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Theory of the Heats of Formation of Transition-Metal Alloys

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A simple expression for the heat of formation ΔH of transition-metal alloys is derived within the tight-binding approximation that has the form $\Delta H = f(\bar{N})\Delta N^2$, where $\bar{N}$ and ΔN are the average and difference in number of valence d electrons, respectively. The prefactor $f(\bar{N})$ is most negative for $\bar{N}$ lying near the middle of the series and it becomes positive towards the edges. The theory gives good agreement with Miedema's semiempirical values of ΔH.

Recently Boom, de Boer, and Miedema[1] have developed a highly successful semiempirical scheme that reporduces the observed signs of the heat of formation of about 500 alloys of the simple and transition metals. It is a natural extension of Pauling's[2] original description of electronegativity in which the heat of formation ΔH was proposed to be proportional to the square of the electronegativity difference ΔX. Boom, de Boer, and Miedema,[1] in order to overcome the problem that Pauling's scheme always predicts a negative ΔH, included a repulsive contribution proportional to the square of the charge-density mismatch at the Wigner-Seitz boundary $\Delta N^{1/3}$. Thus

$$\Delta H_{\mathrm{Miedema}} = -P(\Delta\varphi^*)^2 + Q(\Delta n^{1/3})^2, \qquad (1)$$

where the attractive charge-transfer term was originally[3] assumed proportional to the square of the difference in the work function $\Delta\varphi$. Unfortunately, good agreement with the experimental sign of ΔH could only be achieved by adjusting the experimental work function φ, sometimes by as much as $\Delta\varphi$ itself, to new values[1] φ^*. It was, therefore, not clear what fundamental significance should be attached to the final coordinate φ^*. In this Letter a microscopic theory of the heat of formation of transition-metal alloys will be presented that not only gives good agreement without any adjustable parameters to Miedema's semiempirical values of ΔH, but also suggests a different interpretation of the underlying physics of the coordinate φ^* from that previously[1] ascribed to it.

The cohesive energy of the pure transition-metal constituents arises[4, 5] from the strong bonding of the valence d electrons, which are well described[6] by the tight-binding approximation in which the center of gravity of the d band in the solid is assumed[5,6] equal to that of the atomic d level. The energy in the solid is then given simply by the sum of the one-electron band energies, so that the cohesive energy may be equaled to the d-bond contribution[5,6]

$$U_{\mathrm{bond}}(N) = \int^{E_{\mathrm{F}}} (E - C) n(E)\, dE\,, \tag{2}$$

where N and $n(E)$ are the number of valence d electrons and their density of states respectively, and E_{F} and C are the Fermi energy and center of the d band respectively. By assuming a rectangular d-band density of states of width W, Friedel[4] showed that the bond energy displayed the parabolic trend with band filling,

$$U_{\mathrm{bond}}(N) = -N(10 - N)W/20\,, \tag{3}$$

which is observed experimentally in the cohesive energy across the nonmagnetic $4d$ and $5d$ series. It follows therefore, that the change in energy on forming the AB alloy can be written as the difference in the one-electron band energies

$$\Delta H = \int^{E_{\mathrm{F}}} E n_{AB}(E) dE - \tfrac{1}{2}\int^{E_{\mathrm{F}}{}^{A}} E n_{A}(E) dE - \tfrac{1}{2}\int^{E_{\mathrm{F}}{}^{B}} E n_{B}(E) dE\,, \tag{4}$$

provided the renormalization in the relative position of the d bands $\Delta C = C_B - C_A$ because of charge transfer on forming the alloy can be neglected. The latter is, in fact, a very good approximation in transition-metal alloys as has been demonstrated quantitatively by van der Rest, Gautier, and Brouers[7] who have studied the $3d$ alloys of Fe and Ni within the tight-binding coherent-potential approximation. Figure 4 of their paper clearly illustrates that ΔH is not very sensitive to this renormalization in ΔC. Even though there might be a sizable flow of d charge when the constituents are well separated in the periodic table (see Fig. 1 of Ref. 8), this results in only a small change in ΔH because of cancellation between the change in the sum of the one-electron band energies and the double counting[7] contribution respectively. Thus, as a first approximation, ΔH does not depend *explicitly* on the charge transfer Q, as can be seen from Eq. (4) where only the *total* density of states $n_{AB}(E)$ enters in the alloy sum and not the individual partial contributions.

