JOURNAL OF MATERIALS SCIENCE 3 (1968) 424–435

Immiscibility in Liquid Metal Systems

B. W. MOTT
Metallurgy Division, United Kingdom Atomic Energy Authority Research Group, Atomic Energy Research Establishment, Harwell, Berks, UK

Received 3 January 1968, and in revised form 7 March

A review is given of the various expressions that have been derived to predict the miscibility behaviour of alloy systems, with particular reference to the suggested modifications to the Hildebrand rule for non-polar liquids. The original Hildebrand formula was based on a solubility parameter, δ, and the atomic volume, V, and immiscibility was predicted between two liquids if $\frac{1}{2}(V_A + V_B)(\delta_A - \delta_B)^2 > 2RT$

Mott introduced a correction term in this expression to allow for the difference in electronegativity $(\chi_A - \chi_B)$ between the two component elements and defined a Mott number,

$$\frac{\frac{1}{2}(V_A + V_B)(\delta_A - \delta_B)^2 - 2RT}{23060(\chi_A - \chi_B)^2},$$

where T is the melting point, in degrees absolute, of the more refractory metal. It was postulated that if the calculated Mott number for a given binary alloy system was greater than the number of bonds that could be formed, the two metals would be immiscible in the liquid state. In an earlier paper, the Mott number was compared with the lower Pauling valency of the two elements and when this is applied to 1401 known alloy systems, the overall agreement is 85% compared with 59.9% conforming to the simple Hildebrand rule. In this paper, an alternative suggestion is made that the Mott number can be compared with the mean group valency of the two alloying elements. On this basis, of the 1401 systems analysed, 1181 conform, compared with 1191 on the earlier criterion.

1. Introduction

In 1955 the author [1, 2] proposed an empirical relationship which gave a reasonably accurate prediction of the likelihood of two metals being completely miscible in the liquid state at the melting-point of the more refractory constituent. The relationship was a modification of the simple immiscibility rule proposed by Hildebrand [3] for non-polar liquids and allowed for the possible formation of bonds in liquid alloys formed by two metals of different electronegativities. On the basis of the author's original suggestion, the behaviour of 426 systems was correctly accounted for out of a total of 529 compared with 312 conforming to the simple Hildebrand rule. In 1963 [4], a slightly modified relationship was applied to a total of 1015 systems, of which 857 showed agreement compared with 609 agreeing to the original Hildebrand rule.

Since this second analysis was made, data have become available on a further 400 systems involving a total of seventy-two elements. The 1401 binary systems on which the present analysis is based represents over half of those possible between these elements and enable a fairly reliable test to be made of any proposed relationship. This paper compares the agreements based on the simple and modified Hildebrand rules and a new criterion suggested by the author. A review of the literature on liquid metal immiscibility is also included.

2. Review of Literature

The earliest attempt to obtain a working rule to predict liquid metal immiscibility was by Axon

[5] who considered about eighty binary systems in which no intermediate phases were found. His analysis was based on two factors, one related to the difference in melting-point between the two metals and the other to their relative atomic diameters. He concluded that metals which differed in size by $<30\%$ usually formed simple eutectic-type systems if they had similar melting-points, but had liquid immiscibility when the melting-points were more widely separated. If the size-factor was greater than 30% then the systems were about equally divided between the two types. No account was taken of the electrochemical nature of the elements forming the alloy and no suggestion was made of extending the analysis to ternary systems.

In 1957, Shimoji and Niwa [6] derived an expression for the excess heat of mixing for a liquid alloy which consisted of two terms, one equivalent to the Hildebrand formula for regular solutions together with a contribution due to the difference in the atomic volumes of the alloy constituents. Shimoji [7] used his expression to calculate the variation with composition for the excess heat of mixing of liquid cadmium/lead alloys and also obtained reasonable agreement between the experimental and calculated critical temperatures in the immiscible systems Pb/Zn, Bi/Zn, Tl/Zn and Ca/Cd.

Varley [8] proposed a method of calculating the misfit energy in liquid alloys, formed from two elements of different atomic volume, in terms of their bulk moduli. His equation was applied to systems in which the misfit energy was considered more important than the energy due to electrochemical differences but his calculated heats of solution did not agree very well with the experimental heats of formation for equiatomic alloys.

3. Hildebrand's Rule for Non-Polar Liquids

In 1950, Hildebrand [3] applied his immiscibility rule for non-polar liquids to various alloy systems and although he obtained over 80% success in the case of immiscible systems, nearly 50% of alloys known to be miscible in the liquid state were predicted as immiscible. The basis of the Hildebrand rule is that the excess free energy of formation of a liquid solution is very similar to the theoretical expression for the energy of mixing of a regular solution. The energy of mixing $\varDelta E^{\mathrm{M}}$ is given by

$$\varDelta E^{\mathrm{M}} = V\left[\left(\frac{\varDelta E_{\mathrm{A}}{}^{V}}{V_{\mathrm{A}}}\right)^{\frac{1}{2}} - \left(\frac{\varDelta E_{\mathrm{B}}{}^{V}}{V_{\mathrm{B}}}\right)^{\frac{1}{2}}\right]^{2} \phi_{\mathrm{A}}\phi_{\mathrm{B}} \qquad (1)$$

where V is the average atomic volume of the solution, V_{A} and V_{B} the atomic volumes of components A and B, $\varDelta E_{\mathrm{A}}{}^{V}$ and $\varDelta E_{\mathrm{B}}{}^{V}$ their heats of vaporisation, and ϕ_{A} and ϕ_{B} the volume fractions of the two components. Hildebrand postulated that when the energy of mixing is sufficiently great, separation into two liquid phases will occur and the condition for complete miscibility was deduced as

$$\tfrac{1}{2}(V_{\mathrm{A}} + V_{\mathrm{B}})\left[\left(\frac{\varDelta E_{\mathrm{A}}{}^{V}}{V_{\mathrm{A}}}\right)^{\frac{1}{2}} - \left(\frac{\varDelta E_{\mathrm{B}}{}^{V}}{V_{\mathrm{B}}}\right)^{\frac{1}{2}}\right]^{2} > 2\mathrm{R}T \qquad (2)$$

The term $(\varDelta E_{\mathrm{A}}{}^{\mathrm{V}}/V_{\mathrm{A}})^{\frac{1}{2}}$ was considered to be a measure of the binding energy of component A and was called the *solubility parameter*, δ_{A}.

