

ON THE HEATS OF FORMATION OF THE BINARY HYDRIDES OF TRANSITION METALS

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Summary

It is demonstrated that the available experimental information on the heats of formation of binary transition metal hydrides can be interpreted in terms of an empirical model in which energy effects are treated as contact interactions between metal atom cells and hydrogen atom cells.

From the model it is apparent that, for the various binary metal-hydrogen systems in which stable hydrides occur, the maximum concentration of hydrogen corresponds to approximately the same volume concentration of hydrogen.

Formation enthalpies of binary hydrides of all transition metals, which are required in empirical predictions of ΔH for ternary hydrides, are tabulated.

A connection is made with recent band structure theoretical calculations on hydrides.

1. Introduction

We have recently demonstrated [1] that the heats of formation ΔH of transition metal nitrides can be described in terms of a simple atomistic model. Energy effects are treated as contact interactions between nearest-neighbour atomic cells. Compared with the heats of formation of other inter-metallic compounds those of the transition metal nitrides are special, because experimentally the reference state is gaseous N_2 and not metallic nitrogen as required in the model calculations. Consequently ΔH contains an additional term which is proportional to $\Delta H(\frac{1}{2} N_2 \rightarrow N_{\text{metal}})$.

In this work we will show the similarity between the transition metal hydrides and nitrides. For hydrides, too, the reference state in determinations of enthalpies of formation is gaseous H_2 . The enthalpy difference between gaseous H_2 and metallic hydrogen is expected to be large [2]. This is illustrated in Fig. 1. If hydrogen were a normal metal, the heat of formation of metal hydrides could be represented by a smooth curve (curve (a)), allowing for hydrides to be stable at all different values of the atomic concentration c_H of hydrogen. The transformation energy adds to the smooth curve a term

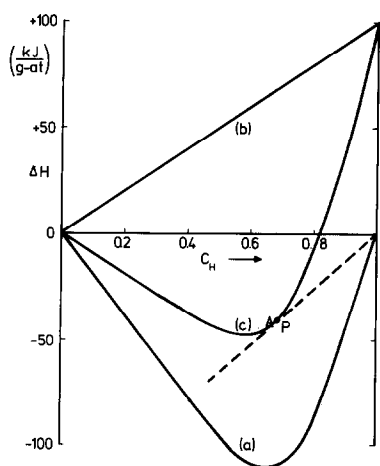


Fig. 1. Enthalpy vs. composition curves for a metal-hydrogen system, in this case the Ti-H system, for which an experimental point is included. If hydrogen were a metal, ΔH could be described by curve (a). Curve (b) represents the transformation enthalpy from gaseous H_2 to metallic hydrogen, while curve (c) represents the sum of curves (a) and (b) (expressions (1) and (3)). Point P gives the maximum composition for a stable hydride.

$$\Delta H_{trans} = c_H \Delta H \left(\frac{1}{2} H_2 \rightarrow H_{metal} \right) \quad (1)$$

(curve (b) in Fig. 1). This results in curve (c) which shows that hydrides to the right of point P are unstable. The position of point P is related to, among other things, the relative sizes of the metal and hydrogen atoms. In Fig. 1 both curves (a) and (b) (and hence also curve (c)) are linear in c_H at low values of c_H . For curve (a) this is the result of the fact that, at low concentrations, hydrogen atomic cells are completely surrounded by metal cells. If the hydrogen concentration is increased gradually in ordered hydrides, at a certain concentration contacts between neighbouring hydrogen atomic cells cannot be avoided and curve (a) starts to deviate from the initial straight line. The position of point P is related to that concentration at which the curvature of curve (a) becomes appreciable, which in turn is determined by the relative sizes of the hydrogen and metal atoms.

In this work we will show that the available experimental information about ΔH of binary transition metal hydrides can be reproduced by means of the empirical formalism given previously [1]. It will be demonstrated that, for the various stable binary transition metal-hydrogen systems, the position of point P corresponds to an approximately constant minimum H-H interseparation of about 2.3 Å. The existence of such a minimum H-H interseparation for stable binary hydrides has been predicted by Switendick [3] on the basis of band structure theoretical investigations.

The present empirical approach makes it possible to predict ΔH for hydrides of arbitrary and sometimes imaginary concentrations, which are of

importance in predictions of the stability of hydrides formed from intermetallic compounds.