The heat of formation is evaluated by assuming that the bonding in the *disordered* AB alloy is well described like that in the pure constituents[4-6] by a simple rectangular d-band density of states, which is centered midway between the two atomic d levels C_A and C_B with a width W_{AB} determined by the second moment of the exact average density of states of the alloy. Because the pth moment of the density of states associated with a given atom can be written[9] within the tight-binding approximation in terms of all the paths of length p that start from the given atom and return to it, I find that W_{AB} must satisfy the equation

$$\tfrac{1}{12}W_{AB}{}^2 = \tfrac{1}{12}W^2 + \tfrac{1}{4}(\Delta C)^2, \tag{5}$$

where W is the width in the absence of diagonal disorder[10] ($\Delta C = 0$). The left-hand side of Eq. (5) is simply the second moment of a rectangular density of states (normalized to unity) of width W_{AB}, whereas the right-hand side contains the contributions to the second moment from the paths of length 2 in the alloy arising from hopping to the nearest neighbors and back and hopping twice on the same site respectively. Thus, the alloy width may be written

$$W_{AB} = [1 + 3(\Delta C/W)^2]^{1/2}W. \tag{6}$$

The heat of formation ΔH may now be evaluated directly from Eq. (4). Expanding Eq. (6) to second order, I find

$$\Delta H = \Delta H_0 + \Delta H_s\,, \tag{7}$$

where

$$\Delta H_0/W = -\tfrac{1}{80}(\Delta N)^2 - \tfrac{1}{4}\Delta N(\Delta C/W) - \tfrac{3}{40}\bar{N}(10 - \bar{N})(\Delta C/W)^2\,, \tag{8}$$

and

$$\Delta H_s/W = -\tfrac{1}{24}(5 - \bar{N})\Delta N(\Delta V/\bar{V})\,, \tag{9}$$

where $\bar{N}$ is the average number of valence d electrons per atom. The first term ΔH_0 is the heat of formation obtained from Eq. (4) assuming that the pure constituents have the same atomic volume as the alloy $\bar{V}$ (assumed determined by Vegard's law), while ΔH_s is the *size*-factor contribution obtained from Eq. (3) in bringing the pure constituents to their observed equilibrium atomic volumes V_A and V_B. It results from the first-order change in the A- and B-band widths as the nearest-neighbor distance changes from that of the AB alloy to that observed for the pure components assuming that the tight-binding hopping parameters fall off inversely with distance to the fifth power.[11] Because of the symmetric nature of the d-bond energy, ΔH_s is zero for $\bar{N} = 5$.

