities are the pure solid and liquid elements, respectively.

Data in parentheses are estimated or otherwise unreliable.

TABLE XIXA.—*Liquid-State Thermodynamic Data: NI Eutectic Systems*

System $A–B$	Ref. (see p. 577)	G^Emax. k cal. g-atom^{-1}	N_B at G^Emax.	S^Emax. e.u.	N_B at S^Emax.	H^Mmax. k cal. g-atom^{-1}	N_B at H^Mmax.	T(°K) at which data quoted	H^Mmax. (solid) k cal. g-atom^{-1}	V^M %	Ref. V^M (see p. 577)
Ag–Cu		+0·71	0·55	+0·26	0·3	+1·0	0·45	1400	(+1·5)	—	
Al–Zn	6–8	0·24	0·5	+0·4	0·5	+0·62	0·5	950	+0·8	±0	
Bi–Cd	9,11	−0·09	0·6	+0·38	0·65	+0·22	0·7	773	—	+1·8	10
Bi–Sn	11	−0·065	0·65	−0·07	0·6	+0·02	0·5	608	(+0·87)	+1·1	
Cd–Sn		+0·22	0·5	+0·28	0·45	+0·45	0·55	773	—	+1·8	10

TABLE XIXB.—*Liquid-State Thermodynamic Data: SI Eutectic Systems*

System $A–B$	Ref. (see p. 577)	G^Emax. k. cal. g-atom^{-1}	N_B at G^Emax.	S^Emax. e.u.	N_B at S^Emax.	H^Mmax. k cal. g-atom^{-1}	N_B at H^Mmax.	T(°K) at which data quoted	H^Mmax. (solid) k cal. g-atom^{-1}	V^M %	Ref. V^M (see p. 577)
Ag–Tl	17, 18	+ve	—	+ve	—	+0·92	0·58	1050	—	—	
Ag–Bi	12, 21	−0·23	0·2	+0·45	0·4	+0·45	0·65	1000	—	+ve	
		+0·17	0·8								
Ag–Pb	13	+0·36	0·5	+0·65	0·5	1·01	0·5	1000	—	+ve	
Al–Sn	7	−0·86	0·55	+0·46	0·48	+0·99	0·45	1000	—	—	
Au–Tl	11	−0·5	0·52	+0·5	0·55	0	—	973	—	—	
Cd–Pb	11, 22	+0·5	0·45	+0·22	0·35	+0·68	0·45	773	—	+0·8	11
Cd–Tl	14	+0·4	0·5	+0·23	0·4	+0·55	0·45	673	—	+1·0	10
Cd–Zn	14	+0·51	0·53	±0·0	—	+0·51	0·53	800	—	+0·6	20
Ga–Zn	14	+0·20	0·55	+0·26	0·60	+0·39	0·55	743	—	—	
Ge–Zn	16, 23	−ve	—	+ve	—	+ve	—	850	—	—	
In–Zn	11, 15	+0·57	0·55	+0·30	0·52	+0·78	0·55	700	—	+0·5	20
Na–Rb	4	—	—	—	—	+0·3	0·40	111		—	
Pb–Sb	11, 30	−0·125	0·5	+0·1	0·33	−0·08	0·67	900	—	—	
Pb–Sn	24	0·3	0·49	0·0	—	+0·33	0·49	773	—	—	
Sn–Tl	11, 29	+0·28	0·45	−0·17	0·6	+0·17	0·42	735	—	—	
Sn–Zn	25–8, 31	+0·41	0·62	+0·56	0·55	+0·8	0·56	700	—	+1·5	20, 29

TABLES XIXC AND D.—*Liquid-State Thermodynamic Data: DI and* 0% *SI Eutectic Systems*

C. *DI Systems*

System A–B	Ref. (see p. 577)	G^Emax. k.cal. g-atom^{-1}	N_B at G^Emax.	S^Emax. e.u.	N_B at S^Emax.	H^Mmax. k cal. g-atom^{-1}	N_B at H^Mmax.	T, °K
Ag–Si	33	+ve	—	—	—	+ve	—	1693

D. 0% *SI Systems*

System A–B	Ref. (see p. 577	G^Emax. k cal. g.-atom^{-1}	N_B at G^Emax.	S^Emax. e.u.	N_B at S^Emax.	H^Mmax. k cal. g. atom^{-1}	N_B at H^Mmax.	T,°K
Bi–Cu	32, 35	+ve	—	+ve	—	+ve	—	—
Bi–Hg	34	+0·18	0·7	−0·07	0·7	+150	0·65	594

TABLE XIXE.—*Liquid-State Thermodynamic Data: Complex Eutectic Systems*

System A–B	Ref. (see p. 577)	Nearest Simple Type	G^Emax. k cal. g-atom^{-1}	N_B at G^Emax.	S^Emax. e.u.	N_B at S^Emax.	H^Mmax., k cal. g-atom^{-1}	N_B at H^Mmax.	T(°K) at which data quoted	H^Mmax. (solid) k cal g-atom^{-1}	V^M %	Ref. V^M (see p. 577)
Au–Bi		DI	(+0·2)	—	(−0·2)	—	(+0·1)	—	723	—		
Au–Pb		NI	−0·57	0·45	0·59	0·28	−0·14	0·73	873	—		
Bi–Pb	42	NI	−0·3	0·5	+0·05	0·5	+0·26	0·5	700	−ve	+0·3	20
Cd–In	41	SI	+0·24	0·45	+0·14	0·45	+0·35	0·45	723	—	+0·7	10
Cs–Na	4, 43	SI	—	—	—	—	+0·24	0·69	384	—	—	
Hg–Pb	8	0% SI	+0·25	0·29						—	−0·9	20
Hg–Sn	34, 36	0% SI	+0·24	0·35	−0·09	0·2	+0·22	0·38	423	—	−0·9	20
Hg–Zn	37	0% SI	+0·21	0·61	(−0·23)	(0·6)	+0·1	0·35	608	—	−1·3	20
In–Sn	11, 19	SI	−0·24	0·4	0·25	0·4	−0·05	0·33	773	—		
K–Na	4	NI	+0·16	0·5	+0·1	0·65	+0·19	0·57	384	−0·15 at KNa_2		
Sb–Tl	38–40	DI	−0·67	0·62	+0·25	0·62	−0·45	0·62	900	—		

TABLE XIXF.—*Liquid-State Thermodynamic Data: Peritectic Systems*

System A–B	Ref. (see p. 577)	G^Emax. k cal. g-atom^{-1}	N_B at G^Emax.	S^Emax., e.u.	N_B at S^Emax.	H^Mmax., k cal. g-atom^{-1}	N_B at H^Mmax.	T(°K) at which data quoted	H^Mmax. (solid) k cal. g-atom^{-1}	V^M, %	Ref. V^M (see p. 577)
Cd–Hg		−0·49	−0·48	−0·26	−0·45	−0·65	0·48	600	—	0·7	20
In–Pb	19, 44, 45	+0·15	0·40	+0·13	0·6	+0·23	0·5	673	—	—	
In–Tl		—	—	—	—	+0·14	0·44	623		—	
Sb–Sn	46	−0·38	0·60	−0·17	0·41	−0·5	0·44	905	—	—	

e.u. = entropy unit = cal. g-atom^{-1} deg^{-1}.
Standard reference states for the solid-state and liquid-state thermodynamic data are the pure solid and liquid elements, respectively.
Data in parentheses are estimated or otherwise unreliable.

TABLE XX.—*Liquid-State Thermodynamic Data: Miscibility-Gap Systems*

System A–B	Ref. (see p. 577)	G^Emax., kcal. g-atom^{-1}	N_B at G^Emax.	S^Emax., e.u.	N_B at S^Emax.	H^Mmax kcal. g-atom^{-1}	N_B at H^Mmax.	T (°K) at which data quoted	Crit. Temp., °K	V^M, %
Bi–Zn		+0·69	0·59	+0·52	0·5	+1·15	0·57	873	878	—
Cd–Ga		+0·64	0·50	±0	—	+0·64	0·48	700	570	—
Cu–Pb		+1·27	0·48	—	—	—	—	1263	1263	−11·8
Na–Zn	47	+1·10	0·48					873		
Pb–Zn	48–50	+1·21	0·55	+0·25	0·3	+1·36	0·50	926	1071	(+1·0)
Tl–Zn		+1·10	0·55	+0·3	0·5	+1·42	0·55	1099	1099	

e.u. = entropy unit = cal g-atom^{-1}deg^{-1}.
Standard reference states for thermodynamic data are the pure liquid elements.
Data in parentheses are estimated or otherwise unreliable.

TABLE XXI.—*Liquid-State Thermodynamic Data: Electron-Compound Systems with no Liquidus Maxima*

System A–B	Ref. (see p. 577)	G^Emax. k cal. g-atom^{-1}	N_B at G^Emax.	S^Emax e.u.	N_B at S^Emax.	H^Mmax. k cal. g-atom^{-1}	N_B at H^Mmax.	T(°K) at which data quoted	H^Mmax. (solid) k cal g-atom^{-1}	V^M, %
Ag–Al	53, 54	−1·6	0·34	+0·66	0·68	+0·17	0·86	1173	—	
						−1·55	0·31			
Ag–Cd		−1·2	0·45	(−0·5)	—	(1·7)	—	1100	−2·0	—
Ag–In		—	—	—	—	−0·8	0·5	723	(−2)	—
Ag–Sn	51	—	—	—	—	+0·06	0·93	1248	(−1)	−4·7 at 25 at.-% Sn
						−0·71	0·2			
Ag–Sb		—	—	—	—	−1·2	0·37	1323	—	—
Ag–Zn	23	−1·3	0·48	(+0·5)	—	(−1)	—	1050	−1·2	—
Cu–Sn	55	—	—	—	—	−1·2	0·22	1423	(−2)	−7.3 at 'Cu_3Sn'
Cu–Zn	23, 52	−1·2	0·47	−0·42	0·52	−1·69	0·49	1200	−2·3	−3·6 at 'CuZn'

e.u. = entropy unit = cal. g-atom^{-1} deg^{-1}.