2. Empirical scheme for calculating heats of formation and volume effects

We will summarize the various steps in the calculation of heats of formation, as introduced in previous work [1, 4, 5]. Energy effects in alloys have been introduced as contact interactions, generated at the interfaces between dissimilar atomic cells. For alloys of two transition metals A and B in which A is clearly the minority metal, the heat of formation can be expressed in terms of the two effective work functions ϕ^* , the cell boundary electron densities n_{ws} and the molar volume of metal A:

$$\Delta H = - \frac{c_A P V_A^{2/3} (\Delta\phi^*)^2}{(n_{ws}^{-1/3})_{av}} + c_A Q_0 V_A^{2/3} (\Delta n_{ws}^{1/2})^2 \quad (2)$$

The first term represents the negative energy of an electrostatic dipole layer. This energy is proportional to the interface area (and hence to $c_A V_A^{2/3}$) and to the square of the difference in the electronic work functions of the two metals and is inversely proportional to the average electrostatic shielding length which can be represented by $(n_{ws}^{-1/3})_{av}$. The second term is determined by the difference in the electron density for A and B cells that has to be smoothed. This term is also proportional to the interface area.

Relation (2) has been used empirically in the form

$$\Delta H = \frac{P c_A V_A^{2/3} f_B^A}{(n_{ws}^{-1/3})_{av}} \left\{ -(\Delta\phi^*)^2 + \frac{Q}{P} (\Delta n_{ws}^{1/3})^2 - \frac{R}{P} \right\} \quad (3)$$

For differences in n_{ws} that occur for metals the second term in relation (3) is equivalent to that in relation (2). The third term is purely empirical; it represents a hybridization energy which is found to stabilize alloys of transition metals with polyvalent non-transition metals. Also for transition metal hydrides the introduction of a non-zero R appears to be essential.

In relation (3) f_B^A represents the degree to which A atoms are surrounded by B atom neighbours. For alloys rich in B, f_B^A is equal to unity. For other compositions f_B^A is found from the average experimentally observed concentration dependence [6] of ΔH in systems in which a number of ordered compositions occur. In Fig. 2 values of f_B^A are tabulated as a function of the atomic concentration of A for the special case of equal-sized A and B atoms. f_B^A is found as the ratio of ΔH at a given composition to the value expected from the linear dependence at low concentrations. For atoms of different sizes the concentration dependence of ΔH is not symmetrical; the extreme value is reached close to a concentration at which the total surface area of A atoms equals that of B atoms ($c_A V_A^{2/3} = c_B V_B^{2/3}$). The tabulated values of f_B^A still apply if, in Fig. 2, atomic concentrations c_A are replaced by surface concentrations c_A^s :

$$c_A^s = c_A V_A^{2/3} / (c_A V_A^{2/3} + c_B V_B^{2/3}) \quad (4)$$

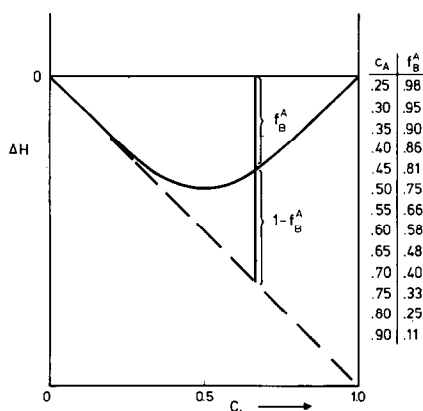


Fig. 2. The average concentration dependence of the heats of formation of a series of ordered intermetallic phases in a binary system for metals of equal molar volume. If the volumes are different it can still be used if C_A is replaced by the surface concentration C_A^s , relation (4). The tabulated values of the degree f_B^A to which A cells are surrounded by B neighbours can be derived from the curve as indicated.

The tabulated empirical values of f_B^A , to a good approximation, can be represented by

$$f_B^A = (1 - C_A^s) [1 + 8 \{C_A^s (1 - C_A^s)\}^2] \quad (5)$$

A problem is that the molar volumes of the constituent metals in an alloy can be different from their pure metal volumes because the formation of the electrostatic dipole layer occurs with a transfer of charge. In calculations of ΔH we need to know the atomic volume in between the values before and after charge transfer. This can be derived from

$$V_A^{2/3}(\text{alloy}) = V_A^{2/3}(\text{pure}) \{1 + a f_B^A (\phi_A^* - \phi_B^*)\} \quad (6)$$

The relative volume change is proportional to the difference $\phi_A^* - \phi_B^*$ in electronegativity and to the degree to which A atoms are surrounded by dissimilar neighbours. Approximate values for the proportionality constant a have been derived from experimentally observed volume contractions in intermetallic compounds to be about 0.14, 0.10, 0.07 and 0.04 for monovalent, divalent, trivalent and higher valent metals respectively [4]. In most cases the volume correction is of minor importance but, because of the relatively large change in volume per transferred electron for monovalent metals, it is important for hydrides. It should be noted that, since f_B^A is a function of $V_A^{2/3}$ (relations (4) and (5)), the calculation of $V_A^{2/3}(\text{alloy})$ in principle requires successive steps.

