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Lang, Peter F. (2020) Applying the soft sphere model to improve the understanding of bonding in transition metals. *Heliyon* 6 (1), e03110. ISSN 2405-8440.

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Research article

Applying the soft sphere model to improve the understanding of bonding in transition metals



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ARTICLE INFO

Keywords:

Inorganic chemistry
Theoretical chemistry
Enthalpy of atomisation
Metallic bonding
Transition metals

ABSTRACT

Development in the understanding of electronic structure and chemical bonding and the importance of metals is outlined. A summary of the main features of the soft sphere model of metallic bonding and structure is provided. The soft sphere model is used to show that there are four main components involved in the bonding of transition metal solids and the enthalpy of atomisation of gaseous transition metal atoms are calculated according to the model and results when compared to literature values give good agreement.

1. Introduction

The nineteenth and early twentieth century witnessed tremendous advances in the development of chemistry into a core modern science. A very important phase in the development of modern chemistry is atomic spectroscopy. Good accurate spectrometers became generally available in the second half of the nineteenth century and rapid progress was made in experimental atomic spectroscopy. The investigation of cathode rays by J.J. Thomson [1] and others led to the discovery of the electron which confirmed the existence of subatomic particles and greatly assisted in the development of a new atomic theory. In 1916 Lewis [2] developed the theory of the electron pair bond and led Langmuir [3] to formally lay down the “octet rule” in chemical bonding. The development of quantum mechanics allowed chemists and physicists to interpret spectra correctly and to a much better understand electronic structure and bonding.

The publication of “The nature of the chemical bond” [4] by Linus Pauling was another step forward in the development and understanding of the theory of chemical bonding. Pauling described in great detail the fundamentals of resonance, covalent bonding, bond strength and bond lengths as well as ionic character in covalent bonds in his book. He discussed the principles of the one electron bond, what he termed the “three electron bond” and three centre bond. The concept of metallic bonding was also included in his description of the various types of chemical bonding but important aspects of metallic bonding were left out.

The development of civilisation as we know it to a very large extent depended on the discovery and ability to extract and make use of metals, especially transition metals. The spread of iron working techniques

around the Aegean [5] is a major factor in the advancement of early civilisation. As from the late nineteenth and early twentieth century large scale extraction and use of transition metals enabled many modern industries including telecommunications, electricity production and supply and aircraft production to be created. It is fair to say that even though transition metals are vital to modern society, bonding in transition metals is not well understood. Currently, the most popular description of metallic bonding being taught to many chemistry students is the “ions in a sea of electrons” model. In this model of metallic bonding, the metal atoms in a metal crystal lose their outer electrons to form a lattice of regularly spaced positive ions surrounded by a “sea” of mobile electrons that move at random around the ions. However, it has been shown very clearly that this model cannot account for many of the common properties of metals. Recently published work [6] has provided overwhelming evidence that the “electron sea” model is a misleading and poor representation of metallic bonding. The aim of this work is to apply the soft sphere model [7, 8, 9] to help further improve understanding of bonding in transition metals in addition to the results of previous work already published [10, 11, 12].

2. Method

A soft sphere model which was developed some time ago [7, 8, 9] has been shown to be a much better description of metallic structure and bonding than the current electron sea model. Essentially the model, as the name suggests, assumes that atoms and ions are not hard spheres but soft or flexible compressible spheres. One or more of the outer electrons

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in each atom of a metal solid are detached or separated from the atom, which forms a positive ion, and the “detached” electron(s) behave like negative ion(s). The detached outermost electron(s) can occupy equivalent positions that are at the midway between the nearest neighbours of the positive ions (as in ionic crystals, where positive ions occupy positions between negative ions). However these electrons are not “free” or completely delocalized but can move within the midpoint positions between ions in a unit cell. Transition metal properties are well known [13] and a more detailed description of and how the model can account for various properties of metals can be found in prior work [6, 12] and not repeated here.