Standard reference states for the solid-state and liquid-state thermodynamic quantities are the pure solid and liquid elements, respectively.

Data in parentheses are estimated or otherwise unreliable.

Table XXII.—*Liquid-State Thermodynamic Data: Electron-Compound Systems with Liquidus Maxima*

System A–B	Ref. (see p. 577).	G^Emax., k cal. g-atom^{-1}	N_B at G^Emax.	S^Emax., e.u.	N_B at S^Emax.	H^Mmax., kcal g-atom^{-1}	N_B at H^Mmax.	T(°K) at which data quoted	H^Mmax., (solid) kcal g-atom^{-1}	V^M, %
Ag–Mg		—	—	—	—	−2·9	0·5	1323	−5·2	
Al–Cu	59	—	—	—	—	−4·4	0·63	1423	−5·5	−6·7 at 'Cu$_3$Al'
Au–Cd		−5·65	0·5	(+1·0)	(0·5)	(−4·5)	(0·5)	1200	−4·7	—
Au–In		—	—	—	—	(−4)	—	—	(−6)	—
Au–Sn		−3·1	0·45	+0·63	0·33	−2·6	0·47	873	−3·65 (at 'AuSn')	—
Au–Zn		(−5)	(−0·5)	—	—	(−3)	—	—	(−6)	—
Cd–Cu	57	(−0·14)	0·7	−0·78	0·45	−0·78	0·48	875	(−1·2) (at 'CuCd$_2$')	—
Cu–Sb	56, 58	—	—	+ve	—	−1·38	0·25	1215	—	−4·3 (max.) at 0·25 Sb

e.u. = entropy unit = cal. g-atom^{-1} deg^{-1}.

Standard reference states for the solid-state and liquid-state thermodynamic quantities are the pure solid and liquid elements, respectively.

Data in parentheses are estimated or otherwise unreliable.

TABLE XXIII.—*Liquid-State Thermodynamic Data: Non-Electron Compound Systems with Liquidus Maxima*

System A–B	Ref. (see p. 577)	G^Emax., kcal g-atom^{-1}	N_B at G^Emax.	S^Emax., e.u.	N_B at S^Emax.	H^Mmax., kcal g-atom^{-1}	N_B at H^Mmax.	T(°K) at which data quoted	H^Mmax., (solid) kcal g-atom^{-1}	V^M, %	Ref. V^M (see p. 577)
Al–Mg	68	(−0·4)*	0·5	(−0·5)* +0·39	0·5 0·79	(−0·9)*	0·5	1000	(−1·0)	−2·7	
As–Cd	73	−1·38	0·55	−0·19 +0·32	0·50 0·20	−1·50	0·51	1000	—	—	
Bi–In	78, 79, 90	—	—	+0·11	0·5	−0·45	0·55	623	—	—	
Bi–Mg		−5·3	0·6	+0·2 −0·1	0·35 0·6	−5·3	0·6	973	−7·35 (at Mg_3Bi_2)	(+2)	
Bi–Na	72	—	—	—	—	(−14·5)	(0·75)	703	(−12)	—	
Bi–Tl	77	−1·12	0·59	0·19	0·25	−1·09	0·6	732	−0·7?	—	
Cd–Na	72	−0·36 +0·12	0·22 0·82	0·70 (inflected)	0·33	+0·45	0·75	668	−2·7 (at Cd_2Na)	—	
Cd–Sb	75, 81	−0·7	0·47	0·45 (inflected)	0·2	+0·06 −0·51	0·1 0·48	773	−1·7 (at CdSb)	+3 (at CdSb)	
Co–Si	63–64	−6·8	0·46	−2·22 (inflected)	0·48	−11·2	0·46	1883	−12·0	−30 (at CoSi)	83
Co–Sn		—	—	—	—	−0·55	0·25	1773	−3·5 (at CoSn)	—	
Cu–Mg		−1·62	0·43	−0·7 (inflected)	0·5	−2·4	0·45	1150	(−2·7)	—	
Fe–Si	63–66, 89	−5·1	0·43	−2·23 (inflected)	0·58	−9·0	0·48	1883	−9·6	−36 (at FeSi)	82
Hg–In	34	−0·50	0·50	−0·11	0·5	−0·54	0·49	433	—	—ve	80
Hg–K	72	−3·15	0·37	−3·9 (inflected)	0·5	−5·3	0·40	600	−6·2	−25	
Hg–Na	72	−3·3	0·43	−5·3 (inflected)	0·38	−6·7	0·4	648	−7 (at Hg_2Na)	−20	
Hg–Tl	34, 69	−0·1	0·35	−0·13 (inflected)	0·4	−0·23	0·4	293	−0·02	—	
In–Na	72	—	—	—	—	(−10·2)	0·49	773	—	—	

In–Sb	84, 90	−0·92	0·45	+0·14 (inflected)	0·5	−0·79	0·45	973	−4·0 (at InSb)	—	
K–Pb	71	−2·9	0·49	−2·7 (inflected)	0·37	−5·1	0·43	873			
K–Tl	72	(−4·3)*	0·6	(+2·2)	0·7	−2·65	0·58	798			
Mg–Pb	69, 85, 86	−1·8	0·38	−0·75 (inflected)	0·38	−2·3	0·38	823	−4·2 (at Mg_2Pb)	(−8)	
Mg–Sn	66, 67, (87), 91	−2·8	0·41	−0·82 (inflected)	0·55	−3·45	0·41	1043	−6·3 (at Mg_2Sn)	(−4)	
Mg–Tl	73	−1·69	0·46	−0·50 +0·18	0·26 0·71	−1·96	0·37	923	(−6·0)		
Mg–Zn	61–63		0·58	0·60 (inflected)	0·62	−1·4	0·56	923	−2·6	−6·3	
Mn–Si	70	−0·87				(−16·0)	(0·5)	?	−16 (at Mn_2Si)	70	
Na–Pb	72, 88	−2·9	0·45	−1·85 (inflected)	0·32	−4·2	0·4	698	−5·8 (at NaPb)		
Na–Sn	72	−3·2	0·43	−2·7 (inflected)	0·43	−5·3	0·43	773			
Na–Tl	72	−2·1	0·55	−0·82 (inflected)	0·35	−2·7	0·50	648	−4·5 (at NaTl)		
Ni–Si	63, 89	—	—	—	—	(−16·0)	(0·33)	?	−10·2	−23 (at Ni_2Si)	83
Ni–Sn		—	—	—	—	−4·7	0·38	1773	(8)		
Pb–Tl	75, 76, 78	−0·2	0·6	−0·21	0·5	−0·4	0·55	773	−0·7 (at 0·75 Tl)	—	
Sb–Zn	75, 20	−0·75	0·5	+0·25 −0·12	0·25 0·52	−0·85	0·52	823		— (+0·4)	
Te–Tl	74	—	—	+0·24	0·8	—	—	—	—	—	

* This system may contain a miscibility gap (see text).
e.u. = entropy unit = cal. g-atom^{-1} deg^{-1}.
Standard reference states for the liquid-state and solid-state thermodynamic data are the pure liquid and solid elements, respectively.
Data in parentheses are estimated or otherwise unreliable.

TABLE XXIV.—*Viscosities of Pure Liquid Metals at 50°C Superheat*

Metal	Viscosity at T^F + 50 degC, centipoises	'Activation Energy' for Viscous Flow kcal. mole^{-1}	Ref. (see p. 579)
Li	0·55	1·33	1
Na	0·68	1·25	1, (2, 31)
K	0·64	1·2	1, 26 (4, 5, 31)
Rb	0·52	1·23	1
Cs	0·53	1·15	1
Mg	1·07	7·3	6, (12)
Ca	1·06	6·5	15
Al	1·13	3·95	3, 7, 27, (9, 10, 35)
Cu	4·1	7·3	3, 3, 35
Ag	3·62	5·3	3
Au	5·38	5·1	7, (11, 2)
Zn	2·82	2·5, 1·6	2, 26, 28, 30, (12, 35)
Cd	2·29	2·6	13, (12)
Hg	1·61	0·6	37, (23)
Ga	1·70	1·0	14
In	1·65	1·2	15, 16, 17
Si	(2·0)	—	22
Sn	1·75	1·3	6, 27, (2, 34, 12)
Pb	1·09	2·35	6, 18, 19, 26, 27, 30, (12, 33, 35)
Sb	1·30	5·25	19, 20, (12)
Bi	1·58	1·75	21, 26, 27, 30, 38, (10)
Fe	5·4	9·9	21, (29, 32)
Co	4·8	10·6	21
Ni	5·0	12·0	15, (29)
Pu	5·5	3·1	24, 25

Sources in parentheses may be unreliable.