The condition for immiscibility therefore becomes

$$\tfrac{1}{2}(V_{\mathrm{A}} + V_{\mathrm{B}})(\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^{2} > 2\mathrm{R}T \qquad (3)$$

The failure of this equation to predict miscibility in many technologically important metal systems for which the nature of the equilibrium diagrams is in no doubt would appear to be largely due to the electrochemical attraction between the elements, of which no account is taken. The present author postulated that if a factor could be introduced into expression 3 to allow for this, many exceptions to the simple rule might be removed.

4. Mott Modifications to the Hildebrand Rule

In 1955, Mott [1] suggested that a correction factor be added to expression 3 to allow for the electrochemical attraction in terms of the electronegativities of the two elements, χ_{A} and χ_{B}, and the maximum number of Pauling bonds [9], n, which they could form. The modified expression for immiscibility then becomes (cal/mole units)

$$\tfrac{1}{2}(V_{\mathrm{A}} + V_{\mathrm{B}})(\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^{2} - 23\,060\, n(\chi_{\mathrm{A}} - \chi_{\mathrm{B}})^{2} > 2\mathrm{R}T \qquad (4)$$

Rearranging this expression we have immiscibility for

$$\frac{\tfrac{1}{2}(V_{\mathrm{A}} + V_{\mathrm{B}})(\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^{2} - 2\mathrm{R}T}{23\,060\,(\chi_{\mathrm{A}} - \chi_{\mathrm{B}})^{2}} > n \qquad (5)$$

provided $n \neq 0$.

TABLE I Selected electronegativities and valencies.

Group	Element	Electro-negativity	Valency Mott Criterion 1	Valency Mott Criterion 2
IA	Li	0.95	1.0	1
	Na	0.90	1.0	1
	K	0.81	1.0	1
	Rb	0.78	1.0	1
	Cs	0.76	1.0	1
IB	Cu	2.00	5.56	1
	Ag	1.90	5.56	1
	Au	2.30	5.56	1
IIA	Be	1.42	2.0	2
	Mg	1.16	2.0	2
	Ca	1.03	2.0	2
	Sr	0.99	2.0	2
	Ba	0.92	2.0	2
IIB	Zn	1.50	4.56	2
	Cd	1.55	4.56	2
	Hg	1.80	4.56	2
IIIA	Al	1.48	3.0	3
	Sc	1.27	3.0	3
	Y	1.20	3.0	3
	La	1.17	3.0	3
IIIB	Ga	1.62	3.56	3
	In	1.48	3.56	3
	Tl	1.46	3.56	3
IVA	Ti	1.62	4.0	4
	Zr	1.48	4.0	4
	Hf	1.48	4.0	4
	Th	1.36	4.0	4
IVB	Si	1.82	4.0	4
	Ge	1.77	4.0	4
	Sn	1.61	4.0	4
	Pb	1.56	4.0	4
VA	V	1.85	5.0	5
	Nb	1.77	5.0	5
	Ta	1.77	5.0	5
VB	As	2.04	5.0	5
	Sb	2.10	5.0	5
	Bi	1.78	5.0	5
VIA	Cr	2.15	6.0	6
	Mo	2.05	6.0	6
	W	2.05	6.0	6
	U	1.30	3.0	3
VIB	Se	2.35	6.0	6
	Te	2.08	6.0	6
VIIA	Mn	1.69	4.0	4
	Tc	2.10	6.0	6
	Re	2.08	6.0	6
Group VIII transition elements	Fe	2.21	6.0	6
	Co	2.26	6.0	6
	Ni	2.24	6.0	6
	Ru	2.12	6.0	6
	Rh	2.12	6.0	6
	Pd	2.08	6.0	6
	Os	2.10	6.0	6
	Ir	2.10	6.0	6
	Pt	2.07	6.0	6
Rare earth elements	Ce	1.21	3.1	3
	Pr	1.19	3.0	3
	Nd	1.19	3.0	3
	Pm	1.20	3.0	3
	Sm	1.18	3.0	3
	Eu	0.97	2.1	2
	Gd	1.20	3.0	3
	Tb	1.21	3.0	3
	Dy	1.21	3.0	3
	Ho	1.21	3.0	3
	Er	1.22	3.0	3
	Tm	1.22	3.0	3
	Yb	0.99	2.0	2
	Lu	1.22	3.0	3
Actinide	Pu	1.28	3.0	3
	Np	1.30	3.0	3
	Am	1.18	3.0	3

For convenience, the numerator of expression 5 is termed the *Hildebrand term*, the denominator is the *electronegativity term* and their ratio the *Mott number*. It was suggested that if the Mott number calculated for a given binary system was greater than the maximum number of Pauling bonds which the two metals could form, then liquid immiscibility could be expected. On both valency and size factor considerations it was concluded that the maximum number of bonds that could form in any system was six, so that this imposed the upper limit of the Mott number for miscibility. Although it was felt that all metals could form at least one bond, a plot of Mott number against difference in atomic size for systems with a Mott number in the range 1 to 6 suggested that all systems with a number lower than 2 should be miscible. The behaviour of those systems with a Mott number of between 2 and 6 was deduced from an arbitrary curve drawn through the plot shown in fig. 1.

