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The Heat of Solution of Hydrogen in Metals and their Ionization Energy*

(Received April 17, 1955)

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Abstract

There are three types of metals which absorb hydrogen.^{(1) (2)} One is the group of salt-like hydride forming metals, which absorb exothermically large, equivalent quantities of hydrogen, other is the group of so called "poor absorber" metals, which absorb endothermically very small quantities, and another is the medium of the both groups. The typical metals of the former group are the alkali and alkali-earth metals, the group of contrast, the poor absorber are the Fe, Ni, Cu, Pt, etc., and the medium are the group of such as Pd, Ti, V, Zr, Th etc. Authors found that the heat of solution of hydrogen in alkali and alkali-earth metals or in poor absorbers are proportional or in inverse ratio respectively to the ionization energy of metals. These facts, together with other phenomena, can be the proof of the negative or positive character of the dissolved hydrogen in the metals.

I. The Heat of Solution of Hydrogen in Hydride-Forming Metals

We shall show the relation between the heat of solution of hydrogen and the ionization energy in the case of alkali earth metals as an extreme example of hydride-forming metals, showing a distinct difference with poor absorber metals. Here we use the heat of formation ($-\Delta H$) of hydride, in place of the heat of solution of hydrogen, as the changes in heat content for the corresponding reactions.

I · 1 The Heat of Formation of Alkali Hydride and Other Thermochemical Quantities

It is well known⁽³⁾ that in crystals of the alkali hydrides which have the sodium chloride arrangement, hydrogen forms the anion, H^- , and the alkali the cation,

* Presented at the meeting of the Japan Institute of Metals in April 1950.

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⁽¹⁾ Borelius, *Annalen der Physik*, 83, 121. (1927)

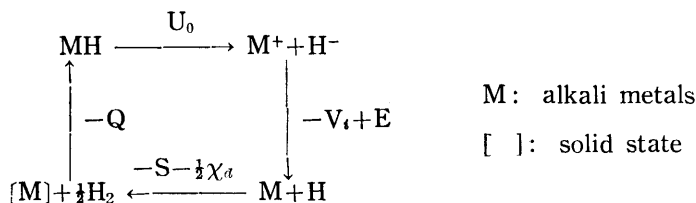
⁽²⁾ H. J. Emeleus and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*, London. Georg Routledge and Sons. I. T. D. (1938) p.13-14.

⁽³⁾ for example:

L. Pauling, *The Nature of the Chemical Bond*, p. 50 (1939)

Emeleus and Anderson, *ibid.*, p. 257.

M⁺. We might accordingly apply the Born-Haber thermochemical cycle.⁽⁴⁾



Here U_0 is the crystal energy, V_i the ionization energy of the metal, E the electron affinity of H (16.4 Kcal/Mole), S the heat of sublimation of metal, χ_a the heat of dissociation of the hydrogen molecule (102 Kcal/Mole), and Q the heat of formation of [MH] from the elements [M] and $\frac{1}{2}\text{H}_2$, which corresponds to $-\Delta H$. The condition that the total change in heat content for the cycle is zero leads to the equation

$$-\Delta H = U_0 - S - V_i - \frac{1}{2}\chi_a + E \quad (1-1)$$

In this equation χ_a is the heat of dissociation of H_2 , E the electron affinity of H, so the heat of formation of hydride ($-\Delta H$) is a function of the crystal energy (U_0) and the heat of sublimation of metal (S) with the exception of the ionization energy (V_i). Therefore we need to relate U_0 and S to V_i .

I · 2 The Crystal Energy of Alkali Hydride and the Ionization Energy

Following Born⁽⁵⁾, the crystal energy (U_0) of the ionic compound is written as

$$U_0 = \frac{N \cdot A \cdot e^2 Z^2}{R_0} \left(1 - \frac{1}{n}\right) \quad (1-2)$$

N : Avogadro number

A : Madelung's constant (for sodium chloride crystal $A=1,747558$)

e : electronic charge

Z : atomic valency

R_0 : the smallest anion-cation distance

n : the Born exponent

The values for U_0 of Alkali Hydride calculated by eq. (1-2) are given in Table (1-1).

Table (1-1) Crystal Energy of the Alkali Hydrides Calculated by the Born's Equation

	$R_0^{(6)}$ [\AA]	n	U_0 [Kcal/Mole]
LiH	2.68	5	172
NaH	3.03	6	160
KH	3.41	7	145

⁽⁴⁾ M. Born, *Verhandl. deut. physik. Ges.* **21**, 13 (1919).

