Electron density and hydrogen solubility in transition metals

It has been shown that by correlating the heat of solution with spectroscopic data of neutral gaseous atoms, the solution process of hydrogen in transition metals involves transfer of an s electron from the metal to hydrogen, or vice versa, with changes in the electronic configurations of the metal.

In a subsequent paper [2], the heat of solution of hydrogen in the metal is also related to the isothermal bulk modulus of the metal at room temperature which is a direct measure of strength of bonding in the metal. When the heat of solution is plotted, the bulk modulus of metallic hydrogen makes a division line which separates (a) those metals dissolving hydrogen exothermically and forming generally stable hydrides, and (b) those metals dissolving endothermically.

The most striking observation made in the previous paper was that dissolved hydrogen in the metal behaved like a metal having a high cohesive energy. Ubbelohde [3] has already pointed out that in the palladium–hydrogen system, the 1s electron of hydrogen is transferred to the energetically lower 4d level of Pd; that is, the hydrogen atom is metallized and converted into a proton. Extending his idea to all the metals, the dissolution process of hydrogen may be interpreted in terms of Wigner–Seitz cellular model. Miedema and co-workers [4, 5] have empirically found that the electron density at the boundary of cells is related to the bulk modulus of metals as shown:

$$N_e = \left(\frac{B}{V}\right)^{1/2}, \qquad (1)$$

and they used it as an approximate measure of estimating the electron densities of various metals. However, $(B/V)^{1/2}$ is also related to the solubility parameter which is a measure of the internal pressure of the metals [6].

In Table I, values of the electron density for transition metals, calculated from bulk modulus and atomic volume data [7], are tabulated with ΔH^0 from [1]. $\Delta(B/V)^{1/2}$, the difference in electron density between the metal and hydrogen at the boundary is also included. The electron density of metallic hydrogen is calculated to be 4.7 from the bulk modulus obtained in the previous paper. This is in good agreement with that of Miedema [4].

The values of $\Delta(B/V)^{1/2}$ in transition metals are shown in Fig. 1a as a function of atomic number for each series. In all three series, $\Delta(B/V)^{1/2}$ increases with the atomic number as far as group VI, after which a difference exists between the first and latter series. In the second and third series, the $\Delta(B/V)^{1/2}$ continues to increase and reaches maximum values. In the first series, $\Delta(B/V)^{1/2}$ of α-Mn is anomalous, as would be expected from its abnormal crystal structure, but otherwise, there is little change on passing from Fe → Co → Ni.

In Fig. 1b, the values of ΔH^0 in transition metals are shown as a function of atomic number for each series. It is readily apparent that the periodic variation of the ΔH^0 in Fig. 1b follows a pattern very

TABLE I Values of ΔH^0 and $(B/V)^{1/2}$ at the boundary of the Wigner–Seitz cell

Element	ΔH^0 (kcal mol H_2)	$(B/V)^{1/2}$ (dens. unit)*	$\Delta(B/V)^{1/2}$
H		4.7	0
Sc	− 20.5	1.7	− 3.0
α-Ti	− 10.8	3.2	− 1.5
β-Ti	− 13.9		
V	− 7.4	4.4	− 0.3
Cr	+ 11.4	5.2	+ 0.5
α-Mn	− 1.9	2.9	− 1.8
α-Fe	+ 6.7	4.9	+ 0.2
γ-Fe	+ 5.4		
Co	+ 4.9	5.4	+ 0.7
Ni	+ 4.0	5.4	+ 0.7
Y	− 20.0	1.3	− 3.4
α-Zr	− 12.2	2.5	− 2.2
β-Zr	− 15.4		
Nb	− 8.6	4.0	− 0.7
Mo	+ 12.3	5.4	+ 0.7
Tc		5.9	+ 1.2
Ru	+ 12.8	6.3	+ 1.5
Rh	+ 6.4	5.7	+ 1.0
Pd	− 2.3	4.5	− 0.2
La	− 22.5	1.0	− 3.7
αHf	− 9.0	2.8	− 1.9
β-Hf			
Ta	− 8.1	4.3	− 0.4
W	+ 5.0	5.9	+ 1.2
Re		6.5	+ 1.8
Os		7.1	+ 2.4
Ir	+ 17.6	6.5	+ 1.8
Pt	+ 4.5	5.6	+ 0.9

*One density unit corresponds to $(B/V)^{1/2} = 10^2$ kg$^{1/2}$ cm$^{-5/2}$ and equals approximately 1×10^{-2} el/(a.u.)^3 or 6×10^{22} el cm^{-3}.