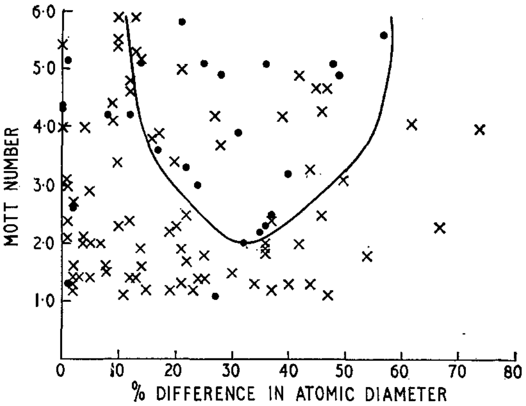

Figure 1 Plot of Mott Number against difference in atomic size; o immiscible, x miscible.

In the original Mott analysis, the values of electronegativity were selected from publications by Pauling [10] and Haissinsky [11] and were expressed to the nearest 0.1 eV. For quite a few systems, this gave a zero electronegativity term and hence a Mott number of ± infinity. In the second analysis made in 1963, Mott followed a scheme suggested by workers [12] at the Los Alamos Laboratory who calculated the electronegativities of eighty-four elements to two places of decimals from the Gordy-Thomas [13] relationship. A further modification to the rule was also made following a suggestion by K. Furukawa [14] that the lower Pauling valency of a given pair of metals might be taken as the maximum number of Pauling bonds which they could form, so that the calculated Mott number could be compared with this figure as a guide to the behaviour of their liquids. Using the data quoted in Mott [1, 2] and some slightly modified values of electronegativity, Furukawa obtained a similar overall agreement to that given by the original concept. There appears to be more theoretical justification for Furukawa's suggestion and it is simpler to apply as it eliminates the need for special treatment when the Mott number falls between 2 and 6. Although the maximum possible number of bonds between two metals is considered to be 6 as before, Furukawa's modification predicts immiscibility in systems containing one of the five Group IA elements if the Mott number is between 1.0 and 2.0 whereas the original rule would predict miscibility. Since the valencies of all other metals are not less than 2.0, this extension in the range of Mott number for immiscibility for the Group IA metals represents the only departure from the original conclusions.

5. Use of Mott Numbers by other Authors

Following initial publication of the suggested modification to the simple Hildebrand relationship, workers [12] at the Los Alamos Laboratory published a set of data for possible binary systems composed of all elements in the periodic table with the exception of halogens, rare gases and those elements of higher atomic number than that of americium. These tables included a Mott number which had been calculated for a temperature of 298° K, instead of T_A, the melting point of the more refractory component of the system as used by the original author. The two methods of calculation give similar values for the Mott number for systems in which the Hildebrand factor, i.e. $\frac{1}{2}(V_A + V_B)(\delta_A - \delta_B)^2 \gg 2RT_A$ but the use of 298° K instead of T_A can have a very marked effect otherwise, particularly if the Hildebrand factor lies between $(2R \times 298)$ and $2\,RT_A$ when the system would conform to the simple Hildebrand rule.

As mentioned in section 4, the Los Alamos workers calculated their electronegativities to two places of decimals from the Gordy-Thomas relationship. This expresses the electronegativity χ in terms of the number of valency electrons, n′ and the single covalent radius of the atom, r, according to the expression

$$\chi = (0.31/r)(n' + 1) + 0.50 \qquad (6)$$

This calculated value was used unless it differed by more than 10% from that selected by Gordy and Thomas in which case the latter was employed. The Gordy and Thomas selected value was only used for fifteen elements, *viz* Fe, Co, Ni, Cu, Zn, Ag, Cd, Sn, Sb, Au, Hg, Tl, Pb, Bi and Po. For some elements of variable valency, the Mott number was calculated for various valency states and these included Cr^{+3}, Cr^{+6}, Mn^{+4}, Mn^{+6}, Sn^{+2}, Sn^{+4}, α-Ce, δ-Ce, $Eu^{+2.1}$, Eu^{+3}, Yb^{+2}, Yb^{+3}, α-Pu, δ-Pu, and ϵ-Pu. No guidance was given as to which valency condition was preferred for a particular element.

The Mott numbers as calculated by the Los Alamos workers have been used by various authors in surveys of the alloying behaviour of various metals in the liquid state. Waber [15] analysed the known systems of plutonium and claimed that the success fell short of the 80% found in the original analysis of the author [1, 2]. Actually the electronegativity of about 1.6 chosen for plutonium would appear to be high and when a value of 1.30 is used, the agreement is 87% of the systems considered (see table II). Gschneidner and Waber (16, 17] have also analysed the behaviour of the rare earth elements with from 60 to 80% success. In their analysis, they considered all systems in which compound formation had been established as showing complete liquid miscibility. This assumption is not necessarily valid although the number of exceptions is likely to be small. On the other hand some of the systems they considered to be immiscible have been shown by other workers to give complete liquid miscibility.

In 1965, Klodt [18] pointed out that the original Hildebrand expression assumes that the binary phase diagrams are symmetrical when based on volume fraction, whereas this is rarely true. By way of example, he quoted the asymmetry of the liquid immiscibility gap in liquid Pb/Zn alloys when plotted on a mole fraction basis. Klodt suggested a modification to the Mott expression (equation 6) which weights the various parameters according to the mole fraction of the components, x_A and x_B. At the composition corresponding to the critical temperature of the liquid immiscibility gap, T_c, he assumed that

TABLE II Agreement obtained for simple and modified Hildebrand rules.