TABLE XXV.—*Coefficients and Activation Energies for Diffusion in Pure Liquid Metals and Alloys*

A Diffusing in *B*		T,° C	$D = D_0 \exp\left(\frac{-E_D}{RT}\right)$			Ref. (see p. 579)
A	*B*		D, cm^2 sec^{-1}	D_0, cm^2 sec^{-1}	$-E_D$, cal.mole^{-1}	
K	K			$1{\cdot}7 \times 10^{-3}$	2550	19, 20
Mg	Mg	700	$2{\cdot}7 \times 10^{-5}$	—	—	
Pb	Pb	—	—	$9{\cdot}15 \times 10^{-4}$	4450	1
Na	Na	—			2430	2
Ag	Ag	—		$5{\cdot}8 \times 10^{-4}$	7660	18
Hg	Hg	20	$1{\cdot}8 \times 10^{-5}$	$1{\cdot}26 \times 10^{-4}$	1160	3, 23, 24
Ga	Ga	—			1122	4
Fe	Fe*	—	—	$4{\cdot}3 \times 10^{-3}$	12,200	5
Fe	Fe†	—	—	$1{\cdot}0 \times 10^{-2}$	15,700	5
In	In	655	$4{\cdot}8 \times 10^{-5}$	—	—	6
		635	$10{\cdot}8 \times 10^{-5}$	—		6
		—	—	$2{\cdot}78 \times 10^{-4}$	2430	7
Sn	Sn	299	$3{\cdot}74 \times 10^{-5}$	—	—	6
		622	$13{\cdot}5 \times 10^{-5}$	$2{\cdot}2 \times 10^{-3}$	4570	6, 22
Zn	Zn	700	$6{\cdot}2 \times 10^{-5}$	—	—	12
		800	$14{\cdot}0 \times 10^{-5}$	—	—	12
		—		$8{\cdot}2 \times 10^{-4}$	5090	21
Ag	Hg	25	$1{\cdot}1 \times 10^{-5}$	—	—	8
Au	Hg	11	$0{\cdot}8 \times 10^{-5}$	—	—	8
Au	Hg	25	$0{\cdot}7 \times 10^{-5}$	—	—	8
Ba	Hg	7·8	$0{\cdot}6 \times 10^{-5}$	—	—	8
Bi	Hg	25	$1{\cdot}5 \times 10^{-5}$	—	—	8
Ca	Hg	10·2	$0{\cdot}6 \times 10^{-5}$	—	—	8
Cd	Hd	20	$1{\cdot}52 \times 10^{-5}$	—	—	9
		99	$3{\cdot}4 \times 10^{-5}$	—	—	8
Cs	Hg	25	$0{\cdot}6 \times 10^{-5}$	—	—	8
Sn	Hg	25	$1{\cdot}06 \times 10^{-5}$	—	—	10
In	Hg	25	$0{\cdot}7 \times 10^{-5}$	—	—	8
K	Hg	22	$1{\cdot}47 \times 10^{-5}$	—	—	11
Na	Hg	22	$0{\cdot}80 \times 10^{-5}$	—	—	11
Pb	Hg	22	$1{\cdot}41 \times 10^{-5}$	—	—	11
Rb	Hg	7·3	$0{\cdot}5 \times 10^{-5}$	—	—	8
Sn	Hg	25	$2{\cdot}1 \times 10^{-5}$	—	—	8
Sr	Hg	9·4	$0{\cdot}5 \times 10^{-5}$	—	—	8
Tl	Hg	25	$1{\cdot}0 \times 10^{-5}$	—	—	10
Zn	Hg	20	$2{\cdot}0 \times 10^{-5}$	—	—	estimated
Ge	Al	630	$9{\cdot}2 \times 10^{-5}$	—	—	13
		666	$17{\cdot}1 \times 10^{-5}$	—	—	13
Mg	Al	670	$6{\cdot}1 \times 10^{-5}$	—	—	14
		700	$7{\cdot}5 \times 10^{-5}$	—	—	14
Si	Al	667	$4{\cdot}0 \times 10^{-5}$	—	—	13
		697	$8{\cdot}7 \times 10^{-5}$	—	—	13
Ag	Bi	—	—	$6{\cdot}2 \times 10^{-3}$	6400	33
Au	Bi	500	$5{\cdot}2 \times 10^{-5}$	—	—	8
An	Bi	450	$5{\cdot}5 \times 10^{-5}$	$5{\cdot}2 \times 10^{-4}$	3200	15
Mn	Fe	—	—	$1{\cdot}95 \times 10^{-4}$	5800	16, 27

* Containing 2·5% C. † Containing 4·6% C.

TABLE XXV—*continued*

A Diffusing in *B*		*T*,° C	$D = D_0 \exp\left(\frac{-E_D}{RT}\right)$			Ref. (see p. 579)
A	*B*		*D*, $\text{cm}^2\,\text{sec}^{-1}$	D_0, $\text{cm}^2\,\text{sec}^{-1}$	$-E_D$, cal.mole^{-1}	
Si	Fe	—	—	$2{\cdot}4 \times 10^{-4}$	8200	16, 27, (25)
Ti	Fe	—	—	$18{\cdot}1 \times 10^{-4}$	11,400	27, (25)
V	Fe	—	—	$6{\cdot}2 \times 10^{-4}$	7200	(25)
Nb	Fe	—	—	$4{\cdot}5 \times 10^{-4}$	7600	(25)
Ni	Fe	—	—		3900	27
P	Fe	—	—		1100	27
S	Fe	—	—		21,000	27
C	Fe	1300	$4{\cdot}0 \times 10^{-4}$	—	—	28
		1400	$4{\cdot}9 \times 10^{-4}$	—	—	28
U	Cd	450	$1{\cdot}3 \times 10^{-3}$	—	—	29
		650	$2{\cdot}3 \times 10^{-5}$	—	—	29
B	Si	1420	$2{\cdot}4 \times 10^{-4}$	—	—	30
Al	Si	1420	$7{\cdot}0 \times 10^{-4}$	—	—	30
Ga	Si	1420	$4{\cdot}8 \times 10^{-4}$	—	—	30
In	Si	1420	$6{\cdot}9 \times 10^{-4}$	—	—	30
P	Si	1420	$5{\cdot}1 \times 10^{-4}$	—	—	30
As	Si	1420	$3{\cdot}3 \times 10^{-4}$	—	—	30
Si	Si	1420	$1{\cdot}5 \times 10^{-4}$	—	—	30
Ga	Ge	940	$1{\cdot}03 \times 10^{-4}$	—	—	30
As	Ge	940	$3{\cdot}0 \times 10^{-4}$	—	—	30
Sb	Ge	940	$1{\cdot}6 \times 10^{-4}$	—	—	30
Se	Te	—	—	$3{\cdot}6 \times 10^{-3}$	5700	31
Hg	Ge	—	—	$2{\cdot}7 \times 10^{-3}$	5200	31
Au	Pb	500	$3{\cdot}7 \times 10^{-5}$	—	—	8
Bi	Pb	450	$5{\cdot}0 \times 10^{-5}$	$9{\cdot}6 \times 10^{-4}$	4200	15
Cd	Pb	450	$3{\cdot}9 \times 10^{-5}$	$1{\cdot}1 \times 10^{-3}$	4800	8
Pr	Pb	490	$2{\cdot}0 \times 10^{-5}$	—	—	15
Rh	Pb	500	$3{\cdot}5 \times 10^{-5}$	—	—	8
Sb	Pb	450	$3{\cdot}1 \times 10^{-5}$	$2{\cdot}5 \times 10^{-5}$	6400	15
Sn	Pb	450	$2{\cdot}6 \times 10^{-5}$	$1{\cdot}2 \times 10^{-3}$	5900	15
Ag	Sn	500	$4{\cdot}8 \times 10^{-5}$	—	—	8
Au	Sn	500	$5{\cdot}4 \times 10^{-5}$	—	—	8
Bi	Sn	450	$3{\cdot}6 \times 10^{-5}$	$1{\cdot}3 \times 10^{-3}$	500	15
Pb	Sn	500	$3{\cdot}7 \times 10^{-5}$	—	—	8
Sb	Sn	450	$3{\cdot}3 \times 10^{-5}$	$3{\cdot}3 \times 10^{-3}$	2800	15
Al	Sn	—	—	$1{\cdot}9 \times 10^{-2}$	5200	17
Zn	Sn	—	—	$6{\cdot}2 \times 10^{-3}$	4880	17
Ag	Sn	—	—	$2{\cdot}6 \times 10^{-3}$	4200	17
Ni	Sn	—	—	$2{\cdot}3 \times 10^{-3}$	4350	17
Cu	Sn	—	—	$1{\cdot}8 \times 10^{-3}$	4200	17
Se	Sn	—	—	$5{\cdot}25 \times 10^{-4}$	3200	32
O	Ag			$14{\cdot}7 \times 10^{-4}$	7100	26
Sn	Ag	—	—	$4{\cdot}4 \times 10^{-4}$	6030	18

TABLE XXVI.—*Viscosities of Solid-Solution Systems*

System	Remarks	Ref. (see p. 580)
Au–Cu	Small +ve deviations of η and E_η	1
Au–Ag		2
Bi–Sb	Small −ve deviations of η and E_η in Bi-rich alloys, becoming small, +ve, above 60 at.-% Sb	3
Cu–Ni	Linear, small −ve deviations in E_η	4
Co–Ni	η linear	5

Deviations are relative to an arbitrary linear-mixing rule (p. 446).

TABLE XXVII.—*Viscosities of Eutectic Systems*

System	Remarks	Ref. (see p. 580)
Ag–Cu	−ve deviations, decreasing rapidly as T increased. No investigation of eutectic minimum.	1, (22), (28)
,,	Eutectic minimum in η.	7
Al–Zn	Strong −ve deviations; insufficient data at eutectic composition.	8
Al–Si	Eutectic minimum in η.	9
,,	−ve deviations.	10
Bi–Cd	Eutectic minimum in η. η_{Bi} sharply decreased by small amounts of Cd. Generally −ve deviations.	3
,,	−ve deviations; insufficient data at eutectic composition.	11, 14
Bi–Sn	Eutectic minimum, −ve deviations in η.	12
,,	Eutectic maximum! Maxima in η at maximum solid-solubility-limit compositions.	10, (20)
,,	Small +ve deviations.	13, (26)
,,	—	(23)
Bi–Pb	Small −ve deviations; insufficient data at eutectic.	14, (25), (27)
,,	Dilute solutions only.	15
Cd–Pb	Dilute solutions only. −ve deviations (?)	15
Cd–Sn	−ve deviations? Eutectic minimum in η.	11, 14
K–Na	Linear composition-dependence (3 alloys only).	16
Pb–Sb	Dilute solutions only.	15
Pb–Sn	Eutectic minimum. Maxima at solid-solubility-limit compositions.	12, 17, (18)
,,	Eutectic minimum specifically sought, but not found.	19
,,	Dilute solutions only.	15
,,	—	14
Sn–Cu	Eutectic minimum in η.	(18)
Sn–Zn	Small −ve deviations.	14
,,	Eutectic minimum. Maxima at solid-solubility-limit compositions?	(18), 20
Pu–Fe	Eutectic maximum in η?	21