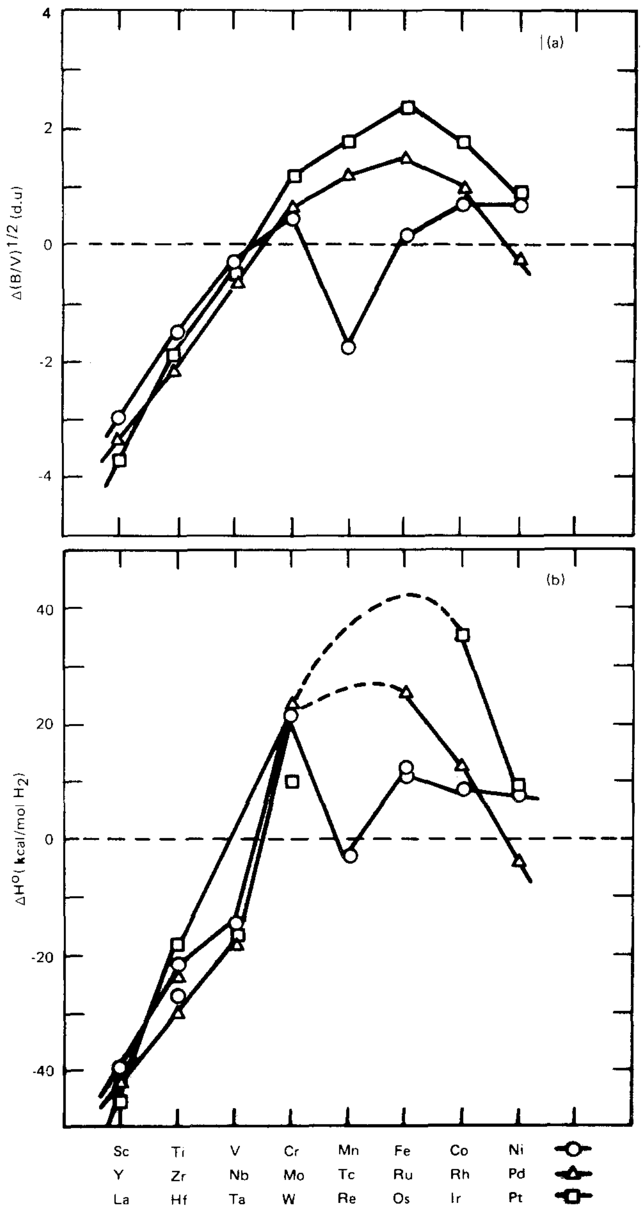

Figure 1 Variation of (a) $\Delta(B/V)^{1/2}$, and (b) ΔH^0, in transition metal series.

similar to those of $\Delta(B/V)^{1/2}$ in Fig. 1a.

A close examination of Fig. 1 reveals the following:

(1) $\Delta(B/V)^{1/2}$, the difference in electron density between metal and hydrogen correctly predicts the signs of ΔH^0;

(2) It is seen that the metals dissolving hydrogen exothermically have lower electron density than hydrogen. Because of the higher electron density of hydrogen, one can scarcely expect a transfer of the 1s electron of hydrogen to the incomplete d electron shell of these metal atoms. Rather, there is only a shift of the hydrogen electrons in the direction of the core of the metal atom and simultaneously a shift of the valency and d electrons of the metal atoms in the direction of the core of the hydrogen atoms. If this is assumed, then during the dissolution process of hydrogen, the dispersibility of the cores of both the metal atoms and the hydrogen atom increases to a corresponding increase in the lattice spacing, a rise in the electrical resistance of the solid solutions compared with the metal atoms themselves, and to an increase in paramagnetism.

