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THERMODYNAMIC STABILITY AND BOND MECHANISMS
IN RELATION TO ELECTRONIC STRUCTURE AND CRYSTAL STRUCTURE

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THERMODYNAMIC STABILITY AND BOND MECHANISMS
IN RELATION TO ELECTRONIC STRUCTURE AND CRYSTAL STRUCTURE

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ABSTRACT

Bonding of metallic systems is considered
in terms of a valence bond model.

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Although in principle all the properties of metals should be deducible from the solution of the Schrödinger equation; in practice there is no hope in the foreseeable future that one will be able to deduce properties of metals from first principles alone. Because of the impracticability of the exact quantum treatment of metals one must resort to various simplified models to aid in the correlation of the properties of metals. Thus the electron-gas theory has provided a useful semiempirical model for the treatment of many electrical properties of metals.¹ However, it is of not much value in predicting stabilities of metallic systems nor in general the structures. Since this paper will deal primarily with the questions of stabilities of metallic phases and their structures, the valence-bond theory will be used to provide the most suitable model.

It is clear from quantum mechanics that electrons are the glue which bond materials together. In dealing with a large variety of materials, both metallic and non-metallic, chemists have accumulated a great deal of information about the way in which electrons bind atoms together. Since this experience has been expressed in terms of the valence-bond model, the examination of metals in terms of the valence-bond theory allows one to put to use all the experience which has been obtained in the consideration of bonding of materials of all types. Pauling^{2,3} is of course the pioneer in the use of the valence bond method as applied to metals.^{4,5} The treatment to be discussed here is similar to Pauling's method but follows a modification of it as suggested by Neils Engel.⁶

The best way to judge the applicability of valence-bond theory is to look at the facts. Table 1 presents the heats of atomization of the solid

elements. In those instances where the elements are solid at room temperatures the values given are the heats required to vaporize one gram atom to the gaseous atomic state. Where those substances are gaseous or liquid at room temperatures, the heats of atomization are given for the solids at the melting point. If one starts at the right hand side of the table one sees that the heats required to atomize the rare gas solids are very small and correspond to Van der Waal's forces acting between atoms with completed octets of electrons. The Van der Waal's type of bonding is an important type in many chemical systems, but as it is rather weak compared to the typical bonds in metallic systems, this type of bonding will not be discussed here. The next column which gives the heats of atomization of the halogens illustrates the strength of bonds involving a single pair of electrons. The halogens have seven electrons per atom and bond together to form diatomic molecules in which one electron pair composed of one electron from each atom binds the two atoms together. It will be seen that the energy of the bond due to a single pair of electrons is of the order of 20-30 kilocalories. The sixth group elements have only six valence electrons and can therefore form two bonds. Structures are obtained corresponding to endless chains or rings in which each sulfur or selenium atom is bonded to two others, each bond involving a single pair of electrons. One sees that the energies required to produce an atom by breaking of two pairs of electrons corresponds to roughly twice that of a single electron pair bond. One will note that for the first row elements, boron through oxygen, there is another way in which the electrons can be used for bonding, namely through multiple bonds between the atoms. Thus for oxygen two pairs of electrons are used to bond a single pair of oxygen atoms. In Table 2 where the structures of the elements are illustrated, the differences in structures are illustrated by a single line

between two atoms for the halogens to illustrate a bond consisting of a single pair of electrons and for sulfur, selenium, and tellurium the bonding is illustrated by two lines from a single atom to illustrate the fact that two bonds are formed with each atom, each bond consisting of a single pair of electrons. At the end of each line there is of course another sulfur or selenium atom which in turn is bonded to the next one giving an endless chain or a ring if the end atom should come around to the initial starting point. For oxygen the double bond character is indicated by a pair of parallel lines between the two atoms indicating the use of two pairs of electrons. The fifth group elements have three electrons missing from a completed octet and three single electron pair bonds can be formed with phosphorus, arsenic and heavier elements forming an infinite plane somewhat similar to graphite, although puckered, whereas nitrogen, as for the other first row elements, forms a multiple bond with three pairs of electrons concentrated between a pair of atoms. This difference between the first row elements and all the others is not only true of the elements but is shown in all the compounds so that one expects multiple bonds for the first row elements whenever possible, whereas the occurrence is much rarer for the heavier elements. It will be noted in Table 1 that the use of three pairs of electrons in bonding yields bonding energies of almost three times those obtained with only a single pair of electrons. The evidence shows clearly that the bonding is stronger the greater the number of electron pairs involved in bonding. For atoms of the fourth group with half of the electrons of the octet missing, there is a possibility of four bonds giving tetrahedrally bonded silicon or germanium whereas carbon, being a first row element with a tendency for form multiple bonds, forms graphite which is indicated as consisting of a carbon atom with