Deviations are relative to an arbitrary linear-mixing rule (p. 446). Measurements which may be unreliable and which, in many cases, cover only limited ranges of composition and temperature have also been reported for the following non-compound systems: Fe–Ni;[6] Cu–Pb;[22] Al–Sn;[24] Fe–Zn;(18) Pb–Zn;(18) Sb–Sn;[6,14] Cd–Zn.[14]

TABLE XXVIII.—*Viscosities of Compound-Containing Systems*

System	Remarks	Ref. (see p. 580)
Ag–Sn	Maximum at $\sim$ 15 at.-% Sn, diminishing with increasing temperature.	29
"	Eutectic minimum; too few experimental points to establish exactly.	(18)
Cu–Sn	Maxima at 20 and 45 at.-% Sn.	30, (26, 27)
"	No maxima.	(18)
Au–Sn	No measurements for $<$ 30 at.-% Sn. Slight maxima at 'AuSn', '$AuSn_2$'.	31
Al–Cu	Smooth +ve deviations.	14
"	23 at.-% Cu only.	32
Cu–Zn	Smooth +ve deviations.	27
Cd–Cu	Maximum in η and E_η, corresponding to γ-phase at 60 at.-% Cd.	33
Al–Ni	Maximum in η at 'AlNi'.	34
Cd–Sb	Maximum in η at 50 at.-% Sb at liquidus temperatures, moving to 40 at.-% Sb at $\sim$ 200 degC superheat.	35
"	—	17, 33
Sb–Zn	Maximum at 'Sb_2Zn_3'.	3
Mg–Pb	Maximum in η and E_η at 'Mg_2Pb'.	36
Mg–Sn	Maximum in η and E_η at 'Mg_2Sn'.	37
In–Sb Ga–Sb Al–Sb	Maxima at 'InSb', 'GaSb', 'AlSb'.	38, 39
Ga–As In–As	Maxima at 'GaAs', 'InAs'.	44
In–Te Ga–Te	Maxima at 'In_2Te_3', 'Ga_2Te_3'.	29
Hg–Tl	Maximum at 'Hg_5Tl_2'?	40
Cu–Sb	Eutectic minimum in? high-Sb alloys only.	41
Fe–C, S, P; other Fe-based alloys.		(42), 45, 49, 52
Mn–Si, Fe, C; other Mn-based alloys.		(43)
Dilute amalgams		22, 47, 48, 50

Sources in parentheses may be unreliable.

Viscosity deviations are relative to an arbitrary linear-mixing rule (p. 446).

Measurements, which may be unreliable, have also been reported for: Al–Na;[24] Al–Mg;[24] Al–Ca;[24] Al–Ti;[24] Cu–Sb;[27] Hg–K;[46] Hg–Na;[46] Ni–Sn;(18) Pb–Tl;[33] Bi–Tl;[33] Mg–Pb;[15] Fe–Si.[51]

TABLE XXIX.—*Thermal Diffusion in Liquid Alloys*

System A–B	T_H, °C	T_C, °C	Initial Concentration of B, at.-%	α (eqn. 4.11)	S_c	Ref. (see p. 581)
Sn–Cu	790–800	360–400	5	+ve	—	2
Sn–Cd	320	270	50	0·30	—	1
,,	900	360	84	+ve	—	2
,,	650	400	?	—	(0·002–0·0005)	7
Sn–Zn	400	350	50	4·10	—	1
,,	790	360	44, 47	+ve	—	2
,,	650	400	4·5–95	—	—	3, 6, 7
Sn–Hg	320	270	50	−9·51	—	1
Sn–Ga	320	270	50	0·18	—	1
Sn–Pb	320	270	50	1·90	—	1
,,	475	425	50	0·83	—	1
,,	600–900	220–400	6–77	+ve	—	2
,,	650	400	4·5–97	—	(0·002–0·0005)	3, 4, 6, 7
Sn–Bi	320	270	50	0·10	—	1

TABLE XXX.—*Atomic Volume, Volume Change on Fusion, Bulk Coefficients of Expansion, and Compressibilities of the Liquid Elements at Their Melting Points*

Element	Atomic Volume cm³ g-atom⁻¹	Vol. Change on Fusion, % of Solid Volume	Ref. (Columns 2 and 3) (see p. 582)	α Solid	α Liquid	α_S/α_L	Ref. (α_L) (see p. 582)	Adiabatic Compressibility (β_A), atm⁻¹ × 10⁶	Ref. (β_A) (see p. 582)
				cm³ g-atom⁻¹ deg⁻¹ × 10³					
Li	13·68	1·65	17	0·17	—	—	—	—	—
Na	24·74	2·5	18	0·22	0·275	0·80	23, 1, 27	17·7	9
K	47·15	2·55	23	0·25	0·29	0·86	23, 1, 27	—	—
Rb	58·00	2·5	17, 18, 49	0·27	0·34	0·79	18	42·7	9
Cs	72·25	2·6	17	0·29	0·365	0·79	28	58·1	9
Be	5·35	7·0	58	0·036	0·093	0·39	58	—	—
Mg	15·29	3·1	7, 19, 55	0·078	0·166	0·62	19, 55	—	—
Ca	—	—	56	0·066	—	—	—	—	—
Ba	32·41	—	50, 56	0·057	—	—	—	—	—
Ce	21·00	0·3	31	0·024	—	—	—	—	—
Al	11·38	6·0	19	0·070	0·122	0·57	19, 29	—	
Si	11·12	−9·6	8, 16, 45	0·23	0·145	1·59	16	—	—
Cu	7·95	+4·15	12, 17, 18, 20, 21, 41, 45, 48	0·051	0·100	0·50	12, 30, 41	—	—
Ag	11·59	3·8	12, 21, 32, 45, 57	0·057	0·097	0·58	12, 21, 32, 57	—	—
Au	(11·50)	5·1	17, 18, 22	0·042	0·069	0·61	22	—	—
Zn	9·95	4·2	24, 25, 45, 40	0·093	0·150	0·60	24, 26, 33	1·95	9
Cd	14·05	4·0	3, 18	0·093	0·151	0·62	3, 23, 26, 32, 33, 35	2·58	
Hg	14·82	3·65	18, 23, 51, 54	0·180	0·182	0·99	1, 23, 36	0·93	1, 2
Ga	11·54	−3·2	1	0·037	0·126	0·29	37	2·19	9
In	16·38	+2·0	3	0·074	0·12	0·62	3	2·90	9
Tl	18·07	2·2	3	0·090	0·14	0·64	3, 23	3·40	9
Ge	13·22	−5·0	5, 6, 16, 45	0·018	0·094	0·19	5, 16	—	—
Sn	17·03	+2·6	18, 21, 23, 15, 40, 43, 45	0·070	0·088	0·80	23, 26, 30, 33, 40, 43	2·79	9, 15
Pb	19·58	3·5	18, 23, 25	0·087	0·127	0·69	3, 23, 26, 33, 35	2·92	9, 15
As		+10·0	53				33, 35		
Sb	18·80	−0·95 +0·5, +0·8	16, 26, 42, 45, 53	0·033	0·096	0·35	16, 21, 34, 42	—	—

Bi	20·90	−3·35	16, 18, 21, 23	0·040	0·11	0·36	16, 23, 44	3·70	9, 15
Se	19·7	+16·8	38, 46	0·18	0·40	0·45	38	—	—
Te	22·01	4·9	3, 6, 45, 13, 52	—	0·096	—	3, 13	—	—
V	—	—	—	0·024	—	—	—	—	—
Cr	8·50	—	—	0·020	—	—	—	—	—
Mn	—	—	—	0·067	—	—	—	—	—
Fe	7·95	3·0	4, 45, 59, (47)	0·036	0·12	0·16	39	—	—
Co	7·65	—	45, (47)	0·037	—	—	—	—	—
Ni	7·62	—	45, 59, (47), (48)	0·090	—	—	—	—	—
Pd	10·14	—	12, 45	0·033	0·120	0·27	12	—	—
Pt	10·32	—	12, 45	0·027	0·153	0·18	12	—	—
U (natural)	13·30	—	55	0·05	0·058	0·86	11	—	—
Pu	14·52	−2·5	10	—	—	—	—	—	—

Data for solid from "Metals Handbook", (Ref. 14).

TABLE XXXI.—*Values of the Integral* $\frac{1}{4k_F^4}\int_0^{2k_F} . a(K) . K^3 \, dK$

Metal	Integral	Metal	Integral
Zn	1·11	Tl	0·97
Cd	1·19	Ge	1·32
Hg	1·12	Sn	1·06
Al	1·04	Pb	0·92
Ga	1·25	Bi	0·90
In	0·97		

(Values calculated from measurements of $a(K)$ at or very near the melting point.) (From General Reference 297.)

TABLE XXXII.—*Resistivities at Constant Pressure of Solid and Liquid Metals at the Melting Point, and the Temperature-Dependence of* ϱ_L