Different transition metals have different electron configurations and so the number of detached electrons is liable to be different for different elements. As has already been described previously [12] Table 1 lists the number of detached electrons per atom for the transition metals which affects the bonding in the individual metal solids. In some instances, the maximum number of detached electrons may not be reached because of the many defects in the solid state. The number of detached electrons per atom may not always be exactly the same for the same reason. Bonding in metals is also influenced by the crystal structure and number of atoms per unit cell, these are listed in Table 2 (elements with distorted hcp structures are marked with (d)). Most transition metals have structures that are described as hexagonal closed pack (hcp), cubic closed pack/face centred cubic (ccp) or body centred cubic (bcc) but some possess more than one structure at room temperature. A few, such as ruthenium, osmium, cobalt, zinc and cadmium possess distorted hcp structures and mercury has a distorted ccp/rhombohedral structure. Chromium and silver are generally recognised to have bcc and ccp structures respectively but in some papers they are reported to they can have alternative cubic or

Table 1. Number of detached electrons per atom in the solid state.

Atomic number	Element	Nr. of detached electrons/atom
21	Sc	½ or 1
22	Ti	2
23	V	3
24	Cr	3 or 4
25	Mn	4
26	Fe	4
27	Co	5
28	Ni	6 or 5
29	Cu	5
30	Zn	4 or 3
39	Y	½ or 1
40	Zr	2
41	Nb	3
42	Mo	3 or 4
43	Tc	5
44	Ru	5
45	Rh	5 or 6
46	Pd	5 or 6
47	Ag	5
48	Cd	4 or 3
57	La	½ or 1
72	Hf	2
73	Ta	3
74	W	3 or 4
75	Re	5
76	Os	6
77	Ir	6
78	Pt	6
79	Au	5
80	Hg	1

Table 2. Crystal structure of transition metals and atoms per unit cell.

Atom	Structure	Atoms per unit cell
Sc	hcp/ccp	6
Ti	hcp	6
V	bcc	2
Cr	bcc/ccp	2 (4)
Mn	complex	58
Fe	bcc/hcp/ccp	2/6/6
Co	hcp(d)/ccp	6/4
Ni	ccp/hcp	4/6
Cu	ccp	4
Zn	hcp(d)	6
Y	hcp	6
Zr	hcp	6
Nb	bcc	2
Mo	bcc	2
Tc	hcp	6
Ru	hcp(d)	6
Rh	ccp	4
Pd	ccp	4
Ag	ccp/hcp	4 (6)
Cd	hcp(d)	6
La	hcp/ccp	6/4
Hf	hcp	6
Ta	bcc	2
W	bcc	2
Re	hcp	4
Os	hcp(d)	6
Ir	ccp	4
Pt	ccp	4
Au	ccp	4
Hg	rhombohedral(d)	4

hcp structures respectively for chromium and silver. Hence, different transition metals possess different specific electrical resistance, atomic volume and hence distinct densities.

This work proposes that there are four major components involved in the bonding of transition metals. They are (a) ionic bonding, (b) covalent bonding, (c) weaker bonding that can be described as three centre bonding and (d) exchange interactions. In a simplistic way, the three types of bonding involved can be viewed as instantaneous which means that at any one time only a third of the bonding electrons contributes to ionic or covalent or three centre bonding.

In a unit cell the detached electrons behave like negative ions and are attracted by the positive ions. So the number of ionic bonds per atom is directly proportional to the number of detached electrons. The strength of the ionic bonds is a function of $1/n$, where n is the principal quantum number, because the larger the positive ion the smaller the attractive force between the electron and the positive ion. The energy B_1 in kJ per mole, associated with the ionic bonding can be approximated to equal to the number of detached electrons per atom, E_d , multiplied by $(1/n)^{3.33}$ and multiplied by a constant E_{H1} and is:

$$B_1 = E_{H1} E_d (1/n)^{0.333} \quad (1)$$

The number of covalent bonds is dependent on the resultant number of parallel spins, E_p , available because electrons that possess anti-parallel spins can pair up and not likely to form bonds with electrons in other atoms in the unit cell. The strength of a covalent bond increases with increasing number of electron shells because ionic character is likely to be reduced. Hence bond strength is a function of the principal quantum number. The d electrons in the outermost or valence shell (which is not completely filled) tend to have the maximum number of unpaired spins