two single bonds and a double bond between it and three other carbon atoms. Actually because of resonance between the various bonds, the three bonds are equivalent in graphite with partial multiple bond character in all. Carbon can also exist under pressures in the diamond structure for which the bonding is due to four single electron pair bonds. In either case whether the electrons are used all in single pair bonds or in multiple bonds the use of four pairs of electrons to bond the carbon atom to neighboring carbon atoms produces very closely the same heat of atomization.

If now for the moment the transition elements which involve d electrons are bypassed, one sees in Table 1 that the alkali metals, which have only one electron per atom available for bonding purposes, have bonding energies or heats of atomization of the same order as that of the halogens, which likewise have only one electron per atom available for bonding. The trends are also similar. As one goes down in the periodic table the internuclear distance increases because of the repulsion of inner filled shells and the bonding energy due to a pair of electrons, which depends upon the electrical interaction between the pair of electrons and the two positive nuclei, decreases as the internuclear distance increases as one sees by examining the trend from sodium to rubidium and chlorine to iodine. The small value for fluorine involves a special repulsive problem which will not be of importance for the metals and therefore will not be discussed further here. If one goes to the second row one finds that these elements, which have two electrons per atom available for bonding, have bonding energies of the same order as those of the sulfur-selenium family which also have two electrons available for bonding. For the third group one again finds a close parallelism between the bonding energies due to three electrons per atom of boron and aluminum

and due to three electrons per atom of nitrogen and phosphorus. It was comparisons of this type that led Pauling to point out that the bonding in metals must be very similar to the covalent bonding that is well characterized for elements like sulfur, chlorine and bromine.

One can best visualize the bonding in terms of orbitals which represent regions of space which can be occupied by electrons. When orbitals from adjacent atoms overlap and are occupied by one electron from each atom, these overlapping orbitals containing a pair of electrons constitute a bond. For the rare gas atoms where each of the four orbitals is filled with a pair of electrons, it is not possible to obtain bonding by means of an electron pair bond between atoms. However, for the halogens where one electron has been removed from one of the four orbitals it is possible to obtain a single electron pair bond by overlapping the two half filled orbitals so that the pair of electrons is occupying both of the overlapping orbitals. Once this bond has been formed between a pair of halogen atoms there are no additional orbitals available for bonding, and the electron pair bond is restricted between the pair of atoms. For the alkali metals, on the otherhand, none of outer orbitals has a pair of electrons in them so that all orbitals are available for bonding between atoms, and the bonding is not restricted to a single pair of atoms. Thus one could visualize the electron pair bond being formed between a sodium atom and one neighbor and then with some other sodium neighbor. Of course through resonance the bonding becomes equivalent to all of the neighbors. However, the bond is still a single electron pair bond and has the same strength as the single electron pair bond for a halogen of comparable radius and this is the basis for Pauling's contention that the bonds in metals involving s and p electrons are essentially equivalent to

the covalent bonds that are so familiar in non-metallic compounds. Whether one goes to the right from the alkali metals or whether one goes to the left from the halogens, the bonding energy is roughly proportional to the number of electrons per atom or the number of electrons that are available for formation of electron pair bonds.

The analysis of the spectra of the gaseous atoms is now complete enough so that for almost all elements, one knows the relative stabilities of electrons of different angular momentum, and one knows how many s, how many p, and how many d or f electrons are present in each gaseous atom. Up to now this discussion has dealt only with s and p electrons which in the diamond structure, for example, mix or hybridize to form all equivalent sp^3 hybrids. The existence of four s and p electrons hybridized to the sp^3 configuration will yield the diamond structure no matter what the nuclei may be. It is the electrons which determine the strength of the bonding and it is the electrons which determine the configuration or structure of the atoms as a result of the bonding.