Element	(1) ϱ_L, ohm-cm	(2) ϱ_S, ohm-cm	(3) $\frac{\varrho_L}{\varrho_S}$ at T_F	Ref. (Columns 1 to 3) (see p. 583)	(4) α_L, μohm-cm. deg^{-1}	(5) β_L, μohm-cm	Ref. (Columns 4 and 5) (see p. 583)
Li	24·0	—	—	1	N.L.	?	1, 31
Na	9·57	6·60	1·45	1	0·038	−4·5	2, 32, (3)
K	12·97	8·32	1·56	1, 4	0·066	−8·6	1, 3, 32, (5)
Rb	22·0	13·7	1·60	4	0·077	−5·0	3, 32, (6)
Cs	36·7	21·7	1·66	4	0·114	0·4	3, 7, 32
Cu	21·1	10·3	2·44	6	0·009	9·1	6, (8)
Ag	17·2	8·2	2·09	6, (33)	0·009	6·2	6, (33)
Au	31·2	13·7	2·28	6	0·014	12·6	6
Mg	27·4	15·4	1·78	6	0·005	22·9	6
Ba	(135)	(80)	1·7	9	No data		—
Zn	37·4	16·7	2·24	6, 26	(−ve) N.L.	?	6, 10, 26
Cd	33·7	17·0	1·97	11, 33, 26	(0) N.L.	?	6, 10, 33, 26
Hg	90·96	Anisotropic	3·74–4·94	12, 13	(+ve) N.L.	?	26
Al	24·2	10·9	2·20	6	0·014(5)	10·7	6
Ga	25·8	Anisotropic	0·45–3·12	14, 26	0·019(5)	19·9	15, 26
In	33·1	15·2	2·18	6, 33	0·025(5)	22·2	6, 33
Tl	73·1	35·5	2·06	6	0·029	56·3	6
Si	80	2400	0·035	16, (17), (34)	0·113	−113·0	16, (17), (34)
Ge	71	1000	0·071	17, 18, 26, 36	(0·047)	(11·0)	26
Sn	48·0	22·8	2·10	6, 33	0·025	35·4	6, 33
Pb	95·0	49·0	1·94	6, 26, 33	0·048	66·6	6, 33, 26
Sb	113·5	183	0·61	6, 33, (26)	0·027	87·9	6, 26, 33
Bi	128·0	Anisotropic	0·35–0·47	19, 26, (6)	0·057	99·0	6, 26, 33
Se	2 × 10^8	2 × 10^8	1·0	20, (21)	N.L.	—	20, (30)
Te	600	Anisotropic	0·048–0·091	22, 26, 28	−ve (N.L.)	?	22, 26, 28, 29
Mn	40	66	0·61	23	No data		—
Fe	138·6	127·5	1·09	24, (8)	0·033	50	8
Ni	85·0	65·4	1·3	8	0·013	63	8
Co	102	97	1·05	8	0·061	−6	8
Pt			1·40				
W	No data		1·08	25	No data		—
Mo			1·23				

TABLE XXXIII.—*Resistivities at Constant Volume*

Quantity in Equation (6.23)	Na	K	Rb	Cs	Hg	Ga
$(\varrho_L)_P$, ohm-cm	9·6	13·0	22·0	36·7	90·96	25·8
$(\alpha_L)_P$, ohm-cm.deg^{-1}	0·038	0·066	0·077	0·114	N.L.	L
$(\alpha_L)_V$, ohm-cm.deg^{-1}	0·021	0·030	0·049	0·084	N.L.	L
$(\varrho_0)_V$, ohm-cm	1·5	3·1	6·7	11·3	—	—
Ref. (see p. 584)	2, (3)	2, (3)	2, (3)	2, (3)	1, 4, (3)	1, 3

N.L. = not linear. L = linear.

TABLE XXXIV.—*Resistivities: Systems with Constant e/a Ratio*

System	Ref. (see p. 584)	Details of Anomaly, at.-% of Second Component (see text)						Remarks
		1st Anomaly			2nd Anomaly			
		1st Max.	Min.	2nd Max.	1st Max.	Min.	2nd Max.	
Ag–Au	1, (8)	28	30	34	67	70	72	ϱ_L isotherm concave downwards, max. at 60 at.-% Au.
Ag–Cu	1, (7)	28	31	—	67	70	71	Anomalies very marked at 66 at.-% Cu; ϱ_L isotherm concave downwards, max. at 70 at.-% Cu.
Au–Cu	1	28	30	32	68	73	75	ϱ_L isotherm concave downwards, max. at 45 at.-% Cu.
Cd–Hg	2, (10), (13)	28	33	36	67	70	72	Approximately linear composition-dependence of ϱ_L, α_L.
Cd–Zn	2, (11), (12)	30	(33)	38	60	(67)	72	Anomalies very marked
Ga–In	2	No significant anomaly			No significant anomaly			Approximately linear composition-dependence of ϱ_L, α_L.
Pb–Sn	3, (8), (5), (6), (15–21)	20	28	33	65	71	74	Approximately linear composition-dependence of ϱ_L.
Bi–Sb	2, (8), (11), (17)	27	30	33	67	71	75	Discontinuity in ϱ_L; α_L isotherm slightly concave downwards.
Average		27	31	34	66	70	78	

General Note: The anomalies in ϱ_L are reported *only* by Refs. 1–3. No other measurements have been carried out in sufficient detail. Other systems with components of equal valence for which less detailed results have been published are: Li–Na;[4] K–Na;[4,5,22] Na–Rb;[4] Na–Ag;[4] Na–Au;[4] K–Rb;[6] Hg–Be;[9] Hg–Mg;[10] Hg–Zn;[32] Ge–In;[14] Co–Ni;[23] Se–Te;[24–28] Cr–Fe;(30) Fe–Mn;(31) Mg–Zn.(46) Data or references in parentheses may be unreliable.

TABLE XXXV.—*Resistivity at Constant Pressure: Systems with Varying e/a Ratio*

System	Ref. (see p. 584)	Valence Electron Concentration of Anomaly 1st Max.	Min.	2nd Max.	Remarks
Ag–Pb	33	2·14	2·23	2·31	$(\varrho_L)_{Ag}$ increased ×6 by 30 at.-% Pb. Shallow maximum in ϱ_L at ∼80 at.-% Pb
Ag–Sn	1, 3, 17	2·16	2·29	2·38	See Table XXXVI.
Au–Pb	33	2·14	2·26	2·35	$(\varrho_L)_{Au}$ increased ×3 by 20 at.-% Pb. Smooth ϱ_L isotherm. Discontinuity in α_L?
Au–Sn	33	2·02	2·14	2·20	See Table XXXIV.
Cu–Sn	1, 12, (7), (18), (40)	2·20	2·25	2·39	See Table XXXIV.
Cd–Pb	2, (11), 5	2·20	2·30	2·44	ϱ_L isotherm slightly concave downwards.
Hg–In	2, 14, 44, (10)	2·20	2·35	2·40	Anomalies very slight, not reported by Ref. (44).
Hg–Tl	3, 14, 45, (9), (32)	2·21	2·28	2·38	Anomalies very slight, not reported by Ref. (45).
Zn–Al	1, 12, 17, (19)	2·22	2·30	2·38	ϱ_L isotherm linear. Anomalies very marked
Zn–Sn	1, 17, 12, (11), (15)	2·30	2·30	2·43	ϱ_L isotherm concave downwards. Marked anomalies.
Average (excluding Au–Sn)		2·20 ±3%	2·28 ±3 %	2·38 ±3%	
Bi–Pb	17, 36, (5), (11)	4·12	4·15	4·20	
Bi–Sn	17, 35, (11), (19)	4·18	4·20	4·23	
Pb–Sb	36, (5), (11)	4·20	4·22	4·25	
Sb–Sn	35, (11), (15)	4·20	4·22	4·24	
Average		4·8 ± 1·5%	4·2 ± 1%	4·23 ± 1%	

General Note: The anomalies in ϱ_L are reported *only* by Refs. 1–3, 33, 35, 36. No other measurements have been carried out in sufficient detail.

Other systems with components of different valence for which less detailed results have been published are:

I–II systems: Hg–Li, Na, K, Ag;[32] Cu–Zn;[7,11,12] Cu–Cd;[7,81] Hg–Cu;[34,37] Hg–Ag;[32,34,38] Hg–Au;[37,38] Cd–Na;[4,15] Hg–Na;[5,39] Hg–K.[5]
I–III systems: Al–Cu;[7,12,40,(19)] Ag–Al.(19)
I–IV systems: Na–Sn;[15] Na–Pb;[4,15] Cu–Pb.[7]
I–V systems: Cu–Sb;[15,41] Ag–Bi.[17]
I–VI systems: Cu–Te;[42,(28)] Ag–Te;[42] Cu–S;[43] Ag–S;[43] Cu–Se.(28)
II–III systems: Hg–Ga.(34)
II–IV systems: Mg–Sn;[46] Zn–Pb;[45,16] Cd–Sn;[11] Hg–Sn;[13,20,32] Hg–Pb;[13,20,32] Hg–Ge.[9,34]

TABLE XXXV—*contd.*

II–V systems:	Zn–Sb;[11,12,17,28,47] Cd–Sb;[11,21,47,75] Cd–Bi;[11,17] Hg–Bi;[1,3] Hg–Sb;[9] Mg–Bi.[66]
II–VI systems:	Zn–Te;[28,48] Cd–Te;[28,48,50] Hg–Se;[23,49] Hg–Te.[28,50]
III–IV systems:	Al–Sn;[17,(19)] Ga–Sn;[14] In–Pb;[8] Al–Si;(19) Al–Ge.(19)
III–V systems:	Ga–Bi;[17] In–Sb;[54–58] Ga–Sb;[28,(54–56)] Al–Sb;(56) In–As;[59] Ga–As;[59] Bi–Tl;[73] Sb–Tl;[73] As–Tl.[73]
III–VI systems:	Tl–Te;[51,52,73] Ga–Te;[53] In–Te;[53] Se–Tl;[73] S–Tl.[73]
IV–V systems:	None.
IV–VI systems:	Pb–Se;(28) Pb–Te;(28) Sn–Te.[42]
V–VI systems:	Bi–Se;(28) Bi–Te;[47,(28)] Sb–Te;[60,(28),(61)] Sb–Se;[62] Sb–S;[62] Sb–S;[63] As–Se, Te.[67]
Other Systems:	Co–S;[43] Ni–S;[43] Fe–S;[64] Ni–Te;(28) Co–Te;(28) Fe–Te;(28) Mn–Si;(31) Mn–C,(31) Cr–Si;(65) Al–Cr;(30) Cu–Ni.[23]

Data or sources in parentheses may be unreliable.