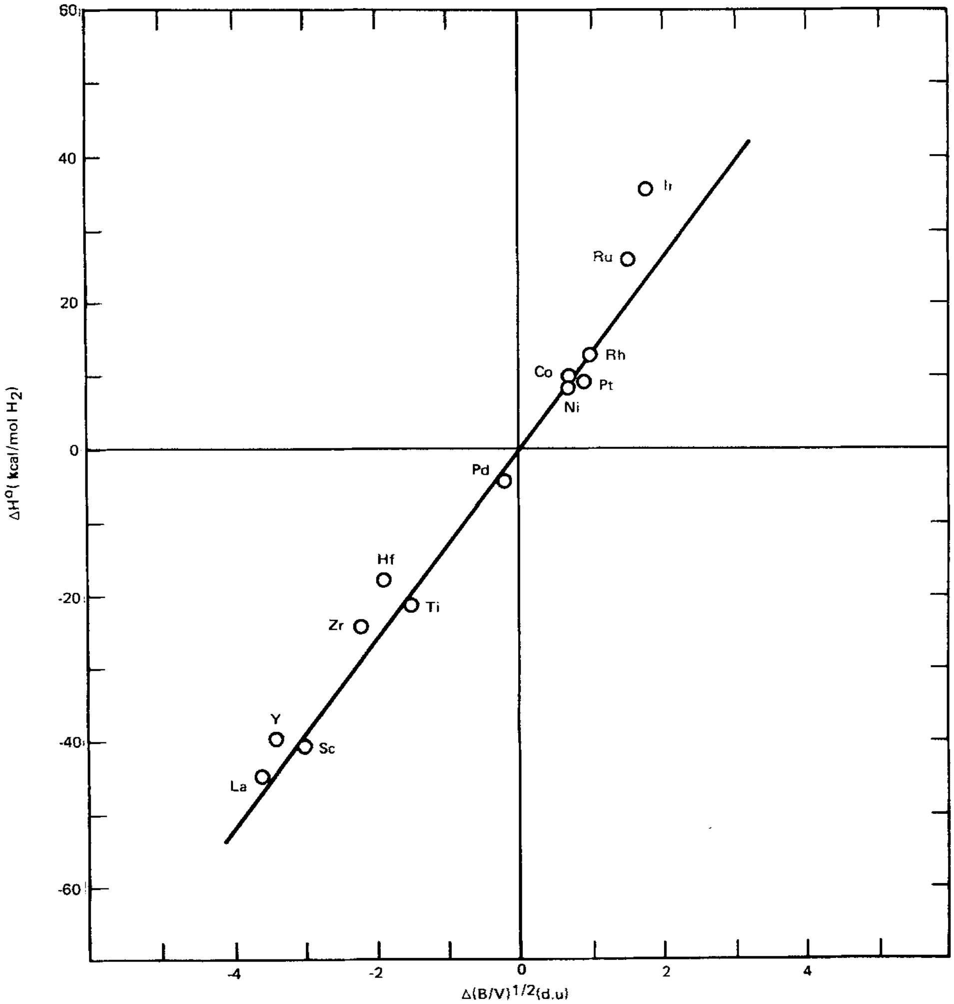

Figure 2 A plot of $\Delta(B/V)^{1/2}$ versus ΔH^0 in f c c and h c p crystal structures.

(3) On passing the borderline, it is seen that the metals dissolving hydrogen endothermically have higher electron densities than hydrogen. The small solubility and endothermic heat of solution in these metals are all attributed to the high electron densities of the metals, which are already crowded with electrons.