F. Harber *ibid.*, **21**, 750 (1919).

L. Pauling, *ibid.*, p. 340.

⁽⁵⁾ M. Born and J. E. Mayer, *Z. f. Phys.* **75**, 1 (1937).

⁽⁶⁾ L. Pauling, *ibid.*, p. 346.

This value, representing the heat of formation of MH crystal from $M^+ + H^-$, may be considered to be uncertain by about several percent. A more refined treatment, involving of Van der Waals forces and use of an exponential repulsive potential, is requested. A direct thermochemical measurement, mentioned section I. 1, provides the values of crystal energy, which are given in Table (I-2).

Table (1-2) Crystal Energy of the Alkali Hydrides Obtained by the Born-Haber Cycle

	$S^{(7)}$ [Kcal/Mole]	V_i [Kcal/Mole]	$-\Delta H^{(9)}$ [Kcal/Mole]	U_0 [Kcal/Mole]
Li	38.3	123.7 ⁽⁸⁾ (123.8) ⁽⁷⁾	21.6	218.3 (218 ⁽¹⁰⁾ ; 219 ⁽¹¹⁾)
Na	26.0	117.3 (118.0)	16.6	195.2
K	21.7	99.5 (99.6)	10.0	165.9

Then, for the hydride of the metals of the same group in the periodic table the value of the crystal energy is seen to be about proportional to the amount $\frac{1}{R_0} \left(1 - \frac{1}{n}\right)$ by eq. (1-2).

The interionic distance R_0 increases in the order of lithium, sodium and potassium, whilst the value of the ionization energy decreases. Therefore it is assumed that the crystal energy (U_0) being proportional to $1/R_0$, is approximately proportional to the ionization energy of metals (V_i). It is seen from Fig. (1-1) that this assumption is not uncertain.

The next equation follows from this result.

$$U_0 = K_u V_i \tag{1-3}$$

(K_u : const.)

I-3 The Heat of Sublimation of Alkali Metal and its Ionization Energy

For the relation between the heat of sublimation of alkali metal and its ionization energy, the next equation has previously been derived by Fröhlich⁽¹²⁾ quantum-mechanically.

$$S = \frac{2}{\rho} - \frac{0.37}{\rho^2} - V_i \tag{1-4}$$

S: the heat of sublimation of alkali metal,

(7) J. Sherman, Chem. Rev. 11, 93 (1932)

(8) Chemical Handbook, Japan Chemical Society p. 633.

(9) Emeleus and Anderson, *ibid.*, p. 260.

(10) L. Pauling, *ibid.*, p. 343.

(11) E. A. Hylleraas, Z. f. Ppys. 63, 771, (1930)

(12) H. Fröhlich, Proc. Roy. Soc., 158 (1937) 97.

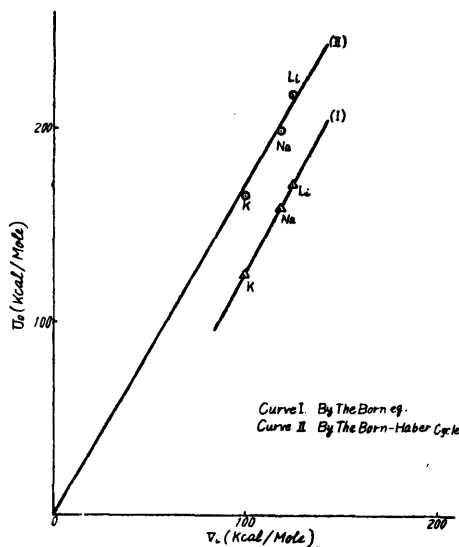


Fig (1-1) Crystal Energy of the Alkali Hydrides and the Ionization Energy of the Alkali Metals

ρ : the radius of the atomic sphere;

the experimental value of ρ is given by $\frac{4}{3}\pi\rho^3 = \frac{\text{atomic weight}}{\text{density}}$

V_i : the ionization energy of alkali metal

In this equation the units are Rydberg's and Bohr's radii; to obtain in c. g. s. units multiply ρ by 0.528×10^{-8} , s by 2.15×10^{-11} .