TABLE XXXVI.—*Resistivities at Constant Pressure: Compound-Containing Systems*

System	Ref. (see p. 584)	ϱ_L	α_L
Ag–Sn	1	Max. at 27 at.-% Sn, 800–1200°C (Solid-state: δ and ε electron compounds at 16 and 25 at.-% Sn, respectively). Anomaly at $e/a = 2{\cdot}3$.	$\alpha_L \sim 0$ at 20 at.-% Sn, becoming +ve with increasing T. Discontinuity at 1100°C, 10–30 at.-% Sn.
Cu–Sn	1, 11	Max. at 25 at.-% Sn, 800–1200°C. (Solid-state: δ and ε electron compounds at 20 and 25 at.-% Sn and η phase at 45 at.-% Sn (NiAs structure)). Anomaly at $e/a = 2{\cdot}3$.	α_L −ve at 20 at.-% Sn at 800°C becoming +ve with increasing Ti; small max. at ∼45 at.-% Sn. Discontinuity at 1100°C, over 10–30 at.-% Sn.
Au–Sn	33	Slight maxima at '$AuSn$', '$AuSn_2$', and '$AuSn_4$', at 450°C. Pronounced max. at 22 at-.% Sn; anomaly at $e/a = 2{\cdot}15$. (ϱ_L)Au increased ×2·8 by 22 at.-% Sn.	$\alpha_L \sim 0$, and invariant with 900°C.
Mg–Pb	1	Sharp increase in ϱ_L of Mg up to 'Mg_2Pb'; ϱ_L varies little with composition, 33–100 at.-% Pb.	Min. at 'Mg_2Pb'.
Mg–Sn	46	Sharp increase in ϱ_L of Mg up to 'Mg_2Sn'; ϱ_L varies little with composition, 33–100 at.-% Sn.	Min. at 'Mg_2Sn'.
Mg–Bi	66	Sharp max. at 'Mg_3Bi_2'.	No data.
Al–Sb	5, 6	Sharp max. at 'AlSb'.	$\alpha_L \sim 0$ at 'AlSb', but large, −ve, at other compns.
Ga–Sb	55, 56	Sharp max. at 'GaSb'.	$\alpha_L \sim 0$ at 'GaSb', but large, −ve, at other compns.
In–Sb	55, 56	Sharp max. at 'InSb'	$\alpha_L \sim 0$ at 'InSb', but large, −ve, at other compns.
Cu–Cd	11	Insufficient data	
Cu–Zn	11		
Cu–Sb	11		
Cd–Sb	11		
Zn–Sb	11		

TABLE XXXVII—*Resistivities at Constant Pressure: Liquid Intermetallic Compounds at the Melting Point*

Compound	ϱ_L, ohm-cm	ϱ_L/ϱ_S	a_S	a_L	Ref. (see p. 584)	V_F, % of Sol. Volume	Ref. (see p. 584)	T_F, °C	Remarks
$MgZn_2$	100	2·0	+	+	46	+4·7	71	590	C14 Laves phase.
$HgSe$	5×10^4	20	+	—	(28)	+5·5	28	680	ZnS (B3).
$HgTe$	(560)	(0·07)	+	—?	(28)	—	—	680	ZnS (B3).
$CdTe$	$1·5 \times 10^4$	0·1	—	—	48	—	—	1050	ZnS (B3).
$ZnTe$	$1·82 \times 10^4$	0·1	—	—	48	—	—	1239	ZnS (B3).
$AlSb$	(85)	0·12	—	+	(56)	—	—	1065	ZnS (B3).
$GaSb$	(62)	0·12	—	+	(54–56)	−6·3	28	706	ZnS (B3).
$InSb$	105	0·24	—	+?	57, (54–56)	−10·4	58	530	ZnS (B3).
$GaAs$	(120)	0·13	—	+	(59)	—	—	1238	ZnS (B3).
$InAs$	(160)	0·64	—	+	(59)	—	—	706	ZnS (B3).
Ga_2Te_3	$6·3 \times 10^3$	$(1·2 \times 10^{-2})$	—	—	(53)	—	—	790	Cation-deficient ZnS (B3).
In_2Te_3	$3·2 \times 10^2$	$(10^{-3}$	—	—	(53)	—	—	667	ZnS (B3) cation-deficient.
Tl_3Te_2	$3·03 \times 10^3$	—	?	—	73	—	—	43	Probably the same compound;
Tl_2Te	$3·3 \times 10^3$	—		—	51, 52	—	—	43	Structures not known.
Tl_2Se	$3·31 \times 10^5$	—	?	—	73	—	—	390	Structure uncertain.
$TlSe$	$8·85 \times 10^5$	— =	?	—	73	—	—	330	Tetragonal (B37).
$PbSe$	$(2·4 \times 10^3)$	(1·0)	—	—	(28)	—	—	1088	NaCl (B1).
$PbTe$	(950)	(0·25)	+	—	(28)	—	—	917	NaCl (B1).
Bi_2Se_3	$1·1 \times 10^3$	(0·70)	+	—	(28)	—	—	706	Rhombohedral (C33).
Bi_2Te_3	$2·4 \times 10^3$	0·43	—	—	47, (28)	—	—	585	Rhombohedral (C33).
Sb_2Se_3	$(\sim 10^5)$	(1·0)	?	—	62	—	—	600	$D5_8$.
Sb_2Te_3	500	0·68	+	—	60, (61)	—	—	622	Rhombohedral (C33).
Sb_2S_3	3×10	—	—	—	63	—	—	546	$D5_8$.
Mg_2Pb	113·6	0·49	+	0	1, 68	—	—	550	CaF_2 (C1).
Mg_2Sn	120	0·0023	—	0	46, 69	—	—	778	CaF_2 (C1).
$CdSb$	$5·0 \times 10^3$	—	?	—	11, 47	—	—	456	Orthorhombic.
$ZnSb$	$5·0 \times 10^3$	—	—	—	11, 47, (28)	—	—	563	Orthorhombic? Melts incongruently.
Cu_2Se	5×10^3	(1·0)	0	0	(28)	—	—	1100	F.C.C.?
$FeTe_2$	$2·9 \times 10^3$	(1·5)	—	—	(28)	—	—	900	Orthorhombic (C18) FeS_2.
$CoTe_2$	$1·6 \times 10^2$	(1·5)	—	+	(28)	—	—	950	FeS_2 (C18) ≡ cation-deficient CoTe (B8).
$NiTe_2$	8×10^2	(1·2)	—	+	(28)	—	—	850	CdI_2 (C6) ≡ cation-deficient NiTe (B8).
$CuTe$	$4·4 \times 10^3$	(1·7)	0	—?	(28)	—	—	860	Orthorhombic. Melts incongruently.

Because of the extensive changes in the properties of the liquid that are reported as taking place over a small range of temperatures above the melting point, some of the values of ϱ_L/ϱ_S may not be reliable. Reference should be made to the original papers before a value is accepted. Note also that in some cases the purity of the materials was not high, and that much of this work is not yet supported by independent observations.

TABLE XXXVIII.—*Thermal Conductivity of Solid and Liquid Metals Close to the Melting Point*

Metal	κL, joule-cm^{-1} sec^{-1} deg^{-1}	$\kappa S/\kappa L$	Lorenz Number, 10^{-8} V^2 deg^{-2} ($\sim 2{\cdot}45 \times 10^{-8}$ V^2 deg^{-2})	Ref. (see p. 585)
Li	0·46	—	2·6	1, 10, 11
Na	0·86	1·31	2·22	2, 4
K	0·45 (200°C)	—	2·07 (200°C)	4
Zn	0·59	1·5	3·2	2
Cd	0·44	2·4	2·5	2
Hg	0·086 (30°C)	—	2·75	3
Al	0·92	1·47	2·4	2
Ga	0·34	1·06 Ref. (6)	2·8	5, (6)
Tl	0·25	2·04	3·2	2
Sn	0·31	1·82	2·9	6
Pb	0·16	1·83	2·44	2, 7, 12
Sb	0·21	1·1	2·6	2
Bi	0·11	0·5 Ref. (6)	2·53	7, (6), 12
Te	0·18	0·17		8, 9

TABLE XXXIX.—*Thermoelectric Properties of Liquid Metals Close to the Melting Point*

Metal	$S_L - S_S$, V. deg^{-1}	x (equation 6.14)	Ref. (see p. 586)
Li	6·0	−8·8	1
Na	0·0	2·9	1, 2, 11
K	2·3	3·5	1, 2, 11
Rb	2·8	1·7	1, 2, 11
Cs	5·2	−1·3	1, 11
Cu	0·5	−3·5	1
Ag	0·0	−1·9	1
Au	0·0	−0·6	1
Zn	−8	+0·3	2, (3)
Cd	—	0·0	2
Hg	−1·5	3·9	4, 11, (2)
Ga	—	0·7	4, (2)
In	—	1·4	2
Ge	70	0	5
Sn	1·2	0·6	2, (6)
Pb	—	2·6	2
Bi	50	0·9	2, (7)
Te	22	—	8, 9, 10

Data or sources in parentheses may be unreliable.

TABLE XL.—*Hall Coefficients near the Melting Point*

Metal	$-R_{\text{Free}} = 1/N\,\lvert e\rvert$ (liquid) e.m.u. × 10^4	$-R_L$ e.m.u. × 10^4	R_L/R_{Free}	$-R_S$, e.m.u. − 10^4	R_S/R_{Free}	Ref. (see p. 586)
Na	25·63	26	1·01	26	1·0	1
Rb	60·08	(60)		60	0·99	2
Zn	5·15	5·2	1·01	−3	−0·58	3, 5, (1)
Cd	7·27	7·2	0·99	−2	−0·27	5, 3, 9, (1)
Hg	7·68	7·6	0·99	9·5	1·2	3, 5, 7, 1, 6, (4)
Ga	3·98	3·8	0·95	—	—	1, 3, 5, 6
In	5·66	5·3	0·94	3	0·54	3, 5, 9, (4)
Tl	6·24	4·8	0·77	—	—	5
Ge	3·42	(3·6)	1·05	$\sim -9{\cdot}75 \times 10^3$	-3×10^3	(1)
Sn	4·41	4·4	1·00	2	0·47	4, 5, 9
Pb	5·07	3·7	0·73	~0	~0	3, 5, (1)
Sb	3·89	(4·4)	(1·13)	~−87	~25	1
Bi	4·33	3·0	0·69	~−1050	~−250	5, (1), (9)
Te	3·80	1·4	0·37	—	—	11, (12)

TABLE XLI.—*Optical Properties of Liquid Metals*

Metal	$\frac{N_{\text{obs.}}}{N_{\text{val.}}}$	$\frac{\sigma_{\text{opt.}}}{\sigma_{\text{elect.}}}$	Ref. (see p. 586)	Metal	$\frac{N_{\text{obs.}}}{N_{\text{val.}}}$	$\frac{\sigma_{\text{opt.}}}{\sigma_{\text{elect.}}}$	Ref. (see p. 586)
Cu	0·84	0·70	3	Bi	1·06	0·99	5
Ag	1·13	0·96	3	Sb	1·22	0·99	5
Cd	1·07	0·79	5	Te	NFE	NFE	6
Hg	0·98	1·01	1, 9, (2)	Zn(*S*)	0·10	0·2	1
Ga	0·98	0·97	1, 8	Al(*S*)	0·45	0·2	1
In	1·00	1·00	1				
In	1·07	0·93	5				
Ge	1·08	0·82	4, (7)				
Sn	1·05	0·95	4				
Sn(*S*)	0·33	0·55	1				
Pb	1·18	0·94	4				
Pb(*S*)	0·32	0·7	1				

(*S*) = solid.
NFE = not free electron.