To elucidate the dissolution process of hydrogen in metals further, in Figs. 2 and 3, ΔH^0, the heat of solution of hydrogen is plotted against $\Delta(B/V)^{1/2}$ for b c c, h c p, and b c c crystal structures. From Fig. 2, it is readily seen that ΔH^0 is linearly proportional to $\Delta(B/V)^{1/2}$ for f c c and h c p crystal structures, and yields an equation:

$$\Delta H^0 = 13\Delta\left(\frac{B}{V}\right)^{1/2}, \qquad (2)$$

and for b c c crystal structure, it is given by:

$$\Delta H^0 = 32.5\Delta\left(\frac{B}{V}\right)^{1/2}. \qquad (3)$$

The values of ΔH^0 for tungsten are incompatible. The experimental values appear to be either too high or too low [8, 9].

The difference in the slopes of Equations 2 and 3 is related to the availability of interstitial sites in the lattice. A b c c crystal structure has more intersitital sites to be occupied by dissolved hydrogen than f c c and h c p crystal lattices. Thus, the variation in ΔH^0 in transition metals depends on crystal structure and the difference in electron density between metal and hydrogen at the boundary of Wigner–Seitz cells.

It is, however, shown that valence electron concentration in metals is correlated to the isothermal bulk modulus of metal, regardless of the structural characteristics, the group, and the period of the

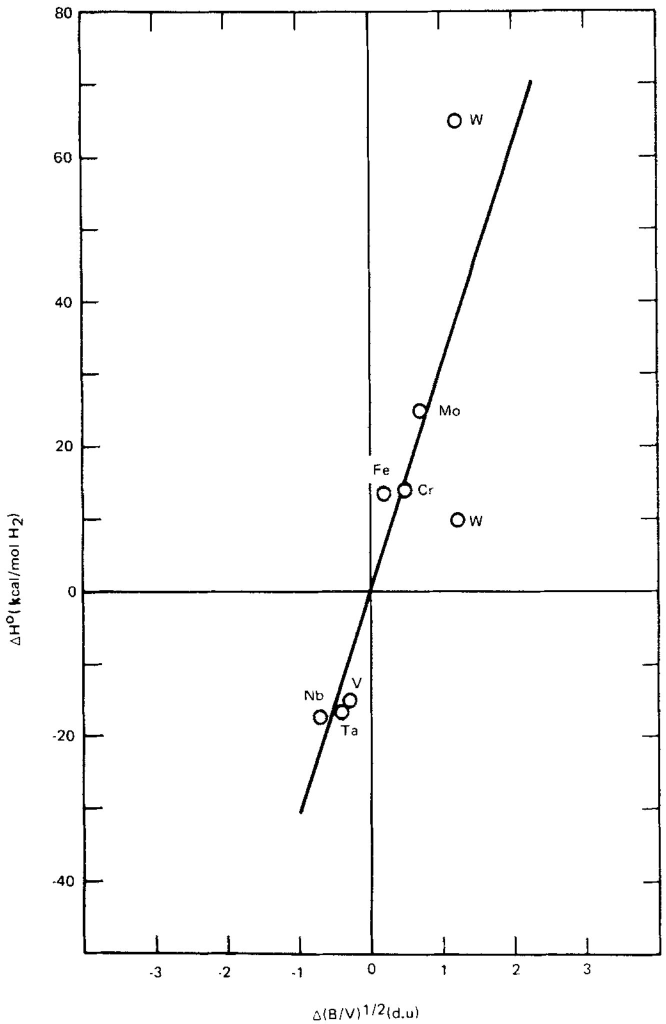

Figure 3 A plot of $\Delta(B/V)^{1/2}$ versus ΔH^0 in b c c crystal structure.

metals [10]. A log–log plot between $(B/V)^{1/2}$ and (n/V) where n is the number of valence electron and V the atomic volume, is shown in Fig. 4. The number of valence electrons in metal was computed based on the three prominent theories on the metallic valences; Engel–Brewer [11, 12], Pauling [13], and Trost [14]. Among those three, the Engel–Brewer theory has resulted in the best linear correlation. From Fig. 4, it is readily seen that $(B/V)^{1/2}$, the electronic density at the boundary, is linearly proportional to the valence electron concentration in metals and yields

$$\left(\frac{B}{V}\right)^{1/2} = 6.92 \times 10^{-4}\left(\frac{n}{V}\right)^{5/6}. \tag{4}$$

α-Mn shows a large deviation as would be expected from its abnormal crystal structure. This reflects the general role played by the valence electron in the solid cohesion, in that they play a major role in holding the solid together as the bonding agent between contiguous atoms.