Group	Element	Immiscible systems				Miscible systems				Total systems			
		Total	Hildebrand	Mott 1	Mott 2	Total	Hildebrand	Mott 1	Mott 2	Total	Hildebrand	Mott 1	Mott 2
IA	Li	12	11	9	6	20	9	17	18	32	20	26	24
	Na	19	18	18	13	18	4	11	12	37	22	29	25
	K	21	21	20	18	10	1	6	4	31	22	26	22
	Rb	23	23	23	23	8	2	3	5	31	25	26	28
	Cs	13	13	13	13	7	1	1	4	20	14	14	17
IB	Cu	11	8	8	8	44	18	40	37	55	26	48	45
	Ag	20	18	13	13	42	20	35	31	62	38	48	44
	Au	5	5	5	5	55	19	45	43	60	24	50	48
IIA	Be	13	13	13	12	24	16	20	19	37	29	33	31
	Mg	13	13	13	12	41	22	35	35	54	35	48	47
	Ca	19	16	15	14	20	9	16	18	39	25	31	32
	Sr	8	8	8	8	15	4	8	7	23	12	16	15
	Ba	8	8	8	8	12	5	7	8	20	13	15	16
IIB	Zn	10	6	5	5	46	21	39	37	56	27	44	42
	Cd	14	12	12	11	38	22	31	30	52	34	43	41
	Hg	10	9	9	9	30	3	21	21	40	12	30	30
IIIA	Al	9	9	9	9	59	19	43	45	68	28	52	54
	Se	7	6	6	6	30	16	29	30	37	22	35	36
	Y	7	7	7	6	48	26	42	44	55	33	49	50
	La	14	13	11	10	41	19	40	41	55	32	51	51
IIIB	Ga	7	7	7	7	35	17	31	32	42	24	38	39
	In	7	7	5	4	44	22	38	38	51	29	43	42
	Tl	14	10	10	7	28	17	22	22	42	27	32	29
IVA	Ti	3	3	2	1	45	24	40	40	48	27	42	41
	Zr	6	6	6	6	40	25	34	34	46	31	40	40
	Th	3	2	2	2	46	22	39	40	49	24	41	42
	Hf	1	1	1	1	31	22	24	24	32	23	25	25
IVB	Si	5	5	5	5	48	20	38	40	53	25	43	45
	Ge	0	0	0	0	48	17	33	33	48	17	33	33
	Sn	4	4	2	2	46	20	36	37	50	24	38	39
	Pb	17	16	16	15	30	16	25	24	47	32	41	39
VA	V	21	21	21	16	33	24	29	29	54	45	50	45
	Nb	17	17	17	17	33	19	23	23	50	36	40	40
	Ta	17	17	17	17	29	22	23	24	46	39	40	41
VB	As	2	0	0	0	17	9	13	13	19	9	13	13
	Sb	0	0	0	0	39	11	26	28	39	11	26	28
	Bi	19	17	17	17	30	11	19	20	49	28	36	37
VIA	Cr	12	11	4	4	33	25	32	32	45	36	36	36
	Mo	14	14	14	13	35	22	32	33	49	36	46	46
	W	11	11	11	10	30	18	23	24	41	29	34	34
	U	26	22	22	22	32	18	30	31	58	40	52	53
VIB	Se	9	5	3	3	15	10	14	14	24	15	17	17
	Te	3	1	1	2	24	10	17	17	27	11	18	19
VIIA	Mn	10	10	8	7	40	19	38	38	50	29	46	45
	Re	4	3	3	3	29	17	24	26	33	20	27	29
	Tc	1	1	1	1	25	16	24	24	26	17	25	25
Group VIII transition elements	Fe	16	16	12	9	42	25	41	41	58	41	53	50
	Co	7	7	6	6	44	20	41	41	51	27	47	47
	Ni	6	6	5	4	48	21	41	43	54	27	46	47
	Ru	3	3	3	3	31	17	30	30	34	20	33	33
	Rh	1	1	1	1	33	19	33	32	34	20	34	33
	Pd	1	1	1	0	55	28	48	48	56	29	49	48
	Os	1	1	1	1	26	15	22	25	27	16	23	26
	Ir	2	2	2	2	33	17	30	31	35	19	32	33
	Pt	1	1	1	0	42	25	37	36	43	26	38	36
Rare earth elements	Ce	9	9	8	7	42	18	37	37	51	27	45	44
	Pr	4	4	3	3	22	14	22	22	26	18	25	25
	Nd	5	5	5	5	30	19	30	30	35	24	35	35
	Pm	2	2	2	1	2	2	2	2	4	4	4	3
	Sm	5	4	3	3	19	6	16	15	24	10	19	18
	Eu	3	3	3	3	11	3	6	7	14	6	9	10
	Gd	7	7	7	7	40	22	38	39	47	29	45	46
	Tb	2	2	2	2	19	14	19	19	21	16	21	21
	Dy	6	5	4	3	26	15	24	25	32	20	28	28
	Ho	2	2	2	2	20	14	19	19	22	16	21	21
	Er	6	6	5	5	28	17	27	27	34	23	32	32
	Tm	2	2	2	2	14	8	12	12	16	10	14	14
	Yb	7	7	7	7	10	5	9	9	17	12	16	16
	Lu	2	2	2	1	16	12	16	16	18	14	18	17
Actinide	Pu	14	13	13	12	50	25	43	45	64	38	56	57
	Np	0	0	0	0	2	2	2	2	2	2	2	2
	Am	0	0	0	0	1	0	0	0	1	0	0	0
Total systems		302	280	260	240	1099	556	931	941	1401	836	1191	1181

$$(x_A V_A + x_B V_B)(x_A \delta_A - x_B \delta_B)^2 - 23\,060\, n\, (x_A \chi_A - x_B \chi_B)^2 = 2RT \quad (7)$$

Rearranging this to solve for n, he obtained

$$n = \frac{(x_A V_A + x_B V_B)(x_A \delta_A - x_B \delta_B)^2 - 2RT_c}{23\,000\,(x_A \chi_A - x_B \chi_B)^2} \quad (8)$$

Using the experimental values of critical temperature and corresponding mole fractions for the Pb/Zn system, the number of bonds at the critical point was calculated to be 0.991, which is consistent with Mott's original postulation that a system could be miscible if the value of n was in the range 1 to 6. For the immiscible systems Zn/Bi, Tl/Zn and U/Th, Klodt calculated values of 1.26, 1.38 and 1.04 for n at the critical temperature.