It is considered for the metals of the same group in the periodic table that the ionization energy (V_i) is approximately proportional to $1/\rho$. It will be shown in Table (I-3) that our assumption is well fulfilled.

Table (I-3) The Radius of the atomic sphere and the Ionization Energy of Alkali metals

	ρ [\AA]	V_i [Kcal/Mole]	V_i
Li	2.0 ⁽¹³⁾ (1.99) ⁽¹²⁾	123.7	247
Na	2.15 (1.13)	117.3	252
K	2.65 (2.60)	99.5	258

Then the substitution in eq. (1-4) of V_i for $1/\rho$ and the assumption* that the second term in eq. (1-4) is shown in a linear function of V_i lead to the following equation for the heat of sublimation:

$$S = K_s V_i + K_s' \quad (K_s, K_s': \text{const.}) \quad (1-5)$$

$$= 0.31V_i - 0.001(112 + \Delta V_i)^2 \quad [\because V_i = 112 + \Delta V_i \dots\dots\dots \text{c. f. Table (1-3)}]$$

$$= 0.31V_i - 12.6 + 0.22\Delta V_i$$

Neglecting the third term, it follows:

$$S \doteq 0.31V_i - 12.6$$

Therefore by this assumption the theoretical value of the heat of sublimation (S) may be considered to be uncertain by about several percent, that is, about 2 Kcal/Mole. We shall test this conclusion using the theoretical value by Fröhlich (the curve II in Fig. (1-2)). The result follows:

$$S = 0.31V_i - 13.2$$

It seems that the two equations fit very well.

To test this eq. (1-5), we use the known value for the heat of sublimation of the alkali metals. The result may be seen from Table (1-4) and Fig. (1-2). It is seen that the agreement is very good for the values found for S by Fröhlich, but for other experiment is not so good. Li is most likely to show deviations from the line.

* Eq. (1-4) follows:

$$S = \frac{329.4}{\rho} - \frac{63.6}{\rho^2} - V_i \quad S, V_i [\text{Kcal/Mole}]; \rho [\text{\AA}]$$

$$= 1.31V_i - 0.001V_i^2 - V_i \quad [\because SV_i \doteq 252 \dots\dots\dots \text{c. f. Table (1-3)}]$$

⁽¹³⁾ Metal Handbook, Japan Inst. of Metals., p. 210. (1952)

Table (1-4) The Heat of Sublimation of Alkali Metals

	theoretical value ⁽¹²⁾	experimental value		
Li	24.5	38.3 ⁽¹⁴⁾	39.0 ⁽¹⁵⁾	46 ⁽¹⁶⁾
Na	22	26.0	26.0	30
K	17	21.7	22.6	26.5

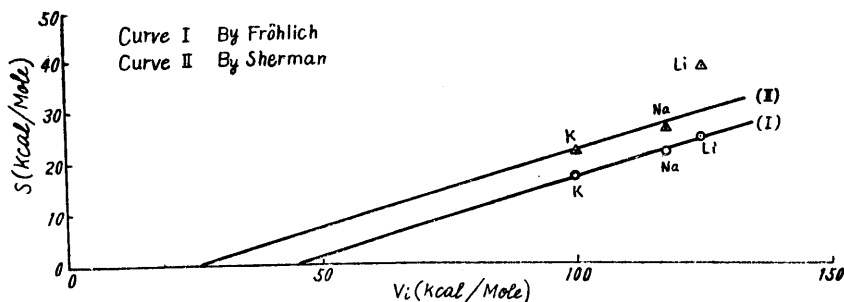


Fig. (1-2) The Heat of Sublimation of Alkali Metals and their Ionization Energy

I · 4 The Heat of Formation of Alkali Hydride and the Ionization Energy

The heat of formation of alkali hydride ($-\Delta H$) is a function of the ionization energy (V_i), the heat of sublimation (S) and the crystal energy (V_0), but we could relate U_0 and S to V_i , so the heat of formation of alkali hydride is a function of V_i only. Substituting eq. (1-3) and eq. (1-5) into eq. (1-1) we obtain the equation

$$-\Delta H = (K_u - K_s - 1) V_i - K_s' - \frac{1}{2} \chi_a + E \tag{1-6}$$

We therefore set for $-\Delta H$

$$-\Delta H = K_h V_i + K_h' \tag{1-7}$$

(K_h, K_h' : const.)