Let us take the example of germanium which has four electrons per atom and therefore forms the diamond structure. If one now produces the compound gallium arsenide in which each gallium provides three electrons and each arsenic provides five, so that one has an average of four electrons per atom, one again gets the diamond type structure in which each gallium atom and each arsenic atom makes four electron pair bonds tetrahedrally oriented to each of its neighbors. If we now consider zinc selenide with again an average of four electrons per atom, one again finds exactly the same structure. Even going as far as cuprous bromide with again four electrons per atom, the same structure is found. The internuclear distances are almost identical for all of these compounds. In germanium the electron pair will be symmetrically

arranged between the germanium atoms. In cuprous bromide one would expect the electron pairs to be polarized so as to be closer to the bromine than to the copper. The copper will have some positive charge and the bromine will have negative charge. The bonding energy of the bond can be described conveniently in two parts, one due to the covalent electron pair bond and another part due to the coulombic attraction between the positive and negative ions. An extreme example of this would be illustrated by the compound NaGa. Here again the diamond arrangement is obtained. Gallium with only three electrons per atom has taken one electron from the alkali atom to obtain the necessary four electrons per atom to produce the diamond structure. This results in a negative charge on the gallium atoms and the resulting positive alkali atoms are held in the lattice by coulombic attraction.

If one considers chemical compounds as a whole one finds variations between the two extreme types of bonding which are illustrated on one hand by sodium fluoride where the electron of the sodium has been transferred virtually completely to the fluorine leaving rare gas configurations for both ions with the bonding energy being due primarily to the coulombic attraction of the positive and negative ions. One sees the other extreme in chlorine or silicon where there can be no charge separation because of the equivalence of all the atoms and the bonding must be due exclusively to covalent bonding. One can find every gradation between these two extremes and most metallic compounds fall in the intermediate class where both covalent bonding to electron pair bonds and coulombic bonding due to the existence of charged ions contribute importantly to the overall bonding energy.

The consideration of the transition elements requires the knowledge of the way in which d electrons contribute to bonding in contrast to s and p electrons that have been considered up to now. Examination of the heats of

atomization in Table 1 in going from potassium to zinc or from rubidium to cadmium shows clearly that the d electrons do contribute importantly to the bonding. For example, vanadium which has five electrons in its valence shell all together has a considerably higher bonding energy than germanium which has only four. In fact one sees that the d electron can be even more effective than the s and p electrons by comparison of titanium and germanium, both of which have four electrons. For the gaseous atoms one knows the exact distribution of electrons among the s, p and d types. For example scandium has two s electrons and one d, titanium has two s and two d, vanadium three d and so on. One also knows from the excited electronic states of the atoms that other arrangements of s and p and d electrons for these elements can be produced without a large difference in energy. Thus one can see that a variety of electronic configurations could be possible, depending upon the environment. In the study of transition metal compounds, this is well understood and has been well characterized through study of the spectra, magnetism, and stability of the transition metal compounds and complexes.

All the transition elements are characterized by the variety of the oxidation states that they can show. One has every reason to expect similar behavior in the metallic systems and one would not expect these elements to show the same valence in all environments. For many of the compounds of the transition metal elements one can often show very clearly from the spectrum alone what the actual resulting electronic configuration is. Unfortunately for the metals one does not have such unambiguous diagnostic tools. However from the knowledge which has been obtained from a variety of compounds and complexes one can draw some conclusions about the relative stabilities of d, s, and p electrons for elements of the various periods. One can make some predictions about the differences between chromium, molyb-

denum and tungsten for example. However, for the most part, we will have to use inductive processes for fixing the electronic structures of the transition metals. Table 2 which gives the crystal structures of the elements shows that there is a fairly good correlation between position in the periodic table and structure. We have already examined the behavior on the far right hand side of the periodic table where the number of electrons per atoms is clearly associated with a given type of structure. On the left hand side of the table one finds a variation of structure with position in the periodic table which is most clearly illustrated by sodium, magnesium, aluminum and silicon which change from the body center cubic to the hexagonal close pack and then to the cubic close pack and finally to the diamond structure with increasing electron to atom ratio. All evidence indicates that the number of electrons per atom that are involved in metallic bonding or covalent bonding are one, two, and three for sodium, magnesium, and aluminum, respectively, and it is clear that silicon uses four electrons per atom bonding. Therefore, these structures corresponding to the 1, 2, 3 or 4 electron per atom bonding arrangements have been labelled with Roman Numerals I, II, III, and IV. For all of the alkali metals where only one electron per atom is available for bonding we do have the body centered cubic I structure. It is interesting to note that this same structure re-occurs in the fourth, fifth, and sixth groups where titanium, zirconium, and hafnium have at low temperature the hexagonal close pack structure but at high temperatures revert to body centered cubic, whereas the vanadium - tantalum, chromium - tungsten groups have only the body centered cubic with the exception of cubic close pack for chromium at very high temperatures. If one follows along after molybdenum and tungsten, there are two groups of elements with hexagonal close pack structure followed by two groups of