The applicability of relation (6) to binary metal hydrides can be verified by comparing the experimentally observed volume changes upon hydride formation with those corresponding to the values of $V_M^{2/3}$ and $V_H^{2/3}$ obtained from relation (6). It must be kept in mind that relation (6) represents the volumes half-way between the values before and after charge transfer, whereas

the experimentally observed volume changes will correspond to the situation after charge transfer. As we show in Section 4, there is good agreement with experiment for the values of V_H and ϕ_H^* assumed.

3. Parameters for hydrogen metal

In our empirical approach we need to know the electronegativity parameter ϕ_H^* of hydrogen metal, the cell boundary electron density $n_{ws}^{1/3}(H)$ in metallic hydrogen, the corresponding molar volume V_H , the transformation energy $\Delta H(\frac{1}{2}H_2 \rightarrow H_{metal})$ between gaseous molecular H_2 and metallic hydrogen and the hybridization energy R . For the two other proportionality constants P and Q we use the values derived for alloys of transition metals with non-transition metals. If in relation (3) ϕ^* is expressed in volts, n_{ws} is expressed in empirical density units (d.u.) (see Table 1 of ref. 1) and ΔH is expressed in kilojoules per gram atom of alloy, then $P = 12.3$ and $Q/P = 9.4$.

In the present calculations we further assume that $\phi_H^* = 5.2$ V, $n_{ws}^{1/3}(H) = 1.5$ d.u., $V_H = 1.7$ cm³, $\Delta H(\frac{1}{2}H_2 \rightarrow H_{metal}) = 100$ kJ (g atom H)⁻¹ and $R/P = 3.9$.

The value assumed for ϕ^* agrees quite well with the position of hydrogen in Pauling's electronegativity scale and with the average relation between X (Pauling) and ϕ^* [5].

The value assumed for n_{ws} agrees quite well with the value for the interstitial electron density in hydrogen metal, derived in recent self-consistent band structure calculations by Moruzzi *et al.* [7], and with the average relation existing between empirical cell boundary densities n_{ws} and calculated interstitial electron densities [8].

The assumed molar volume of hydrogen metal is that derived from experiments on the pressure dependence of the heats of formation of hydrides of metals for which $\Delta\phi^*$ is small, *i.e.* palladium and nickel [9]. The assumed value is slightly smaller than the theoretically predicted molar volume V_H of metallic hydrogen of 1.85 cm³ [2, 7].

The transformation enthalpy $\Delta H(\frac{1}{2}H_2 \rightarrow H_{metal})$ is obtained from the room temperature experimental value of the dissociation energy of H_2 (+215 kJ (g atom H)⁻¹ [10]), from the theoretically estimated cohesive energy without zero point effects for metallic hydrogen of about -135 kJ (g atom H)⁻¹ [2, 7, 11] and from a reduced value of the positive zero point energy of about +20 kJ (g atom H)⁻¹. The zero point energy is reduced because the characteristic Einstein lattice frequencies of hydrogen in transition metal hydrides are considerably lower than the lattice frequencies in pure hydrogen metal. The relatively small temperature-dependent contributions in the transformation enthalpy are neglected.

The value of the hybridization term R is derived as a best-fit value. However, as will be shown in Section 5, it finds a physical interpretation in band structure calculations [12 - 14].

4. Comparison with experiment

We collected in Table 1 experimental information on the enthalpies of formation of binary transition metal hydrides. We used this information to determine best-values of R .