In eq. (1-7), the value of K_h or K_h' is derived from the value of K_u in eq. (1-3) and the value of K_s and K_s' in eq. (1-5), but it is difficult to decide them correctly, because they are very influenced by the experimental value of S or U_0 . Using the values which would be the most reliable, that is, $K_u \doteq 1.72$, $K_s \doteq 0.31$ and $K_s' \doteq -8^*$, we obtained the following equation.

$$-\Delta H = 0.41 V_i - 26.6 \tag{1-8}$$

In eq. (1-8) the unit is Kcal/Mole.

The experimental value of the heat of formation is shown in Table (1-5), and the relation between $-\Delta H$ and V_i in Fig. (1-3). The next equation follows from the curve in Fig. (1-3).

$$-\Delta H = 0.38 V_i - 27 \tag{1-9}$$

* by curve (II) in Fig. (1-1) and curve (II) in Fig. (1-2)

⁽¹⁴⁾ J. Sherman, Chem. Rev. 11, 93 (1932).

⁽¹⁵⁾ S. Harashima. "The Cohesive force in Solid" (in Japanese) p. 166.

⁽¹⁶⁾ Grim and Wolf, Hanab. d. Phys. 24/2 (1934) 1073.

Comparing this experimental equation with the semitheoretical equation (1-8), satisfactory agreement is seen.

Table (1-5) The Heat of Formation (ΔH) of Alkali Hydrides, Kcal/Mole

	Emeleus Anderson ⁽¹⁷⁾	other results
LiH	21.60 ⁽¹⁷⁾ ⁽¹⁸⁾	2.61 ⁽¹⁹⁾ , 21.34 ⁽²⁶⁾ , 21.3 ⁽²⁷⁾
NaH	16.60 ⁽²¹⁾	13.14 ⁽¹⁷⁾ , 12.8 ⁽²⁴⁾ ⁽²⁷⁾ , 13.9 ⁽²³⁾ , 14.44 ⁽²²⁾ , 13.0 ⁽²⁶⁾
KH	10.0 ⁽¹⁷⁾	9 ⁽²⁰⁾ , 13.6 ⁽²⁵⁾ , 14.24 ⁽²⁵⁾ , 14.15 ⁽²²⁾ , 15.16 ⁽²⁶⁾ , 12 ⁽²⁷⁾

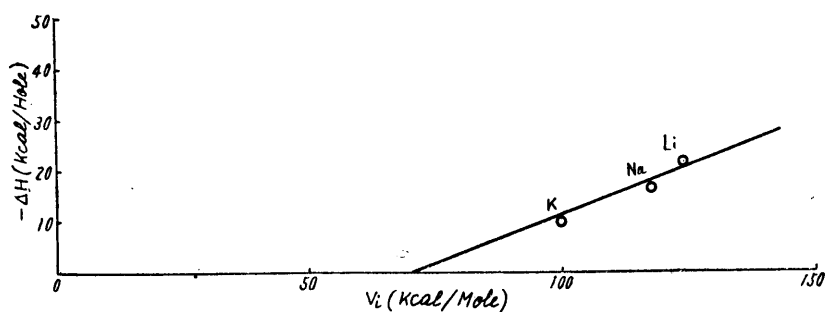


Fig. (1-3) The Heat of Formation of Alkali Hydrides and the Ionization Energy of Alkali Metals

I · 5 The Heat of Formation of Alkali Earth Hydrides and the Ionization Energy

Applying the Born-Haber cycle for the alkali earth hydrides, we lead to the equation

$$-\Delta H = U_0 - S - 2V_{im} - \chi_a + 2E \quad (1-10)$$

Here V_{im} is the mean ionization energy of alkali earth metals. Substituting other experimental values into eq. (1-10), the value of crystal energy is obtained. The result is shown in Table (1-6).

⁽¹⁷⁾ C. J. Smithells, *Metals Reference Book*, p. 384. (1949).

⁽¹⁸⁾ K. Moers, *Z. anorg. allgem. Chem.* **71**, 403 (1911).

⁽¹⁹⁾ A. Guntz, *Comnt. rend.*, **123**, 694 (1896).

⁽²⁰⁾ I. Kasarnowaky and M. Proskwnin, *Z. Physik*, **43**, 512 (1927).

⁽²¹⁾ M. de Forcrand, *Compt. rend.*, **140**, 990 (1905).