The accuracy of this simple analytic expression (8) for ΔH_0 has been demonstrated elsewhere[8,12] by comparison with the tight-binding coherent-potential–approximation results[7] for the $3d$ alloys of bcc Fe and fcc Ni in which the densities of states $n_{AB}(E)$ were computed directly. It, therefore, remains to provide a simple interpretation of the three contributions to ΔH_0. The first two terms represent the result within the virtual-crystal approximation in which all sites in the alloy are equivalent and can be characterized by the average atomic d level $\overline{C}$. The width of the alloy d band in this approximation remains that of the pure constituents, namely W. The *attractive* first term of Eq. (8) results from the fact that Eq. (3) is a concave parabola, so that the d-bond energy for the average number of electrons $\overline{N}$ is always lower than the average of the bond energies for the individual constituents N_A and N_B. The second term in Eq. (8) is *repulsive*, because the center of gravity of the alloy d band lies above that of the more numerously populated pure-metal d band, since the atomic d level becomes more tightly bound as the valence N increases. The first two terms in Eq. (8) give a net *repulsive* contribution for transition metals that is countered only by going beyond the virtual-crystal approximation and including the attractive second-order contribution proportional to $(\Delta C)^2$, which results from treating the A and B site d levels as $\pm\Delta C/2$ with respect to the average background of the virtual-crystal approximation. This attractive contribution to ΔH_0 is very similar to that proposed by Pauling,[2] in that ΔC is clearly a measure of the difference in the free atom's ability to attract d electrons and hence a measure of the electronegativity difference ΔX. In fact, if we exclude the group-VIII metals, then ΔC *is* proportional to ΔX within either the $4d$ or $5d$ series, because both Pauling's[2] electronegativity and the atomic d level[13] vary linearly across the series. Moreover, the prefactor multiplying this contribution to ΔH_0 is directly dependent on the strength of the metallic bond in the alloy $U_{\text{bond}}(\overline{N})$ in a manner reminiscent of Pauling's constant of proportionality that depended on the number of resonating bonds per atom. However, I must stress that this contribution in transition metals is not explicitly associated with the flow of charge[8] Q and so is not directly ionic in character. Rather it reflects the increase in d-bond strength through the widening of the alloy bandwidth W_{AB} compared to the pure constituents due to their electronegativity difference [see Eqs. (3) and (5)]. A similar widening occurs for the energy gap between bonding and antibonding states in covalent systems described by the Hückel[14] (π states in hydrocarbons) and Phillips[15] (sp^3 states in semiconductors) models.

ΔH may be written as a single term by inserting into Eq. (8) the known[13] linear dependence of the atomic d level on valence N, namely

$$\Delta C = -k\Delta N\,, \tag{10}$$

so that

$$\Delta H_0 = \tfrac{1}{4}W[(\hat{k} - \tfrac{1}{20}) - \tfrac{3}{10}\hat{k}^2\overline{N}(10-\overline{N})](\Delta N)^2, \tag{11}$$

where $\hat{k} = k/W$. Thus ΔH_0 is proportional to the square of ΔN with the constant of proportionality dependent on the average band filling $\overline{N}$. ΔH_s may also be expressed in this form by fitting the equillibrium atomic volumes[16] of the $4d$ or $5d$ transition-metal series to

$$V = V_0[1 + \alpha(N - N_0)^2]\,. \tag{12}$$

Substituting Eq. (12) into Eq. (9) and keeping terms to second order in ΔN, we find

$$\Delta H_s = \frac{\alpha}{12}W\left\{\frac{(5-\overline{N})(N_0-\overline{N})}{[1+\alpha(N-N_0)^2]}\right\}(\Delta N)^2. \tag{13}$$

Figure 1 compares the theoretical values of $\Delta H/(\Delta N)^2$ for different average band fillings $\overline{N}$ with Miedema's semiempirical values[17] for the $4d$ alloys with $\Delta N \leq 4$. I have taken $k = 1$ eV,[7] $W = 10$ eV,[6] $\alpha = 0.0308$, and $N_0 = 7.3$.[16] I have not included the alloys with larger values of ΔN in the comparison because in this[8, 12] Letter terms to only second order in ΔN have been retained. (The other two $4d$ alloys that have been studied experimentally besides ZrRu[18] and RhPd[19] mentioned in Fig. 1 are ZrRh and ZrPd[18] with ΔN equal to 5 and 6 respectively. Using the exact expression (5) would lead to an increase in $\Delta H_0/(\Delta N)^2$ of $+0.026$ eV and $+0.033$ eV respectively, which gives values of $\Delta H/(\Delta N)^2$ that are still consistent with the upper bound of -0.01 eV set by the experiment[18].) We see from Fig. 1 that the theory agrees remarkably well with Miedema's results, the main deviation occurring for $\overline{N} = 8.5$ where the experimental value of Myles[18] for RhPd favors the more repulsive theoretical value. This had been a somewhat surprising experimental result. Rh and Pd are neighboring group-VIII metals with the same Pauling[2] electronegativity value of 2.2 and with atomic volumes that differ by only 6%,[15] so that chemically they were thought of as very similar elements. However, because the size-factor contribution ΔH_s increases as $\overline{N}$ moves towards the edges of the series [see Eq. (9)], the 6% volume difference between Rh and Pd is suffi-