among those that are not detached and similarly for those that are detached until there are five or more d electrons and the total parallel spin cannot exceed five. For example, tungsten has a configuration of $5d^4 6s^2$. If there are 4 detached electrons, the most probable distribution of electron spins is $[\uparrow_d \uparrow_d \uparrow_d \uparrow_d] \uparrow_s \downarrow_s$ where $[\uparrow_d \uparrow_d]$ signifies the outer electrons that are not detached and \uparrow_d indicates a d electron and \uparrow_s indicates an s electron. Overall, there are 4 parallel spins. It is most improbable that the 2 detached d electrons will have spins anti-parallel to those of the undetached electrons since that will mean that overall all spins are paired and not likely. If on the other hand there are 3 detached electrons the distribution of electron spins can be $[\uparrow_d \uparrow_d \uparrow_d] \uparrow_d \uparrow_s \downarrow_s$ or $[\uparrow_d \uparrow_d \uparrow_d] \downarrow_d \uparrow_s \downarrow_s$ and the average is 3 parallel spins and the average of 4 and 3 detached electrons is 3.5. Rhenium has a configuration of $5d^5 6s^2$. It is assumed to have 5 detached electrons and the spin arrangement can be $[\uparrow_d \uparrow_d \uparrow_d \uparrow_d \uparrow_d] \uparrow_s \downarrow_s$ or $[\uparrow_d \uparrow_d \uparrow_d] \downarrow_d \downarrow_d \uparrow_s \downarrow_s$ which means an average of 3 parallel spins. As a further example, osmium has a configuration of $5d^6 6s^2$ and has 6 detached electrons. The spin distribution is then $[\downarrow_d \downarrow_d \downarrow_d \uparrow_d \uparrow_d \uparrow_d] \uparrow_s \downarrow_s$ or $[\uparrow_d \uparrow_d \uparrow_d] \uparrow_d \uparrow_d \uparrow_d \downarrow_d \uparrow_s \downarrow_s$ and the average is 3 parallel spins. The average number of parallel spins per atom in the solid state is listed in Table 3.

The total covalent bond energy per mole is then calculated from the following where E_p is the number of parallel spins and n is the principal quantum number and E_{H2} is a constant:

$$B_C = E_{H2} E_p (n)^{0.333} \quad (2)$$

In all cases n , the principal quantum number is equal to 3, 4 or 5 respectively for the $3d$, $4d$ and $5d$ series.

The third type of bonding is weaker three centre bonding and it is assumed to be only half as strong as the other covalent bonds so the value of the constant is equal to half the average of E_{H1} and E_{H2} . A commonly

Table 3. Number of parallel spins and exchange interactions.

Atom	Average parallel spins	Exchange interactions
Sc	1	0
Ti	2	1
V	2	3
Cr	2	10
Mn	3	10
Fe	2	10
Co	2	11
Ni	1	13
Cu	1	20
Zn	0	20
Y	1	0
Zr	2	1
Nb	3	6
Mo	2	10
Tc	3	10
Ru	3	11
Rh	2	13
Pd	0	20
Ag	1	20
Cd	0	20
La	1	0
Hf	2	1
Ta	2	3
W	3.5	6
Re	3	10
Os	3	10
Ir	2	11
Pt	1	16
Au	1	20
Hg	0	20

known three centre bond occurs in diborane [14] where in the bridging hydrogen, two electrons bond a single hydrogen atom to two boron atoms. A more detailed description of three centre bonding is given elsewhere [15] and not described here. In the metal solid, a detached electron and an undetached electron in one ion oscillates between one ion and the mid-point site in one instant and another ion and the same mid-point site in the next instant. So in a way, a bit similar to diborane, two electrons are connected to three sites, thereby bonding the two ions together.

A simple diatomic molecule can be approximated to a harmonic oscillator [16] and the bonding force on the molecule is then directly proportional to the mass. This type of bond can only occur between nearest neighbours so the higher the number of nearest neighbours the greater the probable total bond energy. At the same time, the greater the number of atoms in a unit cell the less likely a bond may form between two particular atoms. Therefore, the three centre bond energy B_A is a direct function of the number of nearest neighbours but an inverse function of the number of atoms in a unit cell. The energy B_A from three centre bonding is then approximately equal to the following:

$$B_A = (E_{Ha} / 2) M^{0.333} (N_e / C_u)^{0.333} \quad (3)$$

In the above Eqn (3), M is the mass number, N_e is the number of nearest neighbours, C_u is the number of atoms in the unit cell. Manganese, unlike other transition metals, does not have a simple structure. When calculating the value of the three centre bond it is assumed that each manganese atom has an average of two nearest neighbours as discussed in the next section.