⁽²²⁾ E. F. Sollers and J. L. Crenshaw, *J. Am. Chem. Soc.* **59**, 2015, 2724 (1937).

⁽²³⁾ F. G. Keyes, *J. Am. Chem. Soc.* **34**, 779 (1912).

⁽²⁴⁾ H. Hagen and A. Sieverts, *Z. anorge. allgem. Chem.* **185**, 254 (1929).

⁽²⁵⁾ F. D. Rossini, et. al., "Selected Values of Chem. Thermodynamic Pronerties" (1952).

⁽²⁶⁾ C. E. M₃sser, L. G. Fasolino and C. E. Thalmayer, *J. Am. Chem. Soc.* **77**, No.17., 4524 (1955).

⁽²⁷⁾ *Chemical Handbook*, Japan Chemical Society. p. 557.

Table (1-6) Crystal Energy of the Alkali Earth Hydrides Obtained by the Born-Haber Cycle

	S [Kcal/Mole]	V _{im} [Kcal/Mole]	-ΔH [Kcal/Mole]	U ₀ [Kcal/Mole]
Ca	39 ⁽²⁸⁾ 48 ⁽²⁹⁾	208.7 ⁽³⁰⁾ (207) ⁽³¹⁾	46.60 ⁽³¹⁾ (46.0 ⁽³²⁾ , 51.1 ⁽³⁰⁾)	572.3 (581.3)
Sr	39	190.5 (202)	42.20 (42.2) ⁽³⁰⁾	531.5
Ba	39	174.8 (175)	40.96 (40.8) ⁽³²⁾	498.7

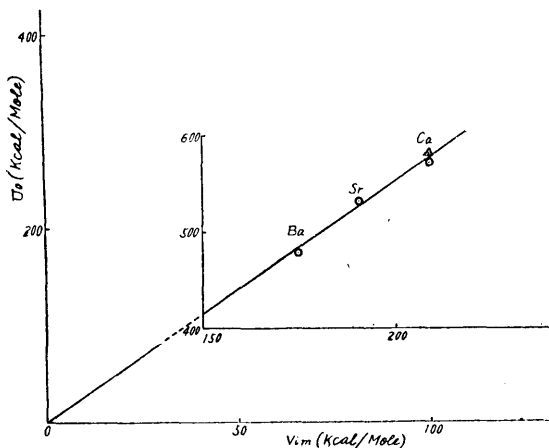


Fig. (1-4) The Crystal Energy of Alkali Earth Hydrides and the Mean Ionization Energy of Alkali Metals

The relation between the crystal energy (U_0) calculated above and the ionization energy is shown in Fig. (1-4). Therefore the next equation approximately follows from this result.

$$U_0 = 2.78V_{im}$$

Then for the alkali earth metals there are a few experimental values of the heat of sublimation, and they are considered to be uncertain. Therefore we cannot obtain the relation between the heat of sublimation of alkali earth metal and its ionization energy,

so firstly we examine the relation between the heat of formation ($-\Delta H$) and the ionization energy.

The experimental value of the heat of formation is shown in Table (1-6), and the relation between $-\Delta H$ and V_{im} in Fig. (1-5). In this case, $-\Delta H$ is shown as a linear function of V_{im} , as the next equation follows.

$$-\Delta H = 0.17V_{im} + 11 \tag{1-12}$$

We led to the same results as those obtained in the alkali metals.

Substituting eq. (1-11) and eq. (1-12) into eq. (1-10) we obtained the equation.

$$S = 0.61V_{im} - 80.2 \tag{1-13}$$

This is very rough equation, but it is considered that the heat of sublimation of the alkali earth metals is approximately proportional to the ionization energy of metals. To test this conclusion we need the reliable values of the heat of sublimation,

⁽²⁸⁾ Grim and Wolf, *ibid.*, p. 1073.

⁽²⁹⁾ S. Harashima, *ibid.*, p. 3.

⁽³⁰⁾ Chemical Handbook, The Chemical Society of Japan p. 633, p. 571. (1952).

⁽³¹⁾ Emeleus and Anderson, *ibid.*, p. 13, p. 260.

⁽³²⁾ Smithells, *ibid.*, p. 384.

but the values we expected are much different from those given by Grim and Wolf⁽²⁸⁾. Calculating the heat of sublimation by eq. (2-13), the next result follows Ca=47.1, Sr=36.0, Ba=26.4.