TABLE 1

Comparison of experimental and calculated values of the enthalpies of formation of binary hydrides^a

<i>Hydride</i>	ΔH_{exp} (kJ (g atom) ⁻¹)	ΔH_{calc} (kJ (g atom) ⁻¹)	$(\Delta V/V)_{\text{exp}}$ (%)	$(\Delta V/V)_{\text{calc}}$ (%)	<i>Reference</i>
Sc _{0.35} H _{0.65}	-66	-63	9	18	15, 16
Ti _{0.33} H _{0.67}	-42	-44	31	41	15, 17
V _{0.67} H _{0.33}	-11	-12	8	10	18, 19
V _{0.33} H _{0.67}	-18	-11	38	49	15, 18, 20
Cr _{0.50} H _{0.50}	-4	-3	19	27	21, 22
Mn _{0.55} H _{0.45}	-2	-11	10	22	23
Fe _{0.50} H _{0.50}		+4		25	
Co _{0.66} H _{0.34}	0	+3		14	24
Ni _{0.67} H _{0.33}	-1	+4		13	9
Ni _{0.50} H _{0.50}		+6	18	26	25
Y _{0.36} H _{0.64}	-72	-63	7	11	15, 16
Y _{0.28} H _{0.72}	-69	-58	18	17	16, 26
Zr _{0.33} H _{0.67}	-55	-63	19	31	15
Zr _{0.41} H _{0.59}	-51	-64	16	22	15, 16
Nb _{0.67} H _{0.33}	-14	-19	6	9	15, 18, 27
Nb _{0.33} H _{0.67}	-20	-28	31	38	15, 20
Mo _{0.51} H _{0.49}	-3	-1	12	20	24
Tc _{0.50} H _{0.50}		+9		19	
Ru _{0.50} H _{0.50}		+11		20	
Rh _{0.67} H _{0.33}	+6	+4		10	28
Pd _{0.67} H _{0.33}	-7	+2	11	9	15, 29
La _{0.27} H _{0.73}	-62	-51	23	13	15, 16
La _{0.36} H _{0.64}	-67	-56	19	9	15, 16
Hf _{0.37} H _{0.63}	-42	-55	17	27	15, 16
Hf _{0.66} H _{0.34}	-21	-33	5	8	30, 31
Ta _{0.67} H _{0.33}	-13	-17	6	9	15
W _{0.50} H _{0.50}		+4		19	
Re _{0.50} H _{0.50}		+13		18	
Os _{0.50} H _{0.50}		+12		19	
Ir _{0.50} H _{0.50}		+10		18	
Pt _{0.50} H _{0.50}		+7		17	
Th _{0.33} H _{0.67}	-49	-65	11	21	15
Th _{0.23} H _{0.77}	-47	-53	44	34	15, 32
U _{0.25} H _{0.75}	-32	-18	70	44	15, 16
Pu _{0.33} H _{0.67}	-52	-36	55	36	15, 16

^a Observed and estimated values for volume expansion $\Delta V/V$ are also included.

As an example of the kind of quantitative overall agreement that can be obtained we plotted calculated curves for ΔH as a function of c_H for the Ti-H system in Fig. 1 and for the V-H and Nb-H systems in Fig. 3.

The curves for the V-H system show good agreement with the results of experiments; in the case of the Nb-H system the negative ΔH values are clearly too high. It should be noted that no elastic size effects were included in the calculations. Hence the calculated values may be somewhat more negative than experimental values obtained for solid solutions or for non-stoichiometric hydride compositions.

Figure 4 gives calculated enthalpy *versus* composition curves for a number of systems in which the hydride phases are either unstable or only just stable. We note that our empirical theory properly includes the non-existence of hydride phases in many binary systems. The curve for rhenium in Fig. 4 also represents those of technetium, ruthenium, osmium and iridium with hydrogen. The calculated enthalpy *versus* c_H curve for Rh-H also represents those of iron, cobalt, nickel, tungsten and platinum with hydrogen; that for Cr-H also represents those of palladium and molybdenum with hydrogen. The differences between the calculated and experimentally observed values for $\text{Co}_{0.66}\text{H}_{0.34}$, $\text{Ni}_{0.67}\text{H}_{0.33}$, $\text{Rh}_{0.67}\text{H}_{0.33}$ and $\text{Pd}_{0.67}\text{H}_{0.33}$ (Table 1) are of the order of the accuracy of the fit to be expected. For instance, the observation that the calculated ΔH value for $\text{Pd}_{0.67}\text{H}_{0.33}$ is more positive than the experimental value can partly be ascribed to the fact that the zero point energy for hydrogen in palladium is considerably lower than that assumed for the average metal in the calculations. A deviation of the characteristic Einstein temperature θ_E (800 K) from the average value corresponds to an enthalpy effect of $10 \text{ kJ (g atom H)}^{-1}$.