Data have also been reported for liquid Fe (Ref. 10). Sources in parentheses may be unreliable.

TABLE XLII.—*Magnetic Susceptibilities of Liquid Metals near the Melting Point*

Metal	χ_L, e.m.u. $g^{-1} \times 10^6$	$(\chi_L - \chi_S)$ e.m.u. $g^{-1} \times 10^6$	$\chi_L - \chi_I{}^* = \chi_E$, e.m.u. $g^{-1} \times 10^6$	χ_P e.m.u. $g^{-1} \times 10^6$	Ref. (see p. 586)
Li	3·4	−0·15	3·5	1·5	1
Na	0·6	−0·04	0·8	2·66	3,13
K	0·5	−0·03	0·9	0·60	3
Rb	0·21	−0·02	0·51	0·32	3
Cs	0·20	−0·02	0·50	0·28	3
Cu	−0·21	−0·12	0·10	0·11	5, 9
Ag	−0·32	−0·10	0·07	0·08	5, 6
Au	−0·23	−0·07	0·07	0·04	5
Zn	−9·10	0·02	0·14	0·16	7, 9
Cd	−0·19	0·13	0·05	0·11	6, 7, 9, 13
Hg	−0·18	−0·06	0·06	0·07	5, 14
In	−0·06	0·06	0·18	0·05	6, 7
Tl	−0·15	0·02	0·05	0·09	5, 6, 9
Si	−0·08	0·03			13
Ge	0·07	0·18	0·22	0·23	7, 13
Sn	−0·04	0·06	0·16	0·16	5, 9, 14
Pb	−0·07	0·03	0·09	0·10	6, 7, 9
Sb	−0·02	0·38	0·15	0·18	6, 7, 9
Bi	−0·05	0·85	0·09	0·12	6, 7, 9, 13
Se					10
Te	−0·03	0·25	0·08	0·11	9, 10
Fe	24·6	−6·2	—	†	12
Ni	5·7	0·0	—	†	12
Co	49·5	−1·5	—	†	12, 14
Mn	15·0	−10·3	—	†	12

*χ_I values are taken from Ref. (8)
† Free-electron model inapplicable.

TABLE XLIII.—*Knight Shift in Liquid Metals*

Metal	K_S, %	K_L, %	Metal	K_S, %	K_L, %
Li	0·026	0·026	Hg	2·45	2·45
Na	0·114	0·116	Al	0·164	0·164
Rb	0·654	0·662	Sn	0·75	0·73
Cs	1·49	1·46			

Data from General Reference (327).

TABLE XLIV.—*Magnetic Susceptibility of Alloys*

System	Ref. (see p. 587)	Results and Remarks
Bi–Sb	1, 2	χ_L linearly dependent upon composition (680°C).
Bi–Pb	1, 2	” ” ” ” ” (380°C).
Pb–Sn	1, 2, 17	” ” ” ” ” (380°C).
Bi–Sn	1, 2, 17	Smooth composition-dependence.
Pb–Sb	1, 2, 17	” ” ”
Fe–Co	3, 4	Anomalous change in χ_L, 40–45 at.-% Co; χ_L roughly composition-dependent at other compositions.
Ni–Co	3, 4	Smooth composition-dependence.
Fe–Ni	3, 4, 7	” ” ”
Cu–Co	5, 6	Smooth composition-dependence. Immiscibility in supercooled liquids.
Cu–Fe	5, 6	Smooth composition-dependence. Immiscibility in supercooled liquids.
Cu–Mn	5	Smooth composition-dependence.
Cu–Cr	5	” ” ”
Bi–Te	1, 2	Minimum in χ_L at 'Bi_2Te_3'.
Pb–Te	1, 2	Smooth composition-dependence.
Sb–Te	1, 2	Minimum at Sb_2Te_3.
Sb–Zn	1, 2	Minimum at 'SbZn', 'Sb_2Zn_3'.
Sn–Te	1, 2	Minimum at 'SnTe'.
Cd–Sb	1, 2	Minimum at CdSb.
Cu–Zn	1, 2	? Minimum at 60 at.-% Zn?
Cu–Sn	1, 2	Minimum at $\sim$ 25 at.-% Sn.
Al–Sb	8, 9	Minimum at 'AlSb'.
In–Sb	9, 14, 15, 16	Minimum at 'InSb'.
Ga–Sb	8, 9, 16	Minimum at 'GaSb'.
Fe–Si	3, 10, 18	? Minimum at 'FeSi'? Two sources disagree.
Fe–Mn	10	Smooth composition-dependence.
Fe–P	10	Minimum at 'Fe_2P'.
Sb–Pd	11	Minimum at 'PdSb'.
Amalgams	12, 13	Ionic behaviour?—see text.
Ga–As	16	GaAs only.
In–As	16	InAs only.
Zn–Te	16	ZnTe only.
Cd–Te	16	CdTe only.
Ga–Te	16	Ga_2Te_3 only.
In–Te	16	In_2Te_3 only.
Ag–Bi	17	Smooth composition-dependence.
Bi–Cd	17	Nearly linear composition-dependence.
Bi–In	17	Slight maxima (?) at 30, 75 at.-% In.
Hg–In	19	Non-Pauli–Landau.

TABLE XLV.—*Electrotransport in Liquid Metals and Alloys*

Solvent	Migrating Solute	Initial Solute Concentration, at.-%	T,°C	Migration Velocity (U_i), cm^{2}V^{-1}h^{-1}	Effective Valence (Z°)	Direction of Migration of Solute	Ref. (see p. 587)
BINARY SOLUTIONS						to:	
Hg	Li	Dilute	25	+0·41	—	C	1
	Na	,,	25	−0·43	—	A	1
	Na	0·85–4·23	232–334	1·3–2·0	—	A, C*	5
	K	Dilute	25		—	C	1, 2
	Ag	,,	,,	2·2	—	C	1
	Au	,,	,,	1·5	—	C	1, 2
	Mg	,,	,,	3·5	—	C	1, 2
	Zn	,,	,,	4·5	—	C	1, 2
	Cd	,,	,,	3·5	—	C	1, 2
	Ga	,,	,,	2·9	—	C	1, 2
	In	,,	,,	3·05	—	C	2
	Tl	,,	,,	0	—	—	1
	Sn	,,	,,	1·9 2·3	—	C	1, 2
	Pb	,,	,,	0	—	—	1, 2
	Bi	,,	,,	−2·9 −3·9	—	A	1, 2
	Ca	,,	,,	0·2	—	C	1
	Cs	,,	,,	4·3	—	C	1
				K_i†			
Na	In	,,		—	—	A	18
	Tl	—	—	$21 \times 10^{+4}$	—	A	13, 17, 18
	Hg	0·6	110	$9 \times 10^{+4}$	−18	A	3, 17
	Hg	1·1	110	$15 \times 10^{+4}$	−7·7	A	3
	Cd	0·21	110	$25 \times 10^{+4}$	−13	A	3, 16
	Pb	0·45	110	$1 \times 10^{+4}$	−21	A	3, 16
	K	1·6	100		−0·8	A	4
	Ba					A	18
	Ag Sr	No migration				—	18
K	Na	5·5	100	$0·5 \times 10^{+4}$	− 0·5	A	4
	Hg	0·4	100	$12 \times 10^{+4}$	−10	A	6, 16, 17
	Tl	0·19	110	$23 \times 10^{+4}$	−20	A	3, 17
	Pb	0·6	100	$26 \times 10^{+4}$	−22	A	6
Cu	H	—	—	—	—	C	11
Cd	Ag	—	—	—	−1·2	A	7
	Au	—	—	—	−2·2	A	7
	Bi	2·1	350	—	—	A	8, 9, 13
	Bi	15–45	?	—	—	A	1
	Sn	60					
	Sn	0·37	360	—	—	A	8, 9
	Sn	25–75	300	—	—	A	1
	Pb	—	—	—	—	A	1
Al	Ag	—	—	—	—	A	1
	Au	—	—	—	—	A	1
	H	—	—	—	—	C	11

* Direction of migration reverses at 4 at.-% Na at temperatures < ~ 300°C, see Ref. (5) for details.

† $K_i = U_i T / D_i$.