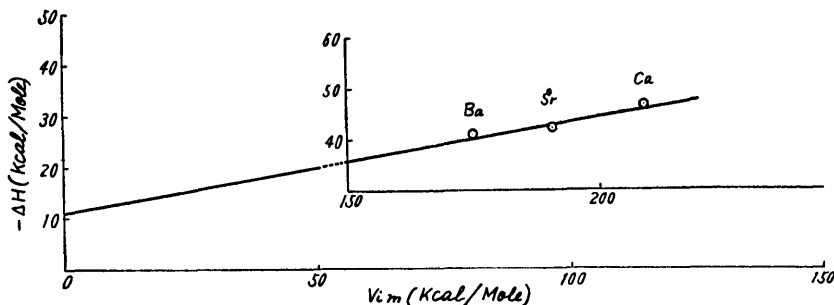


Fig. (1-5) The Heat of Formation of Alkali Earth Hydride and the Mean Ionization Energy

II. The Heat of Solution of Hydrogen in Poor Absorber Metals

In the case of hydride-forming metals, that is, alkali and alkali earth metals, it was seen that the heat of formation ($-\Delta H$) is shown in a linear function of the ionization energy (V_i). Then we examine the solution of Hydrogen in poor absorber.

II · 1 The Solution of Hydrogen in Poor Absorber

According to Borelius⁽¹⁾ the solubility of gas in poor absorber metal is given by the next equation.

$$S = ce^{-\frac{E}{RT}} \quad (2-1)$$

c: const

E: heat of solution [Kcal/gram atom of H]

Therefore solubility increases as the temperature is raised, that is, this solution is an endothermic process in contrast with aqueous solution-gas system.

The explanation of this phenomenon⁽³³⁾ will be shown as follows. The gas absorbed by a metal may be dissociated and distributed as atoms through the metal lattice. Therefore the heat of solution E in eq. (2-1) is, so to speak, an apparent heat of solution, which should be shown as the sum of the heat of dissociation of hydrogen molecule (χ_a) and the heat of solution of hydrogen atom in metal (χ_s). It follows

$$E = \frac{1}{2}\chi_a + \chi_s$$

where the unit is [Kcal/gram atom of H].

Then the dissociation of hydrogen molecule is a great endothermic process, whilst there is a small evolution of heat in metal-hydrogen atom reaction. Therefore the solution of hydrogen in metal is apparently endothermic.

$$\frac{1}{2}\chi_a > E > 0$$

$$\therefore \chi_s = E - \frac{1}{2}\chi_a < 0 \text{ (exothermic)}$$

⁽³³⁾ R. H. Fowler, C. J. Smithells, Proc. Roy. Soc. A 160 37. (1937)

When we examine the solution of hydrogen in poor absorber metals, it is better, according to Fowler,⁽³³⁾ to consider χ_s which corresponds to the potential energy between metal and atomic hydrogen than the apparent heat of solution (E). It is considered that the difference of χ_s shows directly the characteristic of the metal in the solution of hydrogen. We therefore consider χ_s which is the change in heat content for a metal-H reaction, in place of E. Using the value of the heat of solution which Smithells⁽³⁴⁾ calculated of the Borelius equation, the value of χ_s is obtained. The results is shown in Table (2-1).

Table (2-1) The Values of χ_s

	$-\chi_s^{(34)}$ [Kcal/g. atom of H]	$V_i^{(30)}$ (e. v.)	V_i [Kcal/Mole]
Al	28.25	5.94	136.8
Ag	45.20	7.58	174.6
Cu	36.70	7.67	176.5
Ni	48.30	7.6	175
Co	42.50	7.8	179.8
Fe	43.20	7.83	180.2
Mo	49.25	7.2	165.9
Pt	33.30	8.8	202.3

II · 2 The True Heat of Solution (χ_s) and the Ionization Energy (V_i) of the Metals

The relation between χ_s and V_i is shown in Fig. (2-1) and Fig. (2-2). Here V_i is the univalent ionization energy ($M-M^+$), because in simple solution the maximum