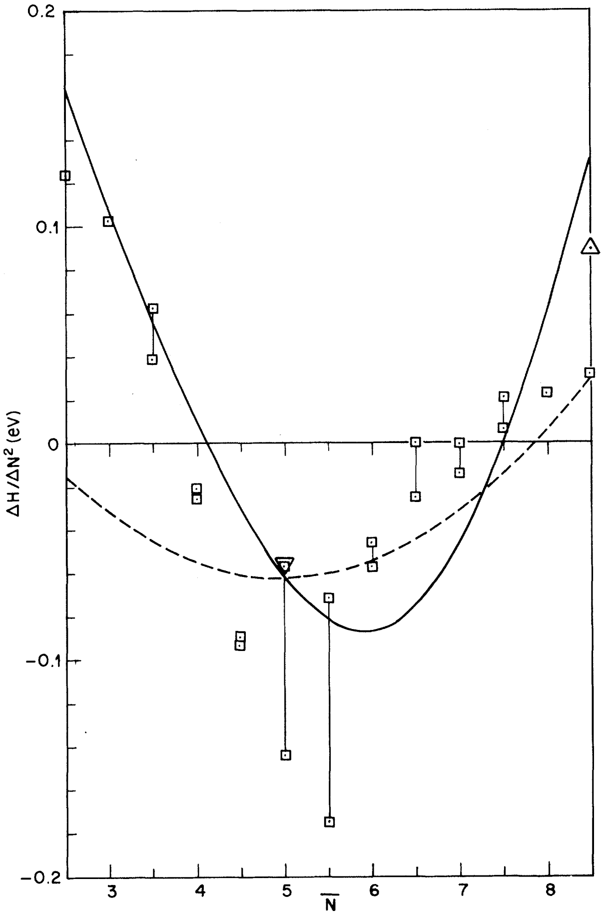

FIG. 1. The heat of formation ΔH for the $4d$ series divided by the square of the difference in number of valence d electrons $(\Delta N)^2$ as a function of the average number of valence d electrons $\bar{N}$. The full curve is the theoretical $\Delta H/(\Delta N)^2$, whereas the dashed curve excludes the size-factor contribution. Miedema's (Refs. 1 and 16) values for $4d$ alloys with $\Delta N \leq 4$ are represented by squares with the points for common $\bar{N}$ connected by lines. The two experimental points are RhPd (Ref. 14) (triangles) and ZrRu (Ref. 15) (inverted triangles), where the latter is from a value for ΔG, not ΔH.

cient to give the large positive heat of formation observed.

The explanation for Miedema's empirical[20] success is apparent from looking at his final choice of parameters φ^* and $n^{1/3}$. Apart from the group-VIII elements his coordinate φ^* is found to vary linearly with N across the $4d$ and $5d$ series, so that the first term in Eq. (1) can be identified directly with ΔH_0. However, because his prefactor P is a constant whereas Eq. (11) passes through zero close to $\bar{N}=8$, Miedema was constrained to choose φ^* a constant for the group-VII and -VIII elements in order to force $\Delta\varphi^*$ to vanish and thereby the contribution ΔH_0. Furthermore, if the other coordinate $n^{1/3}$ is fitted to an expression of the form (12), then Miedema's second term is very similar to ΔH_s, the deviation in $\Delta H_s/(\Delta N)^2$ being less than 0.03 eV for all values of $\bar{N}$ except $\bar{N}=8.5$.