In Table 1 experimental volume effects are compared with calculated volume effects. In the volume expansion $\Delta V/V$ the quantity ΔV is defined as the difference between the molar volume of the hydride (thus per mole

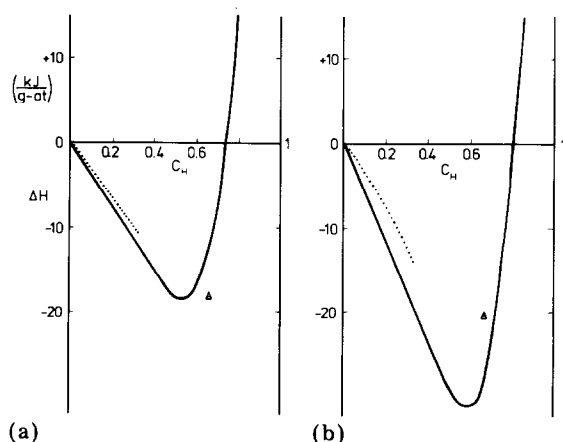


Fig. 3. Comparison of the calculated enthalpy of formation curves with experimental results (... , Δ) for (a) V-H and (b) Nb-H [15, 18, 20].

of metal) and that of the pure metal M. In view of the approximate nature of relation (6) the agreement between the experimental and calculated values is satisfactory.

Large differences between experimental and calculated values occur for the hydrides of uranium and plutonium.

For the actinide metals this can be explained in terms of the molar volumes varying with the 5f-6d mixture of the valence electrons of the metals. For instance, the molar volumes of the different allotropes of elemental plutonium vary between 12 and 15.2 cm³. It follows from the present considerations that hydrides show a tendency to favour the largest possible H-H separation, which will correspond to the largest possible molar volume of the transition metal. Hence we can expect the molar volume of plutonium in PuH₂ to be that of the large-volume allotrope. Remarkably enough, also in the case of UH₃ the volume expansion considerably exceeds the calculated value. We postulate that, although for uranium metal a large-volume allotrope cannot be observed as a function of temperature, such an allotrope has an enthalpy not much above that of the ground state. The experimental volume expansion of 70% in the hydride would correspond to a molar volume of 16.6 cm³ for uranium metal. With this value of V_M the calculated ΔH of UH₃ amounts to -24 kJ (g atom)⁻¹ thus also improving the agreement with ΔH_{exp} . This additional enthalpy lowering, obtained by giving uranium an unusually large molar volume, is sufficiently high to stabilize a metastable uranium modification.

For thorium hydrides the experimental and calculated volume changes agree rather well; apparently variations in molar volume are less important here.

5. Discussion

For the relatively stable hydrides the present model yields a maximum concentration of hydrogen. In Fig. 1 we find the critical value of c_H in the Ti-H system at $T = 0$ K (point P); for other temperatures the procedure given previously [1] can be followed, as illustrated in Fig. 5. The difference between zero and non-zero temperature can be taken into account by drawing the tangent to the ΔH versus c_H curve starting from the point $c_H = 1$, $\Delta = -T\Delta S$. For metal-hydrogen reactions ΔS is about 65 J K⁻¹ (g atom H)⁻¹ and is fairly independent of the metal host. For $T = 300$ K the limiting value of c_H is indicated by the position of P¹ in Fig. 5.

For the metals that form stable binary hydrides the maximum hydrogen concentrations at $T = 0$ K and at $T = 300$ K are collected in Table 2. A maximum value of c_H corresponds to a minimum H-H separation if a given lattice type is assumed for the ordered hydrogen atom positions. The minimum H-H distances of Table 2 are those for a simple cubic arrangement of hydrogen atoms. It is demonstrated that, for the more stable transition metal hydrides, the calculated minimum H-H separations are approximately constant (2.3 Å at 0 K and 2.5 Å at 300 K and 1 atm).

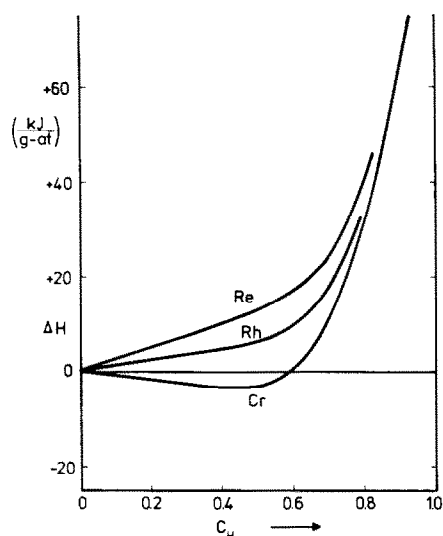


Fig. 4. Calculated enthalpy of formation *vs.* composition curves for some binary systems in which there are only weakly stable or unstable hydrides.