Klodt also extended expression 7 for immiscibility to a ternary system assuming that the total heats of mixing and binding energies are the sums of the pairwise energies of the binary alloy pairs. Using his equation to calculate the critical temperatures of the liquid immiscibility gap for three compositions in Pb/Zn/Sb alloys and one Pb/Zn/Sn alloy, Klodt obtained only moderate agreement between the calculated and experimental values of T_c, as shown below.

System	Mole fraction			Critical temp. (°K)	
	x_A	x_B	x_C	calculated	observed
Pb/Zn/Sn	0.200	0.718	0.082	625	875
Pb/Zn/Sb	0.207	0.669	0.125	945	850
Pb/Zn/Sb	0.169	0.658	0.181	1050	745
Pb/Zn/Sb	0.145	0.612	0.242	425	790

Klodt also constructed diagrams for a number of metals in which the solubility parameter was the ordinate and the electronegativity was the abscissa. The position of liquid immiscible and simple eutectic systems were plotted on the diagram and it was found that in the majority of cases examined, a line could be drawn which divides the diagram into two regions, each containing only one of the two types of system. The slope of the dividing line was essentially the same for all the diagrams, with the liquid immiscible system lying above the simple eutectic systems, as illustrated by fig. 2 which shows the plot for lead alloys. The two most notable exceptions to this were the plots for copper and aluminium alloys for which no dividing line could be drawn.

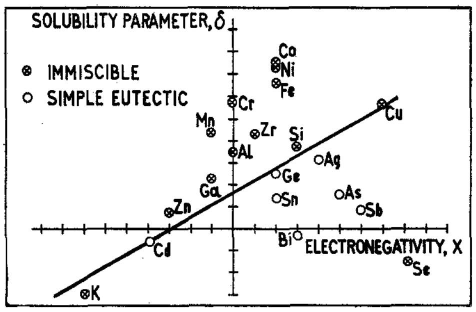

Figure 2 Plot of δ versus χ for Pb-base alloys (Klodt).

Efimov [19] considered the likely interaction in the liquid state between vanadium and eighty-three elements on the basis of the simple and modified Hildebrand rules. He concluded that the agreement with experiment was poor if the Mott numbers were calculated for a temperature of 298° C but was considerably improved if calculated at the melting-point of the more refractory metal. A diagram was constructed similar to that of fig. 1 to enable predictions to be made for vanadium systems having a Mott number between 2 and 6, and it was noted that most systems in this category were of the simple eutectic type, with no compounds in the solid state.

6. Application of the Mott Criterion to known Binary Metallic Systems

6.1. Choice of Parameters

For the application of the Mott criterion, the parameters involved are the heat of vaporisation, the melting-point of the pure metal, the atomic volume, the electronegativity and the valency. The most reliable data for the heats of vaporisation were chosen [12] by the Los Alamos authors and were accepted for the present work. The melting points have been selected from various standard tables of physical constants with the exception of the values for the rare earth metals which were taken from Gschneidner's book [17]. The remaining three parameters are interdependent and are to a large extent determined by the choice of valency. There is ample evidence from the present state of alloy theory that the valency of a given element, particularly if it belongs to one of the B-subgroups or a transitional series, can vary according to its environment. The assignment of a unique electronegativity value to every element is therefore an impossible task and the best that can be done is to select either a most probable value or an average value from the possible valency states. If a most probable electronegativity is selected, then Mott numbers calculated for systems to which the corresponding valency condition applies are explicit but could be markedly in error for systems where the valency is considerably different. On the other hand, the Mott numbers obtained from an average electronegativity would give a moderate guide to the possibility of immiscibility for most systems but could give a completely false impression in borderline cases.

Thus, exceptions to the rule would be expected for all systems involving a metal of variable valency when the Mott numbers are calculated using a series of selected electronegativity values. The course followed in the 1963 [4] paper to give an overall assessment of the agreement obtained in about 1000 binary systems was to use a set of electronegativity values which are close to those generally accepted by various workers. The valency used for comparison with the Mott number was in each case that employed in the calculation of electronegativity using the Gordy-Thomas equation [8]. The criticism has been raised that the valency and electronegativity values chosen for certain elements are "rather unconventional", but in the absence of an acceptable and comprehensive electronegativity scale for all the elements, some compromise is necessary. As pointed out by Hume-Rothery [20] the Pauling electronegativities are not electrochemical constants but bond energy terms expressing the difference between the energy of an A-B bond and the mean of A-A and B-B bonds. They are generally derived from nonmetallic compounds and it is by no means certain whether their exact values should be used in a discussion of either solid or liquid alloys.