It has been shown [17, 18] that exchange interactions need to be taken into account in evaluating ionisation energies of atoms and atomic ions. Repulsion between electrons at a constant distance from each other is the same whether they have parallel or anti-parallel spins. However, assuming that they are not in a confined space there is much less probability of finding two electrons with parallel spins in the same region of space than if they possess paired spins. Since electrons with parallel spins tend to occupy space far apart from each other, a gaseous atom gains exchange stabilisation when it is separated from a solid where it is tightly bound and electrons in the same atom and neighbouring atoms cannot move as far apart from each other even if they have parallel spins. Hence the appropriate amount of exchange energy has to be deducted from the total enthalpy of atomisation. From the results obtained in earlier work on ionisation energies [19, 20] it is estimated in this work that for each additional exchange interaction a neutral transition metal atom gains approximately between 10 to 15 kJ per interaction per mole. The number of exchange interactions for a particular transition metal atom in the gaseous state is dependent on the number of d electrons in each individual neutral transition metal atom and is a straight forward calculation [19, 21] and is listed in Table 3. The exchange energy term E_c is then:

$$E_c = E_i d_E \quad (4)$$

E_i is the number of exchange interactions and the energy d_E is estimated to be just slightly higher than 12 (± 2) kJ per interaction per mole. To keep the calculations simple and consistent only one value for d_E is used even there may be a slightly different value for each transition metal series.

The simplest bond between two atoms is bond in the hydrogen molecule. All other molecules are more complicated and in a naive sense other bond energies between identical atoms may be a function of the hydrogen bond energy and E_H is assigned some fraction of the hydrogen bond energy. The bond dissociation energy of the H_2 bond has reported by Herzberg [22] to be 4.47eV (presumably derived from data of observed spectra of the hydrogen molecule) which is equivalent to 435 kJ per mole. Since there are two atoms in a hydrogen molecule and in atomisation individual atoms are produced the figure of 435 kJ has to be divided by two. Additionally, it is likely that in an atom in the unit cell at any instant only one of the three types of bonds occur or more likely that

an electron in an atom involved in one type of bonding may not be involved in the other two types. Therefore, a more appropriate value of the constants E_{H1} and E_{H2} should be no greater than one third of the value of 435/2 kJ. The value of E_{H1} and E_{H2} is rounded to 72kJ per mole and is the figure used in preliminary calculations. Since three centre bonding is most likely to be weaker than ionic or covalent bonds the value of E_{Ha} (which is the average of E_{H1} and E_{H2}) is further divided by two in expression (3). The enthalpy of atomisation of a transition metal is then given by:

$$\text{Enthalpy of atomisation per mole} = B_I + B_C + B_A - E_c \quad (5)$$

In the above expressions the values of E_p , n , M , N_e , C_u , E_d and E_i are considered to be pure dimensionless numbers. For example, n is a number showing the number of electron shells or principal quantum number and E_i is the number of exchange interactions, E_d is the number of detached electrons, M shows the number of nucleons in the atom and they have no dimensions. Crystal structure data, ionisation energies and enthalpies of atomisation are taken from the open literature and details are described in [Appendix 1](#).

For each individual element, a particular number of atoms per unit cell, number of detached electrons, number of nearest neighbours per atom etc. are required to be input into the formulas (1) to (4) to calculate the enthalpy of formation. The following assumptions are necessarily made for this purpose. Iron occurs in all three structures but mainly bcc and it is assumed to have an average value of four atoms per unit cell. Cobalt is assumed to have the hcp (hexagonal closed packed) structure and nickel the ccp (cubic closed packed) structure. Scandium, yttrium and lanthanum are assumed to have exactly one detached electron per atom. Elements with distorted hcp structures have only six nearest neighbours. Manganese has a highly complex structure containing 58 atoms per unit cell. In each unit cell there are four different “types” of atom, each possessing a particular site symmetry and to simplify matters each atom is estimated to have an average of two nearest neighbours. Mercury has a rhombohedral/distorted ccp structure and assumed to have four atoms per cell.