elements with the cubic close pack structure. In going from sodium to aluminum the structure changes from I to II to III as the number of electrons per atoms is increased. In going from zirconium and hafnium to silver and gold we know that the total number of electrons per atom is increased and we find a similar sequence of structures from I to II to III. This repetition of sequences of structures demonstrates a relationship between structure and electronic configuration, although the detailed relationship of the structural changes to electronic changes has still not been definitely established. It would be a little difficult to do it just from the evidence presented here. However, Dr. Niels Engel⁶ considered not only structural data of the kind presented here but also structural data for the various phase diagrams among the transition elements, magnetic data and a variety of other data and presented a rather interesting and stimulating proposal. His proposal was an extension of the Hume-Rothery rules which, as you recall, go along the same lines as those presented here in that a characteristic structure is associated with a given number of electrons per atom.

Now it is interesting to note that the hexagonal ϵ phase which according to the Hume-Rothery rules has a electron to atom ratio of 1.75, is of the same structure as the hexagonal close phase for the elements that are labelled II here and apparently can be obtained for a range of electron to atom ratios in the vicinity of two. Likewise the β phase with an electron to atom ratio of 1.5 has the body centered cubic structure indicating that the I structure is not restricted to exactly 1 electron per atom but may be found for a wide range of electron concentrations below a ratio of 1.5. Engel suggested that the structure is determined by the s and p electrons and not by the d electrons, although the d electrons contribute importantly to bonding energy. Thus, on this basis, Engel assigned to the VI group elements, chromium through tungsten,

the electronic configuration d^5s^1 in the metallic state which is a low lying configuration for the gas. He proposed that these elements have the body centered cubic structure of the alkali metals because they have approximately one s electron per atom as in the case of the alkali metals. He pointed out from consideration of data of the type given in Table 1 that the d electrons must contribute importantly to the bonding and that more stable metals are obtained if one uses as many d electrons as possible in bonding. Thus for vanadium, niobium, and tantalum he proposed the electronic configuration d^4s^1 in agreement with structure I, and the configuration d^5s^2 for Tc and Re with structure II.

Turning now to the left hand side of the table the sequence sodium, magnesium, aluminum, silicon proceeded quite simply because there were no d electrons available for bonding. Electron configurations involving d electrons are very high in energy for such light elements. However, as one proceeds beyond potassium not much energy is required to excite electrons to levels involving d electrons and the occurrence of the body centered cubic structure for calcium, strontium and barium instead of the hexagonal close pack structure of magnesium would be interpreted in the terms of having one d electron involved in bonding and only one s electron. Likewise the occurrence of scandium, yttrium and lanthanum in the hexagonal close pack II structure contrasting to the cubic close pack structure III of aluminum would be an indication that one electron is used in d bonding. By the time one reaches the IV group the d electrons have become stabilized enough as would be anticipated from the behavior of the electronic structures of the gaseous atoms that even two or three electrons can be put into the d state as indicated by the appearance of I and II structures. The occurrence of cubic close pack III structures for calcium and strontium are not explainable

on this basis. The presence of the hexagonal close pack structure for strontium and the cubic close pack structure for lanthanum would be indicative of the possibility of metallic structures not involving an appreciable amount of d electrons under those conditions where the structures exist. However, by comparing the Hume-Rothery rules with the rules that Engel has suggested for the elements, one sees that these structures are not limited to the integral number of electrons per atom. Thus a III structure for lanthanum does not mean that all of electrons are s and p electrons. There could be as many as perhaps an average of 0.5 d electrons per atom with 2.5 sp electrons per atom. The contribution of d electrons to the bonding of the alkaline earth metals and of the third group metals below magnesium and aluminum is indicated by looking at Table 1. In contrast to the gradual reduction of the bonding energy that one would anticipate as the sizes increase, one finds the expected drops from beryllium and boron to magnesium and aluminum and then a rise to calcium and scandium. The bonding energies are higher and the internuclear distances are smaller than one might expect in support of Engel's contention that d electron bonding must play some role for the alkaline earth metals, calcium to barium, and for the third group metals, scandium to lanthanum. The d electrons become increasingly more effective in bonding as one goes to the heavier elements as can be seen by comparing titanium to hafnium, chromium to tungsten, etc.