The selected electronegativity and valency values (*Mott Criterion* 1) are listed in table I, from which it will be noted that the selection of electronegativity values for the A-subgroup elements appears to present little problem and those adopted throughout have been calculated from their group valencies. The only exception to this is uranium which has been treated as an actinide group element with a valency of 3.0. In general, the accepted values for the elements of subgroups IB, IIB and IIIB, are fairly close to those given by their Pauling valencies but do not necessarily coincide with them. For the higher B-subgroups, the normal group valencies appear to give the most appropriate electronegativities. For the Group VIII transition elements, the electronegativity calculated from the Gordy relationship for a common Pauling valency of 6.0 has been used in each case.

6.2. Results using Criterion of Lower Pauling Valency

The Mott numbers have now been calculated for 1401 systems on which sufficient data are available to make a reasonable judgement as to whether liquid immiscibility exists or not. This does not imply that the full equilibrium diagram is known in each case, but for example, that sufficient alloys have been prepared over a wide range of composition as to make the incidence of immiscibility highly improbable. In a few cases, liquid immiscibility has been postulated between two metals, one of which boils at atmospheric pressure before the other melts but the solubility of the latter in the liquid of the other is known to be extremely low. No special treatment has been made of immiscible systems in which compound formation has also been reported, as a special study is required to elucidate their peculiar behaviour.

In addition to the alloying behaviour of the fifty-five elements considered in the original publication, a further seventeen elements have now been included in the analysis. The additional elements include hafnium, technetium, plutonium, neptunium, americium and the remaining twelve rare earth elements after praseodymium. On the basis that, for immiscibility the Mott number should be greater than the lower Pauling valency of the two elements, the 1401 systems analysed, 1191 conform, representing a total of 85% agreement compared with 59.9% conforming to the simple Hildebrand rule (836 systems).

The agreement on the above basis ("Mott 1" columns) for each of the seventy-two elements is tabulated in table II, which shows that the A-subgroup elements generally give better agreement than those of the B-subgroup. The Group VIII transition elements give the best overall agreement of about 91% while that given by the elements of Groups VB and VIB is only about 67%. This may be partly due to the variable behaviour of these elements and of arsenic, antimony and bismuth in particular, or to the incorrectness of some of the alloy diagrams in view of the handling difficulties for materials such as selenium and tellurium. It may be noted that of the nine selenium systems reported immiscible, four do not conform to the simple Hildebrand rule, while two out of the three immiscible tellurium systems are exceptions also. This may be due to the suggestion made by Hume-Rothery and Anderson [21] that the reason for the formation of immiscible liquids in alloys based on these elements may not stem from a reluctance of the two kinds of atom to pack together to form a liquid. On the contrary, they can form liquids of high stability but immiscibility results from an inflection in the free energy curve. They suggest that discrete molecules may form in liquid alloys involving these elements or alternatively definite ratios of oppositely charged ions may predominate.

The behaviour of chromium is of interest because whereas only one of twelve reported immiscible systems gives a negative Mott number, only four of the remaining eleven systems obey the Mott rule. The exceptions include five rare earth alloys and may indicate a special behaviour or incorrect determination. In the case of the thirty-three miscible systems involving chromium, only one does not agree with the Mott analysis. When the Mott numbers are calculated for an electronegativity of 1.63 corresponding to a valency of 3.0, three of the exceptions in immiscible systems with rare earth elements for a valency of 6.0 now conform and the other two give Mott numbers of 2.7 and 2.3 which are not far removed from the required figure of 3.0. Three further exceptions among miscible systems are found for a valency of 3.0 so that the overall agreement is the same for the two possible valency states of chromium.

6.3. Further Correction of Simple Hildebrand Rule for Atomic Volumes

In the case of aluminium, all nine immiscible systems conform but for miscible systems, the agreement is only 73%, i.e. forty-three systems out of fifty-nine. In this case, five of the sixteen miscible exceptions are with the elements of Group IIA. Where the systems between the remainder of the Group IIIA and Group IIA elements are known, reasonable agreement is obtained (seven out of eight). For the five aluminium systems, the ratio of the atomic volumes varies from 1.4 for Mg/Al to 3.81 for Ba/Al whereas the original Hildebrand expression assumes nearly equal atomic volumes. The more accurate Hildebrand analysis for immiscible non-polar liquids was given as

$$2RT < \frac{4x_A x_B V_A^2 V_B^2}{(x_A V_A + x_B V_B)^3}(\delta_1 - \delta_2)^2 \qquad (9)$$

where x_A and x_B are the molar concentrations of A and B respectively. The expression 9 simplifies to condition 2 for the equimolecular point provided that the atomic volumes V_A and V_B, are nearly equal. It can be shown that the Hildebrand term obtained from expression 2 does not deviate from the correct value by more than 10% until the ratio of the atomic volumes, V_A/V_B, exceeds about 1.6, so that this has no significant effect on the Mott number calculation for the majority of alloy systems. For metals whose atomic volumes differ greatly, however, the Hildebrand term and hence the Mott number may be appreciably greater when estimated from expression 5 than the true value from expression 9. The rate at which the simplified Hildebrand term deviates from the true value with change in the ratio of the atomic volumes can be seen from table III. When these corrections are applied to the five systems between aluminium and the Group IIA elements, although significant reduction in the Mott numbers were obtained, e.g. from 8.9 to 3.2 for the exceptional case of Al/Ba alloys, in no case was the reduction sufficient to bring the value below 2.0 for conformity.

TABLE III Error in Hildebrand term with increased ratio of atomic volumes.

Ratio V_A/V_B	$\frac{\text{True Hildebrand term}}{\text{Simplified Hildebrand term}}$
1.0	1.000
1.5	0.923
2.0	0.790
2.5	0.667
3.0	0.572

A further series of alloys which do not conform to the simplified expression in which marked variations in atomic volume occur, is that of the elements of Group IA when alloyed together. Thus complete miscibility has been shown for the system Na/K, Na/Rb, Na/Cs, and K/Cs but the Mott numbers range from 3.8 to 25. When these are corrected for the atomic volume ratio, the Mott numbers are considerably reduced but are still greater than 1.0 as shown in table IV. One possible explanation for miscibility in the case of these alloys is that the alkali metals have high compressibilities and may be able to accommodate themselves more readily than other metals.