TABLE XLV—*continued*

Solvent	Migrating Solute	Initial Solute Concentration, at.-%	T,°C	Migration Velocity (U_i), cm^{2}V^{-1} h^{-1}	Effective Valence (Z°)	Direction of Migration of Solute	Ref. (see p. 587)
In	Ag	—	—	—	−0·74	to: A	7
Tl	Ag	—	—	—	+0·64	C	7
	Au	—	—	—	−0·28	A	7
Sn	Co	—	—	—	—	A	14
	Sb	—	—	—	—	A	15
	Cu	—	—	—	—	C	1
	Ag	—	—	—	−1·07	A	1, 7
	Au	—	—	—	−2·2	A	7
	Zn	—	—	—	—	C	1
	Ga	0·17	300	—	+0·6	C	8, 9
	Bi	2·85	350	—	−0·8	A	8, 9, 13
Pb	Ag	0·02	360	—	+0·33	C	8, 9, 14
	Ag	—	—	—	+0·48	C	7
	Ag	35–70	1000	—	—	C	1
	Au	—	—	—	−0·1	A	7
	Zn	0·13	360	—	0·5–0·9	C	8, 9
	Sn	—	—	—	—	C	11, 13
	Bi	—	—	—	—	A	1
	Se	0·22	300	—	−0·9	A	8, 9
Sb	Ag	—	—	—	—	C	1
	Au	—	—	—	—	C	1
	Zn	—	—	—	—	C	1
Bi	Ag	0·02	300	—	0·1–0·2	C	8, 9
	Ag	—	—	—	±0·2	C	7
	Ag	45	—	—	—	C	1, 15
	Au	—	—	—	−0·18	A	7
	Cd	4·6	300	—	+1·36	C	8, 9, 13
	Se	0·23	300	—	−0·9	A	8, 9
	Cr	—	—	—	—	A	12
	Fe	—	—	—	—	C	12
	Te	—	—	—	—	A	13
Fe	H	wt.-% —	—	—	—	C	11
	C	3·65 C 1·72 Mn 1·88 S 0·07 P				C	10
	S					C	
TERNARY SOLUTIONS							
Hg	Na, Sn					Na, Sn → C	1
Cu	Be, Fe					Be, Fe → C	1
Pb	Cu, Zn					Cu, Zn → C	1
Sn	Cu, Ag					Cu, Ag → C	1
	Cu, Bi					Cu → C	1
	Cu, Pb					Cu → C	1
	Al, Fe					Fe → C	1

TABLE XLVI.—*Surface Tension of Pure Liquid Metals at or near the Melting Point*

Element	γ, dyne-cm^{-1}	$\frac{d\gamma}{dT}$ dyne-cm^{-1} deg.$^{-1}$	Ref. (see p. 588)	Element	γ, dyne-cm^{-1}	$\frac{d\gamma}{dT}$ dyne-cm^{-1} deg.$^{-1}$	Ref. (see p. 588)	Element	γ, dyne-cm^{-1}	$\frac{dT}{d\gamma}$ dyne-cm^{-1} deg.$^{-1}$	Ref. (see p. 588)
Li	398	N.D.	14	Pb	480	−0·26	13, 14, 60	Pt	1800	(−0·17)	16, 37, 49, 53
Na	200	−0·05	14, 15, 25, 27, 60	Sb	384	0	5, 43, 60	La	(700)	N.D.	—
K	101	−0·06	14, 25, 56	Bi	390	−0·13	4, 25, 58, 60	Ce	(700)	N.D.	—
Rb	77·5	N.D.	40	Te	178	N.D.	45	Pr	(700)	N.D.	—
Cs	(68)	−0·046	48	Se	105	N.D.	17, 34	Nd	675	N.D.	38
Be	1100	N.D.	3	Ti	1600	(−0·26)	(12), (41), 50, 51	Pm	(650)	N.D.	—
Mg	570	−0·3	9, 2, 40	V	1750	(−0·31)	(41)	Sm	(600)	N.D.	—
Ca	337	−0·068	20, 26, (40)	Cr	1700	N.D.	(7), 28	Eu	(450)	N.D.	—
Sr	290	−0·106	39	Mn	1100	0	28, 42	Gd	(650)	N.D.	—
Ba	224	−0·095	26	Fe	1850	(−0·43)	9, 33, 36, 49, 96	Tb	(650)	N.D.	—
B	1060	N.D.	46	Co	1890	(−0·92)	6, 32, 49, 36, 52	Dy	(650)	N.D.	—
Al	914	−0·135	2, 25, (60)	Ni	1800	(−0·98)	6, 16, 28, 36, 49, 54	Ho	(650)	N.D.	—
Sc	(900)	N.D.	—	Zr	1400	(−0·20)	12, 28, 30, (41), 49, 51	Er	(620)	N.D.	—
Y	(900)	N.D.	—	Nb	1900	(−0·24)	49	Tm	(620)	N.D.	—
Si	860	−0·5	11, 22	Mo	2250	(−0·30)	49, 51	Yb	(850)	N.D.	—
Cu	1350	−0·18	8, 23, 36, 43, 52, 49, 55, (60)	Ru	2250	(−0·31)	49	In	(950)	N.D.	—
Ag	930	−0·13	23, 43	Rh	2000	(−0·30)	49	Ra	(450)	N.D.	—
Au	1130	−0·10	23	Pd	1500	(−0·22)	49	U	1550	−0·14	31, 44
Zn	810	−0·25	2, (60)	Hf	1650	(−0·21)	49, (12)	Th	(1050)	N.D.	—
Cd	560	not linear	5, 58, (60)	Ta	(2400)	(−0·25)	18, 49, (51)	Pu	550	N.D.	31, 44
Hg	480	−0·20	4, 14	W	2300	(−0·29)	18, 49				
Ga	735	N.D.	10, 20, 21, 47	Re	(2700)	(−0·34)	49				
In	560	−0·09	13, 20, (29)	Os	2500	(−0·33)	49				
Tl	490	−0·07	9, 20, 59	Ir	2250	(−0·31)	49				
Ge	620	−0·20	11, 20, 87								
Sn	575	−0·075	13, 14, 20, 35, 52, (60)								

References to earlier work will be found in Ref. (4).
N.D. = no data available.

Data in parentheses are estimated or otherwise unreliable.

TABLE XLVII.—*Effect of Alloying upon Surface Tension in Dilute Solutions*

Solvent	Type	
Mercury	Surface-active:	Cd, Ag, Sn, Pb, Mg, Tl, Sr, Ba, Na, Li, K, Rb, Cs, Se
	Surface-inactive:	Co, Bi, Zn, Cu
Tin	Surface-active:	Bi, Te, Na, Pb, Sb, Tl, O, Se, S
	No effect:	In, Ge
	Surface-inactive:	Cd, Zn, Al, Mn, Cu
Bismuth	Surface-active:	Na, K, Te, O
	Surface-inactive:	Pb, Zn
Iron	Surface-active:	O, B, Se, Te, S, Sn, Cu, N ?
	No effect reported:	W, Cu, Co, Ni, Cr
	Surface-inactive:	C
Aluminium	Surface-active:	Zn, Li, Bi, Pb, Cu ?
	No effect reported:	Fe, Ni, Si, Mn, Cr
	Surface-inactive:	Mg, Sb, Sn
Copper	Surface-active:	Sb, Sn, Ag, Au, S, O, Se, Te
	Surface-inactive:	?
Silver	Surface-active:	?
	Surface-inactive:	Cu
Gold	Surface-active:	?
	Surface-inactive:	Cu ?
Antimony	Surface-active:	?
	Surface-inactive:	Cd, Zn, Pb
Zinc	Surface-active:	Sb, Sn, Bi, Pb, Li
	No effect reported:	Fe, Co
	Surface-inactive:	Al ?
Lead	Surface-active:	Bi, K, Na, Ca, O, Te, Se
	Surface-inactive:	Sn

TABLE XLVIII.—*Surface Tensions: Alloy Bibliography*

The qualitative results listed in Table XLVII were taken from the following sources, and from earlier references listed by the authors mentioned in General References (8), (450) (for amalgams), and (497). Much of the work reported has been carried out over very limited ranges of composition and temperature. For list of references see p. 588.

Solid-Solution Systems

Au–Cu;[23] Fe–Ni;[57,60,97] Fe–Mn;[60,97,100,(62)] Cr–Fe;[60,97,(62)] Fe–V;[62] Bi–Sb; Cu–Ni;[60,63,64] Fe–Co;[60,97] Co–Ni.[60]

Eutectic and Miscibility-Gap Systems

Ag–Cu;[23,60] Al–Si;[65] Al–Sn;[70] Al–Zn;[2] Bi–Cd;[66] Bi–Sn;[66,67,70,76,99,(24)] Cd–Sn;[68,70] Ag–Bi;[55] Ag–Pb;[55,(105)] Cu–Pb;[55] Cd–Pb;[70] Pb–Sb;[5,73,(69)] Pb–Sn;[13,66,(24)] Sn–Zn;[2,70] Bi–Pb;[75,76,(24)] Sn–Tl;[71,99] Ge–Sn;[72] Ge–In;[74] In–Sn;[72] K–Na;[75] In–Pb;[13] Sb–Sn;[71,99] Co–Cu;[60,77] Cu–Fe;[61,97] Ag–Ni;[80] Ba–Na;[92] Ba–Ca;[92] Cr–Ni;[60] Co–Cr;[60] Fe–Sn.[61]

'*Electron-Compound*' *Systems*

Ag–Al;[78] Al–Cu;[79,85] Cu–Sn;[76,81] Cu–Sb;[76,81] Ag–Sb;[81] Ag–Sn;[82] Cu–Zn.[2]

'*Compound*' *Systems*

Hg–Tl;[83,84] Hg–In;[84] Al–Mg;[2,85] Sn–Te;[4,71,86,99] Sn–Se;[4,75] Al–Ni;[79] In–Sb;[88] Co–Sn;[89] Ni–Sn;[95] Co–Si;[60] Fe–Si;[60,90,98] Ni–Si;[60] Mn–Si;[90] Mg–Zn;[2] Fe–Te;[91,97] Fe–Se;[91,97] Cd–Sb;[5,(69)] Sb–Zn;[(69)] Sn–Ti;[94] Fe–Ti;[94] Na–Sn;[99] Be–Ni;[79] Cu–Se;[102] Cu–Te.[102]

Miscellaneous Systems

Zr–rare earths;[93] Al–Ti;[94] Fe–C;[33,60,91,101,(106)] Fe–S;[61,91,97] Fe–N;[91] Fe–O;[91,96,97] Fe–W;[60,97] Ni–W;[60] Co–W;[60] Fe–Mo;[60] Ni–Mo;[60] Co–Mo;[60] Co–C;[60] Ni–C;[60,101] Cu–S;[102] Cu–O;[102,104] dilute alloys in Al, Zn.[103]

Amalgams. See Refs (4), (99), (107).

Sources in parentheses may be unreliable.

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TABLE XIV

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