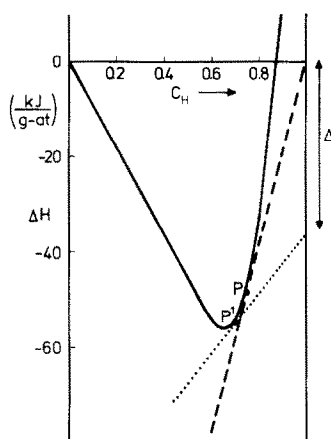


Fig. 5. Calculated values of the enthalpies of formation of ordered La-H hydride phases as a function of the hydrogen atomic concentration c_H . The points P and P' indicate limiting values of c_H at $T = 0$ K and at $T = 300$ K respectively. The parameter Δ equals $T\Delta S$, where in practice ΔS is the entropy of hydrogen gas.

TABLE 2

The distances between hydrogen atoms for the maximum hydrogen concentration at which hydrides are calculated to be stable^a

<i>M</i>	Maximum concentration (% H)		<i>H-H</i> distance (Å)	
	<i>T</i> = 0 K	<i>T</i> = 300 K, <i>p</i> = 1 atm	<i>T</i> = 0 K	<i>T</i> = 300 K, <i>p</i> = 1 atm
Sc	73	67	2.27	2.45
Ti	69	62	2.25	2.43
V	60	49	2.32	2.61
Y	75	70	2.35	2.53
Zr	73	67	2.29	2.46
Nb	67	50	2.31	2.60
La	75	71	2.43	2.58
Hf	72	66	2.29	2.46
Ta	65	55	2.36	2.63
Th	76	71	2.39	2.56
U ^b	68	59	2.39	2.65
Pu ^b	68	61	2.33	2.52

^aFor convenience it is assumed that the hydrogen atoms occupy the lattice positions of a simple cubic lattice.

^bFor uranium and plutonium the molar volume used in the calculations is that of the allotrope stable at room temperature.

The concept of a minimum H-H distance was introduced by Switendick [3]. He noted that the hydrogen positions in the hydride are determined by the requirement of an optimum H-H separation as well as by the availability of interstitial positions. As a consequence of the oversimplification made by estimating a simple cubic hydrogen lattice at maximum c_H , the value for the critical H-H separation found from Table 2 can be a point of discussion, but the underlying principle is in agreement with Switendick's suggestion.

Gelatt *et al.* [13], Switendick [3, 12] and Kulikov *et al.* [14] have discussed the stability of transition metal hydrides in terms of the electronic band theory of solids. The essence of their results can be represented by Fig. 6. Upon the formation of for example a monohydride MH, the density of states *versus* energy curve of the transition metal is changed. As a consequence of the hydrogen implantation a low-lying band of states with spherical symmetry around the hydrogen sites is formed. The position of this low-lying s-type band is of central importance to the stability of the hydride. For a given transition metal the position of the s-type band, relative to the d-type conduction band, is independent of the hydrogen concentration c_H for low c_H values. In higher hydrides (large c_H) the low-lying level is displaced upwards, in this way determining a maximum value of c_H up to which hydrides can be stable. In different metals with a fixed value of c_H (e.g. the dihydrides of the transition metals) the position of the top of the additional s-band relative to E_F can be significantly different (δ in Fig. 6). For dihydrides Switendick has found a correlation between δ and ΔH . He has interpreted the calculated change of δ with hydrogen concentration as a repulsive H-H interaction.

We note that there is a marked similarity between the way Switendick arrives at a maximum concentration (and a minimum H-H separation) in stable binary hydrides and the way it is found in Fig. 1 or Fig. 5. The value of δ in band structure calculations corresponds to the value of R in our empirical approach. As long as the hydrogen concentration is sufficiently low, so that hydrogen atomic cells are completely surrounded by metal atom neighbours, the parameter δ is found to be constant while R results in a negative contribution to the heat of formation per hydrogen which also is independent of c_H . At concentrations at which the ΔH *versus* c_H curve becomes curved, δ starts to change. The close correspondence is illustrated by the fact that Switendick's value for the minimum H-H separation is 2.2 Å, quite close to that concluded from Table 2.