TABLE IV Corrected Mott numbers after allowing for atomic volume ratio for Group IA elements.

System	Atomic volume ratio	Mott no. Uncorrected	Corrected
Na/K	1.91	16.0	6.5
Na/Rb	2.36	19.0	12.0
Na/Cs	2.91	25.0	13.0
K/Cs	1.52	3.8	1.9

A survey of the remaining miscible exceptions shows that about 10% borderline systems can be made to conform by applying a correction to the Hildebrand term to allow for a size difference between the atoms. At the best therefore the use of the more accurate expression [9] would only result in an overall improvement of 1% in the agreement obtained.

Gschneidner [17] claimed an agreement of less than 70% when the Mott analysis was applied to the rare earth alloys. Out of the 416 systems analysed here for the elements lanthanum to lutetium, 383 conform representing an agreement of 90% which is better than the average result for the seventy-two elements considered. The main reason for this difference is the fact that the Mott numbers calculated for this paper correspond to temperatures at which both metals are liquid and not for a standard temperature of 25° C as used by Gschneidner. Any differences in the electronegativities used here and by the Los Alamos workers may also account for some of the discrepancy. Gschneidner [15] has also referred to the poor success of the Mott analysis on plutonium alloys. From table II, it will be seen that fifty-six out of sixty-four plutonium systems show agreement (87% correct) and this result is no doubt largely due to the electronegativity of 1.28 adopted here compared with the Los Alamos figures in the range 1.54 to 1.68.

It is interesting to note that of the 280 immiscible systems (out of 302) which conform to the simple Hildebrand rule, only twenty fail to give agreement on the present modified rule. For the miscible systems, 168 of the 543 which the Hildebrand rule would predict as immiscible fail to fit in on the Mott analysis. The percentage (86.1%) for immiscible systems on the present concept is only slightly better than that for miscible systems (84.7%).

6.4. Results using Criterion involving the Number of Free Electrons per Atom

Since the original suggestion of a modified Hildebrand rule was put forward, a considerable improvement has taken place in our knowledge of the liquid metal state and the position was reviewed by Cusack [22] in 1963 and by Wilson [23] in 1965. On the basis of various physical property measurements and particularly from the changes at the melting-point, it is considered that pure liquid metals consist essentially of positively charged ions in a sea of electrons. The valency electrons are considered to be free to move with mean free paths ranging from a few Ångströms to several interatomic spacings, depending on the metal. All the valency electrons are generally free to take part in conduction processes as shown by the measurements of electrical resistivity, Hall coefficient, Knight shift, etc. On alloying, although the mean free path of the electrons may decrease and increase in electrical resistivity may occur at some particular alloy composition, the valency electrons are still considered to be in an essentially free state. There is ample evidence from thermodynamic data, however, that some form of bonding can occur in liquid alloys for which the electronegativities of the two elements are different. The nature of this bonding has not yet been fully elucidated but could be of a resonating covalent type, the effect of which on the thermodynamic and electrical properties of the alloys does not necessarily reach a maximum at the equiatomic composition. In the absence of precise data on a particular system, however, it might be considered that for the 50:50 alloy, the number of bonds could be assumed to be proportional to the number of free electrons, per atom, i.e. the mean of the valencies for the two pure metals.

The criterion postulated by Mott in 1963 and used in section 3.2. of this paper, *viz* that for liquid immiscibility the Mott number should be greater than the lower Pauling valency for the two constituents, was quite arbitrary. If a better knowledge of bonding in liquid metals were available, it might be possible to define explicitly the number of bonds in an equiatomic alloy. It seemed of some interest however in the absence of a true picture to test the agreement of immiscibility in terms of the Mott number and the average number of valency electrons likely to be present. This assumes that all alloys obey the free electron theory and that each element contributes a constant number of electrons per atom irrespective of composition and alloying element.

The valency adopted for each element is given in the fifth column of table I (*Mott Criterion* 2) and in most cases conforms to the standard group valency. The main exceptions to this are manganese for which a valency of 4 was taken, and uranium, which was assumed to be trivalent, as well as the three trans-uranium metals, Pu, Np and Am. The nine transition metals of Group VIII were all considered to be hexavalent although this is less reasonable for Fe, Co and Ni than the other six elements. The agreement for each element based on the Mott number calculated as before using the electronegativities quoted in table I is given in table II under the column headed Mott 2. The criterion used for immiscibility was Mott no. > average group valency for the two elements (subject to the exceptions quoted above).

A comparison of the overall agreement obtained on this basis (*Mott* 2) with that considered in section 6.2 (*Mott* 1) is given in table V.

TABLE V Overall agreement according to two possible criteria.

	Immiscible systems	Miscible systems	Total no. of systems
Total considered	302	1099	1401
No. conforming to Mott 1	260	931	1191
No. conforming to Mott 2	240	941	1181
% conforming to Mott 1	86.1	84.7	85.0
% conforming to Mott 2	79.5	85.7	84.3

Table V shows that using the second criterion, the number of systems conforming out of a total of 1401 is only ten less than on the first criterion. As would be expected, the number of immiscible systems conforming is less, but this is partly counterbalanced by an increase in the number of miscible systems brought into line. For any valid scheme proposed, it would be expected that the percentage agreement for immiscible and miscible systems should be approximately the same. It is interesting to note that whereas there is only 1.4% difference in the agreement for the two types of system on the first criterion, there is 6.2% difference for the second.