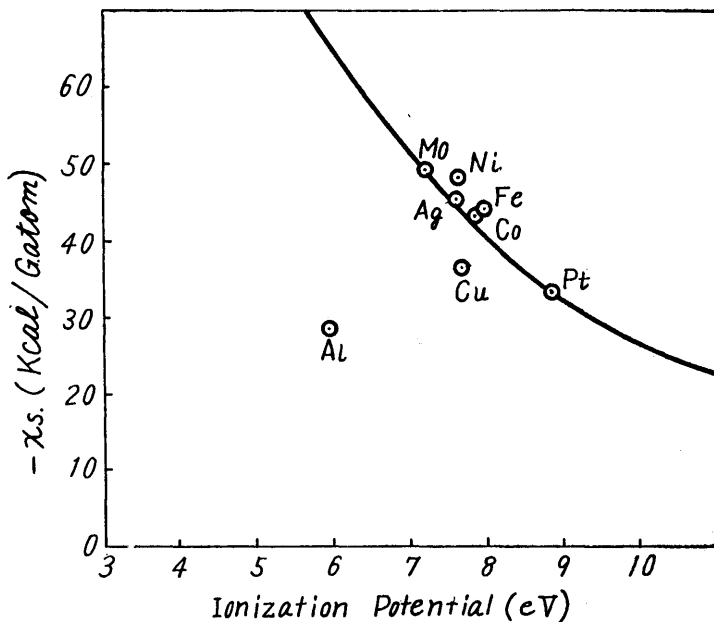


Fig. (2-1) The Relation Between $-\chi_s$ and V_i

⁽³⁴⁾ C. J. Smithells, Gases and Metals, p. 152.

quantity of gas taken up at atmospheric pressure corresponds to about one atom of hydrogen to 10000 atoms of metal.⁽³⁴⁾

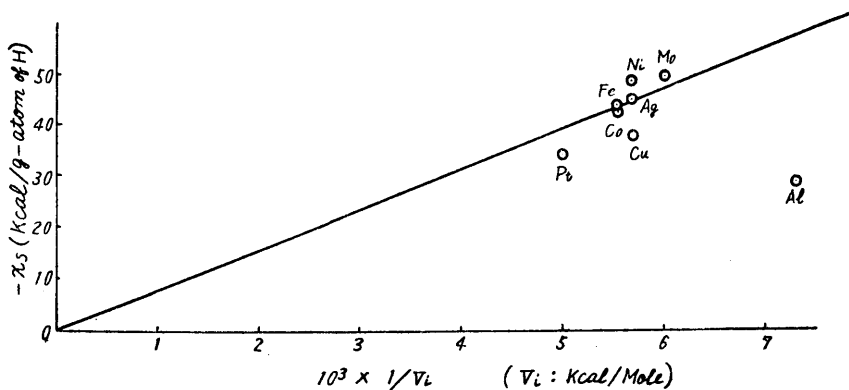


Fig. (2-2) The Relation Between $-\chi_s$ and $1/V_i$

It is clearly seen from Fig. (2-2) that χ_s is approximately proportional to $1/V_i$. In the case of hydride-forming metals the result is just the converse.* Therefore it is assumed that in simple solution the hydrogen has a positive charge (H^+). And in this case the positivity of hydrogen is the matter, because the hydrogen forms the anion H^- in hydride-forming metals. This assumption has been experimentally verified, for example, by the experiments on the decrease of the magnetic susceptibility or the decrease of resistance of metals by absorbing hydrogen.^(1,5)

III. Summary

The results obtained follow :

1) The heat of formation of alkali and alkali earth hydrides is a linear function of the ionization energy of metals, that is, it follows.

$$-\Delta H = KV_i + K' \\ (K, K' : \text{const.})$$

There is a satisfactory agreement between the semi-theoretical equation and the experimental.

2) Whilst the heat of solution ($-\chi_s$) of hydrogen in poor absorber metals is approximately proportional to $1/V_i$, that is, it follows.

$$-\chi_s = K/V_i \\ (K : \text{const.})$$

3) These facts can be the proof of the negative or positive character of dissolved hydrogen in metals.

* In the case of alkali metals, $-\Delta H + 1/2\chi_d$ corresponds to χ_s , so the results obtained on $-\Delta H$ are consistent with $-\chi_s$. Therefore $-\chi_s$ is proportional to V_i , too.

⁽³⁵⁾ S. Yanagisawa, M. Seki, H. Tanaka, and H. Kawase, "The decrease of the susceptibility and resistance of metals by absorbing hydrogen" read at the meeting of Physical society of Japan, May (1951).