3. Results and discussion

An initial set of enthalpies of atomisation for the transition metals were calculated by expression (5) with the assumption that both E_{H1} and E_{H2} are equal to 72 kJ per mole and a value of 12.5 kJ for the exchange energy per exchange interaction for all three series. The results agreed fairly well with literature values, however absolute differences between literature values and calculated values exceeded 20% for six metals.

By varying the values of E_{H1} and E_{H2} , and by trial and error a better set of results was produced with E_{H1} being equal to 78 kJ/mol and E_{H2} being equal to 65, 73 and 77 kJ respectively for the 3d, 4d and 5d series. In all cases d_e , the exchange energy term, is equal to 12.5 kJ. The values together with accepted literature values of atomisation enthalpies in kJ per mole are shown in [Table 4](#). A comparison between the values in the Table shows that for 60% of the metal elements the absolute differences between Literature and Calculated are 10% or less and differences exceeded by 20% occur for only three elements (namely chromium, manganese and silver, the difference for palladium is exactly 20%).

The enthalpy of atomisation of an element is essentially the enthalpy change when one mole of atoms in the gaseous state is formed from the element in its standard state. Basically, to all intents and purposes for this work, this means the energy input needed to break all the bonds in one mole of the metal solid turning them to individual atoms in the gaseous state. A model (for example “the ions in a sea of electrons”) that is created to describe the bonding in a metal solid (and in this case transition metals) should be able to predict to a fair degree of accuracy the enthalpy change when a mole of the solid is converted to individual gaseous atoms. This is simply because for metal atoms in the solid state to transform into individual gaseous atoms all the bonds must be broken.

Table 4. Accepted open literature and calculated enthalpies of atomisation.

Atom	Literature enthalpy kJmole ⁻¹	Calculated enthalpy kJmole ⁻¹
Sc	377.8	307.7
Ti	473.0	446.4
V	514.2	522.2
Cr	396.6	490.3
Mn	280.7	416.8
Fe	416.3	450.7
Co	424.7	459.4
Ni	429.7	455.9
Cu	337.4	319.6
Zn	130.4	110.2
Y	421.3	376.9
Zr	608.8	531.2
Nb	725.9	690.8
Mo	658.7	577.1
Tc	678.0	687.2
Ru	642.7	631.4
Rh	556.9	569.6
Pd	378.2	302.5
Ag	284.9	370.3
Cd	111.8	128.5
La	431.0	429.6
Hf	619.2	616.3
Ta	782.0	709.8
W	849.4	871.5
Re	769.9	776.2
Os	791.0	766.1
Ir	665.3	721.4
Pt	565.3	528.9
Au	366.1	434.3
Hg	61.4	54.8

The equations derived from the soft sphere model are very simple and does not need the use of any form of advance computing power, just very basic calculators. So, even though in many cases agreement between the calculated and literature values are not perfect the results are still fairly remarkable. When two atoms approach each other both attractive and repulsive forces may come into play. When the charges are doubled it does not mean that the bond energy is necessarily doubled or a double bond between two identical atoms is twice the strength of a single bond. Therefore, it is most unlikely that the bond energy will increase or decrease linearly with the principal quantum number n or the mass number/atomic number of the atom but only by a fraction of it. Hence, a simple exponent of one third is used in expressions (1), (2) and (3) as an approximation to otherwise may be a very complex calculation.

Transition metal crystals are not ideal or perfect structures. There are different kinds of defects in the solid state, some metals possess more than one crystal structure which in some cases may be elongated or distorted. Or, say for technetium which is radioactive, that radioactivity may increase or decrease the bond energies. In the solid state there is a possibility that under experimental conditions the electronic configuration may be different from that of the free gaseous atom.

Consider the cases of chromium, manganese, palladium and silver, there is only “fair” or can be even described as “poor” agreement between values calculated by the model and literature values with differences of 23.6, 48.5, 20 and 30% respectively. However, manganese has a highly complex structure, each unit cell has 58 atoms and unlike most other transition metals, the mean number of nearest neighbours is less than three. The majority of atoms in the unit cell have larger internuclear distances than the nearest neighbours. So, a large proportion of the bonds formed between the atoms in the unit cell are much weaker than the

bonds formed by the nearest neighbours and the average bond strength may be up to a third lower. If this is lower average bond strength (estimated to be 66% of the previous calculated) is taken into account the calculated enthalpy of atomisation is reduced and different from the literature value by only 2%.