The choice of a valency of 6 for Fe, Co and Ni is debatable and a value of 2 might be preferable as a general choice for these elements. If these metals are considered divalent then five new systems Fe/Ag, Fe/Ca, Fe/Cr, Co/Ag, and Ni/Ag conform but this is exactly counterbalanced by the non-conformity of the systems Co/In, Ni/Ca, Ni/In, Ni/Sm, and Ni/Eu. In the case of the higher transition elements Ru, Rh, Pd, Os, Ir, and Pt where there is more justification for the higher valency, the nett loss in systems conforming for a valency of 2 is 13.

7. Conclusions

The data presented illustrate the usefulness of the application of the Mott number concept to immiscibility in liquid metal systems. When the suggestion was first put forward in 1955, the amount of published data on the constitution of alloy systems was somewhat restricted and the immiscibility analysis was confined to 529 systems. Since then our knowledge has been extended to many more alloys and the present paper is based on 1401 systems involving a total of seventy-two elements, which represents about 53.3% of the total number possible. If the three systems involving neptunium and americium are omitted, then the analysis covers about 56.1% of the systems possible between the remaining seventy elements. Thus the need for a method of predicting immiscibility in binary alloys is considerably less now than twelve years ago, but the possible extension to multicomponent systems to increase or decrease the extent of immiscibility could still be quite useful.

The present analysis is used therefore mainly as a means of testing various possible criteria employing the Mott number concept. It is clearly shown that it is not necessary to invoke a size factor relationship for systems with Mott numbers between one and six as originally proposed. The shape of the envelope dividing miscible and immiscible systems in fig. 1 is very arbitrary and the basis on which it was conceived was not well founded. On the other hand, the amended criterion proposed in 1963, in which the Mott number is compared with the lower Pauling valency of the two elements forming the alloy was also somewhat arbitrary. The suggestion in this paper, to compare the Mott number with the average number of valency electrons per atom in the alloy, gives almost as good agreement as the 1963 proposal and may be more consistent with the current free-electron theory for liquid metals and alloys. It certainly removes the objection that unconventional valencies were originally adopted although the choice of the number of free electrons for the Group VIII transition elements is very open. As discussed in section 6.1, the criticism that some of the electronegativities chosen are unconventional may still apply but the Pauling values are not necessarily the correct ones for use in either solid or liquid alloys. Although the mean valency may be a good approximation for the number of free electrons per atom in the equiatomic alloy, this may not bear any relation to the number of bonds for which allowance must be made. Until a more precise knowledge of bonding in liquid alloys is available, however, there is little that can be done to improve the proposed concept.

Whichever criterion is chosen, on the basis of the 1400 systems considered it appears that the behaviour in the liquid state can generally be predicted to an accuracy better than five systems out of six. For some elements, e.g. the Group VIII transition elements and the rare earths, the accuracy is at least nine out of ten correct while the worst prediction applying to a few elements only is two out of three correct. The overall agreement obtained gives the rule an empirical status for predicting to a reasonable degree of certainty whether two metals will form immiscible liquids or not, using a set of unique parameters for each element. One of the most important parameters in determining the Mott number is the electronegativity and as so many different scales and individual values for a given element have been proposed, it is impossible at present to determine their relative merits. There is always the possibility of a given element, particularly if a member of one of the B-subgroups, having a different valency state according to the metal with which it is alloyed and the specific case of chromium has been discussed. Another possibility is that valency of a metal may change with its concentration in a given alloy system and this could be the reason for immiscibility over a limited composition range with compound formation outside of it. In some cases, the electronic structure in the liquid state could be such as to lead to immiscibility whereas a change to another configuration in the solid state could result in compound formation. This could explain the occurrence of compounds under a liquid immiscibility gap as found for some alloy systems. Such deviations need careful analysis and will not be dealt with in this paper.

Of the other parameters used in the calculation of the Mott number, small errors in the heat of vaporisation are not likely to affect the overall agreement to any large extent as borderline cases could be affected either way. For example, the Los Alamos workers report [9] that subsequent to the preparation of their tables, a new estimation of the ΔE^V for thorium gives a value of 136.6 kcal/mole compared with a value of 127.0 kcal/mole used in their calculations. When the new value is used, out of the forty-two systems considered, only one is affected and this is also made to conform by applying an atomic volume ratio correction. The parameter which could have a more marked effect on the overall agreement, however, is the atomic volume. The values used throughout the calculations are those estimated from data on the solid phase, whereas the correct procedure should be to use the atomic volume of the liquid phase at the temperature used for each calculation. This would involve a knowledge of the density coefficients for all the elements in the liquid state and this is not available. A partial correction factor to the atomic volumes used could be made by allowing for the volume change on fusion and taking an average value for the temperature coefficient. With a few exceptions, most metals expand by about $4 \pm 2\%$ by volume on melting so that the error involved in estimating the Mott number using the solid atomic volumes is not very large. For the metals such as gallium, bismuth and antimony which contract on melting, the errors in calculating the Mott numbers will be the greatest. In the absence of more precise data on the liquid atomic volumes, however, the scheme adopted is not unreasonable.

Another factor which could affect the overall agreement is an incorrect assessment of whether or not immiscibility exists in a given system. The form of the equilibrium diagram for some systems can be markedly affected by even trace amounts of impurity, so that some of the early results obtained with somewhat impure materials may be in doubt. The experimental techniques which can now be employed have also greatly improved and redetermination of several systems initially reported as immiscible has shown them to be incorrect in recent years. The number of systems which have been incorrectly categorised in this paper is most likely to be less than twenty so that when this number is combined with those brought in line by correcting for deviation from equiatomic volumes of the two constituents, the overall agreement is not likely to exceed 88%, or seven systems correct out of eight.

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