One might consider now why the maximum heat of atomization occurs in the fifth group with vanadium and niobium and then switches to the sixth group for tungsten. This would seem to be related to this clear trend in the effectiveness of d electrons in strengthening of the bonds as the atomic number is increased. The effect of the extra d electron in the sixth group is not so important with the lighter elements so that chromium and molybdenum

actually appear to lose in bonding energy compared to vanadium and niobium where in the case of tungsten, the d electrons have become so effective that the extra d electron can clearly be utilized. When one goes beyond the sixth group the data for the gaseous atoms indicate that the elements prefer to maintain a half filled shell of five d electrons and to put the extra electrons into the s levels of the next higher shell. This also shows up clearly in the crystal structures with the transition from I structure for chromium, molybdenum, and tungsten to II structure for technetium and rhenium with a variety of structures, some quite complex, for manganese which would indicate that for manganese the various possible electronic configurations are so close in energy that manganese cannot make up its mind as to which structure it would prefer. It perhaps occurs in several different electronic configurations in the same structure. As additional electrons are added Engel would explain the gradual transition from I to II structure to III structure as being due to the need to maintain as many d electrons as possible in an unpaired state and therefore the promotion of as many electrons as possible to s and p states. Engel characterized copper, silver and gold as being three electron elements. These elements are commonly described in the metallurgical literature as being one electron metals. Examination of Table 1 shows that this is clearly not possible. One could never explain the very high heats of atomization of copper, silver and gold on the basis of only one electron per atom. Internuclear distances and bonding energies clearly require that copper, silver and gold have more electrons per atom for bonding than zinc, cadmium and mercury. Even if one compares them with elements of known trivalence and comparable size such as copper with arsenic and silver with antimony or copper with aluminum, one concludes that there must be contribution of d electron bonding in addition to that of the three sp

electrons.

The copper zinc diagram is a very interesting one to consider in this connection, and Engel has pointed out that copper can dissolve zinc and that when zinc dissolves in the cubic close pack structure of copper it would be expected to contribute at least two and possibly as many as four electrons per atom. The zinc might well promote electrons to allow d electrons to become unpaired and available for bonding with d electrons in copper. With increasing zinc it becomes impossible to maintain the cubic close pack structure and then a transition to the β phase takes place. In a phase with so much zinc, the zinc is expected to be divalent and to have completely shared d electrons. Thus there is no advantage to the copper to maintain unpaired d electrons since they cannot bond with their neighbors. In a zinc lattice, then, the copper would behave as a one electron metal since the stability due to the unpaired electrons is lost. Thus from the point of view of the Hume-Rothery rules, copper in an environment of other metal atoms which do not have unpaired d electrons will behave as a one electron metal. However copper in compounds with transition metal or in pure copper will behave as a 3 electron metal so as to take advantage of the additional stability given by the bonding due to unpaired d electrons. This variability of valence is not surprising; one sees this all the time in the compounds of the transition metals. Copper itself can form cuprous compounds in which the d electron shell is left intact or cupric compounds in which one electron is removed from the d shell to leave an unpaired d electron behind. It is this variability of the valence of the transition metal elements, depending upon the environment, which makes the chemistry of the metallic system so complicated. One must examine carefully the relative advantages that would accrue to having more or less d electrons and more or less s and p electrons. This is the

type of reasoning which is necessary for dealing with the halides of these elements, since one knows clearly that the metal can turn in a variety of oxidation states depending on the environment. Clearly the same reasoning must be used in treating the inter-metallic compounds. The structures and heats of atomization will be two of the most important clues as to the actual valence adopted by the element in a given structure. Engel in his manuscript goes into considerable detail in the discussion of various binary phase diagrams to show the relationship between structure and bonding. His manuscript was fairly widely circulated in a mimeographed form and more and more of his ideas are appearing in the literature.

It is of interest to compare the atomization energies of the transition metals with the atomization energies of bonds, carbides, silicides, and nitrides of the transition metals.⁷ It is significant that the peak of maximum stability gradually moves from the metals of the fifth and sixth groups to the metals of the fourth group as one adds non-metals with increasing numbers of electrons as in the sequence B, C, N. This would indicate an increasing tendency to donate electrons to the metallic bonding system.

In the case of the nitrides, apparently one to two electrons per nitrogen are used to convert the electronic structure of the fourth group metals to the electronic structure of optimum bonding strength characteristic of the pure fifth and sixth group metals.