Assuming that as reported in some original papers chromium and silver also exhibit the ccp and hcp structures respectively, the average number of atoms per unit cell for the two metals then become three and five respectively and the calculated enthalpies for the two metals are then different from literature values by only 17% for chromium and 23% for silver. The electronic configuration of a gaseous palladium atom is normally $4d^{10}5s^0$ but under experimental conditions and/or where there are defects in the solid state some of the atoms in the unit cell may acquire outer electronic configurations similar to nickel or platinum. Assuming that this may be the case it is probable that there is an average of 0.5 covalent bonds per atom (as opposed to none for the $4d^{10}5s^0$ configuration). The calculated the enthalpy of atomisation then only differs from the literature value by 5%.

Enthalpies of atomisation that have been derived from experimental measurements were reported by different researchers. Experimental methods and conditions may not be the same for all cases and there is a chance that the degree of purity of the samples used may not be high enough in some cases. No crystal is 100% perfect and there are many defects of different types in the solid state. The calculations assume a single set of conditions and it is not practicable to take into account all the different crystal defects/imperfections which impact on the enthalpies of atomisation. The value of each exchange interaction d_E is assumed to be the same for all the three transition series. There is of course a probability that the value of the exchange interaction can be different for each transition series or it may be slightly different between the first and second half of each series or indeed for each element. Hence, it is impossible to produce a set of calculated results to be identical with values derived from experimental measurements.

In general, transition metals are hard and possess higher tensile strength and higher melting points than most other elements. It is the combination of the different types of bonding which gives transition metals such properties. Especially, in a way not unlike carbon (in the diamond structure), it is likely that the equivalent bonds in all three dimensions which make transition metals into hard and strong materials. In addition, transition metals are malleable and ductile because the “negative ion” in the metal solid is only a detached electron. Since at any instant not all available sites are occupied by detached electrons, when a metal is twisted or bent the “volume” of the site can change and the detached electrons can move from one site to another within a unit cell, allowing the shape of the metal to change without any bonds being broken.

Band theory, which correctly describes the mechanism of electrical conduction in metals, is based on quantum mechanics. The soft sphere model does not contradict band theory but provides a non-mathematical and pictorial representation of it. In band theory, the highest energy band in conducting materials, (the conduction band) is only partly occupied so that random movement of electrons which are in the highest band is allowed. In the soft sphere model, the detached electrons are those electrons which occupy the highest energy band and only some these electrons in the highest energy level can move at random within the unit cell. The two bonding electrons in a three centre bond which under ordinary conditions may move aimlessly between the three atoms forming the bond and enable metals to be good conductors of heat. When a potential difference is applied between the ends of such a solid (say a metal wire) the electrons which form the three centre bonds, instead of only moving about the particular three atoms at random, freely move down the potential gradient from atom to atom forming an electric current.

As a final point, it is of interest to note that there appears to be no correlation between the internuclear distances in the structures of metals (or metallic radii) and their ionic or covalent radii or the average of the

two. Part of the reason is that the number and type of bonds formed for each particular metal as discussed above depends on the crystal structure, number of atoms per unit cell, average number of parallel spins per atom, number of nearest neighbours etc. and not directly dependent on bond lengths/internuclear distances. Secondly, assuming that there should be some correlation it is not possible to show whether there is any correlation nor the degree of correlation because there is no universally agreed set of ionic or covalent radii available and published values are inconsistent. It has also been shown that the apparent ionic or covalent radius of a metal can appear to “vary” [7, 8, 9] depending on the surrounding environment. Appendix 2 provides a more detailed discussion regarding to ionic and covalent radii of metals.

4. Conclusion

The “ions in a sea of electrons” model was developed some time ago when there was much less experimental data available. From previous work [6, 10, 11, 12] it is evident that the ions in a sea of electrons model or any similar model of metallic bonding cannot clarify many of the properties of the transition metals nor can any equations be derived from it which can replicate values such as enthalpies of formation (atomisation), densities, heat capacities, electrical resistivities etc. The soft/flexible sphere model can be used to explain many metallic properties. Equations derived from the soft sphere model can reproduce values such as densities, heat capacities, coefficients of expansion, electron work functions etc. of transition metals. This work which forms part of the model also provides very compelling evidence that what is usually termed metallic bonding is not a single bond type but actually consists of covalent and ionic bonds and three centre bonds. Values of enthalpies of atomisation calculated from simple equations derived from the model produce good agreement with literature values. All this is very good evidence that the form of metallic bonding detailed above is a good physical representation of real transition metal bonding.