Inserting Equation 4 into Equations 2 and 3, one obtains

$$\begin{aligned}\Delta H^0 &= 90\left[\left(\frac{n}{V}\right)_{\mathrm{Me}}^{5/6} - \left(\frac{n}{V}\right)_{\mathrm{H}}^{5/6}\right]\\ &= 90\left(\frac{n}{V}\right)_{\mathrm{Me}}^{5/6} - 61,\end{aligned} \tag{5}$$

for f c c and h c p crystal structures and

$$\begin{aligned}\Delta H^0 &= 225\left[\left(\frac{n}{V}\right)_{\mathrm{Me}}^{5/6} - \left(\frac{n}{V}\right)_{\mathrm{H}}^{5/6}\right]\\ &= 225\left(\frac{n}{V}\right)_{\mathrm{Me}}^{5/6} - 153,\end{aligned} \tag{6}$$

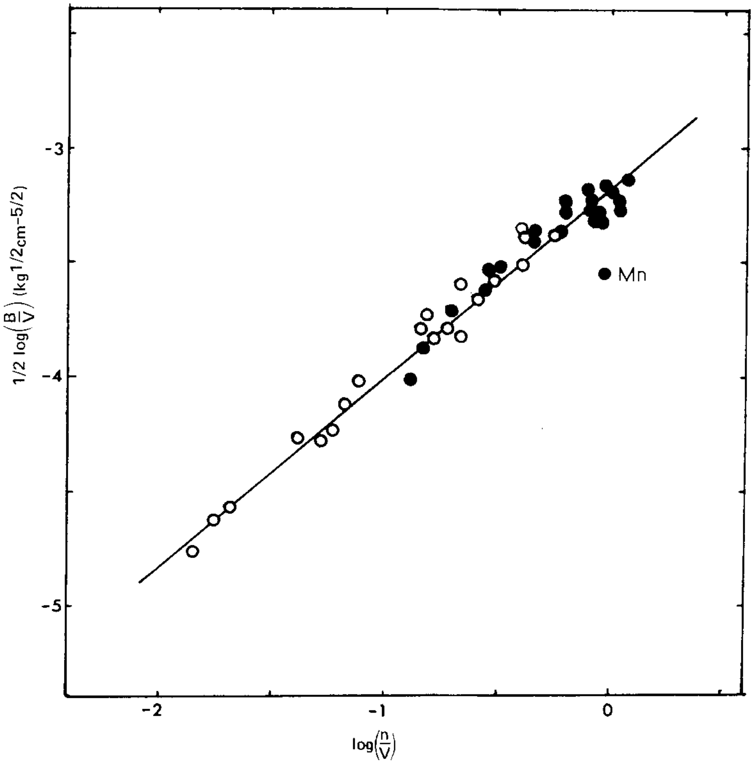

Figure 4 A log–log plot of $(B/V)^{1/2}$ versus (n/V). ● Transition metal; ○ Non-transition metal.

for a b c c crystal structure. The subscripts are for metal and hydrogen. The term $(n/V)_{\mathrm{H}}^{5/6}$ was calculated to be 0.679 from Equation 4.

It should be, however, noted that the term $(n/V)_{\mathrm{H}}^{5/6} = 0.679$ is much higher than expected from $n = 1$ and $V = 14.1\,\mathrm{g\,cm}^{-3}$ for hydrogen. This high value indicates that the dissolved hydrogen behaves like a highly charged atom in the metals. A dissolved hydrogen atom is extremely small, but the associated force field could produce a considerable dilation of the surrounding metal atoms with the result that the apparent size of the hydrogen may be considerable.

In conclusion, $(B/V)^{1/2}$, the electron density at the boundary of the cells, is related to the valence electron concentration in metals. It can be described that the dissolution process of hydrogen in metals depends on the crystal structure, the number of valence electron, and the atomic volume of metal and hydrogen.

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