In conclusion, the theory has provided the first *a priori* justification for the use[21] of the coordinates $\bar{N}$ and ΔN to describe transition-metal alloy behavior. The present tight-binding theory can be extended to include the sp-bonded materials as well, so that a fully microscopic theory of metallic heats of formation within the periodic table may be achieved.

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Cosmological Production of Baryons

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Departures from thermal equilibrium which are likely to occur in an expanding universe allow the production of an appreciable net baryon density by processes which violate baryon-number conservation. It is shown that the resulting baryon to entropy ratio can be calculated in terms of purely microscopic quantities.

It is an old idea[1] that the observed excess of matter over antimatter in our universe may have arisen from physical processes which violate the conservation of baryon number. Of course, the rates of baryon-nonconserving processes like proton decay are very small at ordinary energies, but if the slowness of these processes is due to the large mass of intermediate vector of scalar "X bosons" which mediate baryon nonconservation, then at very high temperatures with $kT \simeq m_X$, the baryon-nonconserving processes would have rates comparable with those of other processes. However, even if there are reactions which do not conserve C, CP, T, and baryon number, and even if these reactions proceed faster than the expansion of the universe, there can be no cosmological baryon production once the cosmic distribution functions take their equilibrium form, until the expansion of the universe has had a chance to pull these distribution functions out of equilibrium. This can easily be seen from the generalized Uehling-Uhlenbeck equation[2] for a homogeneous isotropic gas,

$$\begin{aligned} dn(p_1)/dt = \textstyle\sum_{kl} \int dp_2 \cdots dp_k dp_1' \cdots dp_l' \\ \times \{ \Gamma(p_1' \cdots p_l' \to p_1 \cdots p_k) n(p_1') \cdots n(p_l')[1 \mp n(p_1)] \cdots [1 \pm n(p_k)] \\ - \Gamma(p_1 \cdots p_k \to p_1' \cdots p_l') n(p_1) \cdots n(p_k)[1 \pm n(p_1')] \cdots [1 \pm n(p_l')] \}, \end{aligned} \tag{1}$$

where n is the single-particle density in phase space; p labels the three-momentum and any other particle quantum numbers, including baryon number; and Γ is a rate constant, equal, for $k = l = 2$, to the cross section times the initial relative velocity. The factors $1 \pm n(p)$ represent the effect of stimulated emission or Pauli suppression for bosons or fermions, respectively. If at any instant, $n(p)$ takes its equilibrium form, then $n(p)/[1 \pm n(p)]$ is an exponential of a linear combination of the energy and any other conserved quantities; so for any allowed reaction with $\Gamma \neq 0$, we have

$$n(p_1') \cdots n(p_l')[1 \pm n(p_1)] \cdots [1 \pm n(p_k)] = n(p_1) \cdots n(p_k)[1 \pm n(p_1')] \cdots [1 \pm n(p_l')]. \tag{2}$$

Under T invariance, Γ would be symmetric, and the two terms in the integrand of Eq. (1) would cancel. But even without T invariance, unitarity always gives

$$0 = \textstyle\sum_l \int dp_1' \cdots dp_l' [1 \pm n(p_1')] \cdots [1 \pm n(p_l')][\Gamma(p_1 \cdots p_k \to p_1' \cdots p_l') - \Gamma(p_1' \cdots p_l' \to p_1 \cdots p_k)], \tag{3}$$

so that the p' integrals in (1) still cancel.[3] For an expanding gas there are also terms in Eq. (1) which represent the effects of dilution and red shift, and these terms can produce departures from equilibrium, but of course they have no direct effect on the baryon number per co-moving volume.

This note will describe a mechanism for production of a cosmic baryon excess, based on the departures from thermal equilibrium which are likely to have occurred in the early universe. It is assumed