Declarations

Author contribution statement

Peter Lang: Conceived and designed the analysis; Analyzed and interpreted the data; Contributed analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

I thank Professor C. D. Flint for helpful discussions and advice.

Appendix 1. Data Sources.

It is worth mentioning that some sets of values published in even very recent compilations contain data originally published many years ago. For example, values of ionisation energies provided by the Handbook of Chemistry and Physics [23] listed as a main source of reference Ionization potentials and ionization limits derived from the analysis of optical

spectra [24] which in turn listed Atomic energy levels [25] as the principal source of data.

Crystal structure unit cell data are taken from Structure of the elements [26] which provides a very comprehensive and detailed compilation of the various crystal structures of all metals with references to original work. To ensure that the data used in this work are reliable two other publications are consulted (a) Crystal Data Determinative Tables [27] which provided a some details of unit cell measurements and Structural Inorganic Chemistry [28] which only gave a brief description of crystal structure and does not give reference to original work. The other main data source is the Handbook of Chemistry and Physics which listed values of enthalpies of formation and ionisation energies. Again, the data are compared with values, where available, provided in various issues of the Journal of Physical and Chemical Reference Data. In general, data from the different publications are found to agree closely or in many cases exactly the same.

The data sources showed that many of the solid metallic structures reported are distorted and not exact close packed arrangements and very often this fact is not mentioned some reference/text books. In some cases where there are even very small amounts of impurities present in the metals being examined the observed structure(s) can be different from the usually recognized one(s). It has to be emphasized that some of the crystal structures and unit cell measurements were made over eighty years ago and in some instances the authors performing the original investigations disagree on the precise structures/shapes or reported different structures for the same transition metals being studied.

Enthalpies of formation and ionisation energies are mainly derived from experimental measurements or calculated using theoretical sound methods and there is little reason to doubt their reliability. Although, there is always a very small probability that in a few cases measurements may not have been taken correctly or incorrect figures being input into equations used in calculations. More importantly, when the enthalpies were derived from measurements taken from impure samples the resulting values obtained would be different from values obtained from pure samples.

Appendix 2. Ionic, covalent and metallic radii of metals.

There are a large number of published sets of reference ionic and covalent radii and the value of the (covalent and/or ionic) radius of any particular element can be wildly different between any two sets. Pauling, Goldschmidt and Ladd, to name but a few, have published sets of reference radii showing fairly different values for most elements. Two reference sets of covalent radii were published fairly recently and the values of one set have been shown to be completely different from that of the other [8]. All the different sets of reference (covalent and ionic) radii cannot be equally accurate or correct and it is simply impossible to determine which set is more reliable. Cordero and coworkers [29] pointed out that for many elements there are “no clearly established covalent radii” and gave examples of inconsistencies in a widely used and well known database of covalent radii, including cases where the bond length of two atoms X and Y is larger than the sum of the individual covalent radii of X and Y.

Schomaker and Stevenson [30] were amongst the first to point out that covalent radii are not additive. It has been clearly demonstrated [7, 8, 9] that the internuclear distance between two atoms A and B forming an ionic or covalent bond can be calculated by the following:

$$D\{AB\} = (\{A\}^k + \{B\}^k)^{1/k} - C$$

In the above formula, $D\{AB\}$ is the internuclear distance between atoms A and B which has formed an ionic/covalent bond, $\{A\}$ is the ionic/covalent radius of atom A and $\{B\}$ is the respective radius of atom B, k is a constant which varies from 1 to 2 depending on the chemical environment, for example for Group I halides k is equal to 5/3 or 1.6667.

C is the square root of the absolute difference in electronegativity between the two atoms. In the case of an ionic bond C is equal to zero. Hence, ionic/covalent radius of an atom may appear different in different chemical environments and trying to determine the correlation between the internuclear distances in the structures of metals (or metallic radii) and the sum of their ionic or covalent radii or the average of the two is not straight forward especially there is no universally agreed set of reference radii and that the published literature values of ionic/covalent radii do not represent the actual radii.

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