The brief discussion given here shows the usefulness of the valence bond model in extending bonding behavior which is well established in non-metallic compounds to metallic systems. Metallic systems use the same electronic glue as do other types of systems and one would expect that any theories of bonding in metals be consistent with more general bonding theories.

Li	Be	B
38.4	77.9	135.
Na	Mg	Al
25.9	35.6	77.5

Table 1

Heat of atomization of the solid elements in kcal/gram atom at 298.15°K or at the melting point, whichever temperature is lower.

C	N	O	F	Ne
170.9	113.7	60.4	19.7	0.50
Si	P	S	Cl	Ar
108.	79.8	66.	32.2	1.84

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
21.5	42.2	90.	112.7	123.	95.0	67.2	59.5	101.6	102.8	81.1	31.2	65.3	90.	69.	49.4	28.1	2.55
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sr	Sb	Te	I	Xe
19.5	39.1		146.	173.	157.5		144.	133.	91.	68.4	26.75	58.	72.0	62.	46.	25.5	3.57
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
18.7	42.5	100.2	168.	186.8	200.	187.	(165.	155.	135.2	87.3	15.32	43.0	46.8	49.5	34.5		
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
97.	80.	77.		50.	42.	84.	87.	62.	70.	66.	58.	40.	95.
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md		Lw
136.6	126.	125.	105.	92.	66.								

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Li	Be	B
I	II	*
Na	Mg	Al
I	II	III
K	Ca	Sc
I	I	II
Rb	Sr	Y
I	II	II
Cs	Ba	La
I	I	III
Fr	Ra	Ac

Table 2
Crystal Structures of the Elements

I Body Centered Cubic
 II Hexagonal Close Pack
 III Cubic Close Pack
 IV Diamond
 * Complex

C	N	O	F	Ne
IV	≡	≡	—	
Si	P	S	Cl	Ar
IV	↖	<	—	
Ge	As	Se	Br	Kr
IV	↖	<	—	
Sn	Sb	Te	I	Xe
*	↖	<	—	
In	Pb	Bi	Po	At
(III)	IV	↖		
Tl	Pb	Bi	Po	At
I	III			

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
III	III?	II		(II)	I	II	II	II	II	II	II	III	II
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md		Lw
I		I	I?	I									
III	*	**	**	**									

L. Brewer, 1961
 after N. Engel

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APPENDIX : Thermodynamic and Structural Data for the Elements

Table 1 presents the heats of atomization of the solid elements in kcal/gram atom at 298.15°K for elements that are solid at 298.15°K. For the liquid and gaseous elements, the heats of atomization are given for the solid at the melting point. Thus the value tabulated is ΔH° for the reaction $M(s) = M(g)$. Virtually all values given have been taken from Lewis, Randall, Pitzer, and Brewer.¹ The values given for Sr, Ru, Os, Ge, P, As, Po, and the rare gases and the value of the enthalpy of fusion of Hg were obtained from Stull and Sinke.² The Rh value given by Stull and Sinke agrees with the average of recent determinations reviewed by Dreger and Margrave.³ The values given for Ga, In, La, Ce, Nd, Sm, Eu, Tm, and Yb with extrapolation to 298°K if necessary were obtained from Hultgren et al.⁴ The value for Nb is from Speiser, Blackburn, and Johnston.⁵ The Pd value is from Dreger and Margrave.⁶ The Sc value was obtained from a third law treatment of the data of Spedding et al.⁷ The values for Gd, Tb, Dy, Ho, Er and Lu are from White et al.⁸ Their Nd value agrees well with the one given by Hultgren.⁴ The Dy value seems low and the Lu value high. The Pr value is an average based on White et al.,⁸ Spedding and Daane,⁹ and Johnson et al.¹⁰

Table 2 presents the crystal structures of the elements. Only structures obtained for pure elements are listed. Non-equilibrium structures obtained by cold working are not listed. The symbol $\bullet \text{---} \bullet$ represents a diatomic molecule with a single electron pair bond. = and $\equiv$ represent diatomic molecules with double and triple bonds, respectively. The symbol $\angle$ represents a structure containing atoms which form two single bonds per atom to form rings or infinite chains. The symbol ∇ represents three single bonds

per atom and corresponds to a puckered planar structure. The symbol $\triangleright \equiv$ represents the graphite structure where one resonance form consists of two single and one double bond per atom. Symbols in parentheses represent structures that are slight distortions of the type represented by the symbol. The structures given are based on Table B given by Hansen¹¹ except for the addition of the high temperature form of Cr claimed by Bloom, Putnam, and Grant.¹²

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