It is not easy to establish a quantitative connection between the value of the present hybridization term R and that of δ . Our value of R for a hydrogen atom completely surrounded by transition metal neighbours amounts to about 100 kJ (g atom H)⁻¹.

There is a connection with the results of molecular orbital calculations of hydrogen-transition metal clusters, as shown in Fig. 7 for Ni₄H [33]. This figure shows energy levels for Ni₄ clusters, which can be correlated with the density of states *versus* energy curves of nickel metal, the energy level of the ground state of the hydrogen atoms and the energy levels of Ni₄H

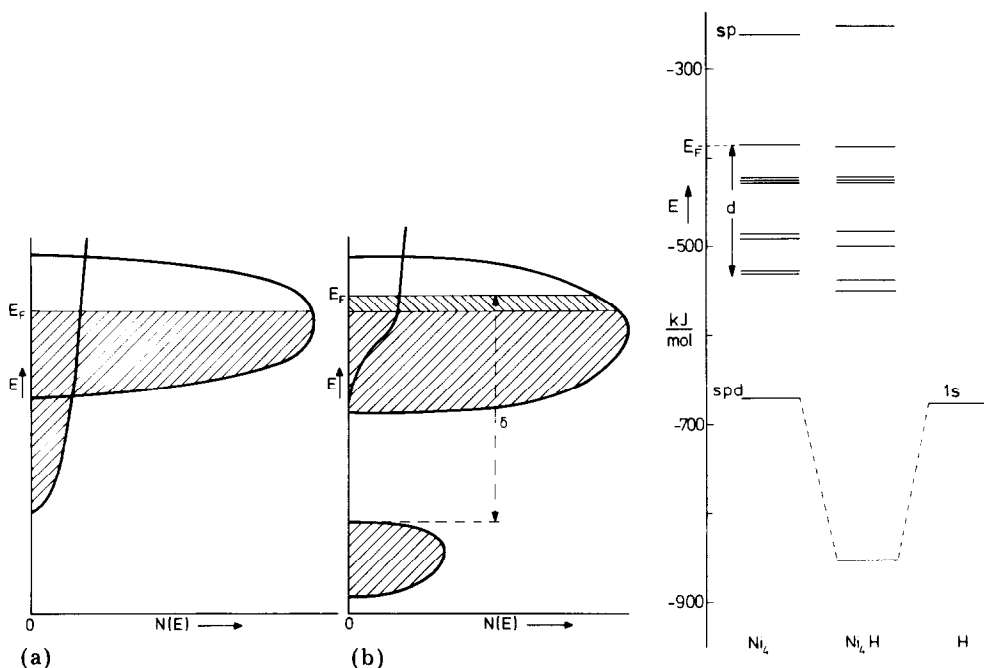


Fig. 6. An illustration of the density of states in (a) a transition metal and (b) a transition metal hydride. The states associated with the low-lying band in (b) have s-type symmetry around the hydrogen site. δ is the distance between the top of this s-type band and the Fermi energy E_F . Because hydrogen adds electrons to the system, the d band in (b) is more filled [3].

Fig. 7. An energy eigenvalue diagram obtained from molecular orbital calculations on a tetrahedral Ni_4 cluster with a hydrogen atom in its centre [33].

clusters. The lowest level in Ni_4H has been lowered with respect to the lowest levels of Ni_4 and hydrogen by an amount $0.14 \text{ rydberg} = 180 \text{ kJ}$. Messmer *et al.* [33] have reported similar energy reductions for Pd_4H and Pt_4H . It would be expected that the energy lowering of the $1s$ level in Fig. 7 would correspond approximately to the sum of the cohesive energy of metallic hydrogen, the zero point energy and the R term; this amounts to $190 \text{ kJ (g atom H)}^{-1}$ in our empirical description.

6. Application to ternary hydrides

In terms of a model in which energy effects in metallic alloys are treated as contact interactions between dissimilar metallic atoms, the heats of formation of ternary hydrides can be derived from those of two binary hydrides and the binary intermetallic compound. In their paper on hydrogen absorption in $LaNi_5$ and related compounds van Mal *et al.* [34] have demonstrated that, for this class of compounds, the heat of hydride formation can be calculated from

$$\Delta H(AB_nH_{2m}) = \Delta H(AH_m) + \Delta H(B_nH_m) - \Delta H(AB_n) \quad (7)$$

where n is assumed to be much greater than unity. Metal A is a transition metal that forms stable binary hydrides and metal B is a second transition metal.

In successive steps Miedema *et al.* [35, 36] have generalized relation (7) in order to be able to estimate ΔH for hydrides formed from compounds AB_n with values of n down to unity.

$$\Delta H(AB_nH_{x+y}) = \Delta H(AH_x) + \Delta H(B_nH_y) - (1 - F) \Delta H(AB_n) \quad (8)$$

where x , y and F depend on the atomic composition (*i.e.* on the value of n) of the intermetallic compound AB_n as well as on the size of the hydrogen-attracting atom A. As binary A hydrides are supposed to be more stable than the binary hydrides of B, there is a tendency to have more A-H contacts than B-H contacts if originally there were A-A contacts. For compounds AB_n with small n and/or reduced m , the factor $(1 - F)$ is introduced, accounting for the fact that not all A-B contacts are lost upon absorption of hydrogen. Values for x , y and F proposed in ref. 36 are given in Table 3. It can be seen that F , $x + y$ and x/y all vary smoothly with n .

TABLE 3

Values of the parameters needed in calculations of the enthalpies of formation of hydrides formed from intermetallic compounds AB_n (relation (8))^a

Metal A	AB_n	AB_nH_{x+y}	x	y	F
Ti, Hf, Zr, V, Nb, Ta, Sc	AB_5	AB_5H_5	2	3	0.1
	AB_3	AB_3H_4	2	2	0.2
	AB_2	$AB_2H_{3.5}$	2	1.5	0.4
	AB	ABH_2	1.5	0.5	0.6
La, Y, rare earth, Th, U, Pu	AB_5	AB_5H_6	2.5	3.5	0.1
	AB_3	AB_3H_5	2.5	2.5	0.2
	AB_2	AB_2H_4	2.5	1.5	0.4
	AB	$ABH_{2.5}$	2	0.5	0.6

^aThe two groups of metals correspond to metal atoms of different size (size in the alloy).

Values of $\Delta H(AH_x)$ and $\Delta H(B_nH_y)$ that are needed in calculations of $\Delta H(AB_nH_{x+y})$ can be calculated from the foregoing section. The results are collected in Table 4; for convenience those for the A hydrides are expressed in units of kilojoules per formula unit. Calculated values of $\Delta H(AB_n)$ can be derived from data given in ref. 4; for AB_3 and AB compounds a table of the relevant calculated ΔH values has been published previously [35].

On the whole [36] there is good agreement between the stabilities of ternary hydrides calculated by means of relation (8) and the experimentally observed stabilities.

TABLE 4

Calculated values of the heats of formation of binary hydrides used in the calculations of ΔH of ternary hydrides, relation (8)

ΔH (kJ mol ⁻¹)				ΔH (kJ (g atom H) ⁻¹)	
A	AH _{2.5}	AH ₂	AH _{1.5}	B	B _n H _y (n > y)
Sc	-192	-185	-158	V	-37
Y	-205	-188	-153	Nb	-59
La	-185	-173	-135	Ta	-54
Ti	-125	-136	-120	Cr	-7
Zr	-197	-188	-160	Mo	-3
Hf	-165	-161	-138	W	+8
Th	-218	-196	-158	Mn	-25
U ^a	-95	-96	-80	Tc	+18
Pu ^a	-123	-123	-103	Re	+26
V	-12	-34	-42	Fe	+7
Nb	-74	-83	-78	Ru	+21
Ta	-65	-75	-72	Os	+24
				Co	+9
				Rh	+12
				Ir	+21
				Ni	+10
				Pd	+5
				Pt	+13

^aFor uranium and plutonium molar volumes of 16.6 and 15.2 cm³ respectively were used in the calculations.

7. Conclusions

Experimental data on the heats of formation of the binary hydrides of transition metals can be interpreted in terms of an empirical model in which energy effects are treated as contact interactions between neighbouring atomic cells. The introduction of a large enthalpy contribution, representing the transformation of molecular H₂ into metallic hydrogen, is of central importance. It leads to the concept of a minimum H-H separation below which the hydrides are not stable. In addition there is a large negative hybridization energy which may be related to the lowering in energy of the s-like electron states observed in metal hydride band structure and cluster calculations.

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