APPROXIMATION OF THE ADSORPTION HEATS OF HYDROGEN ON TRANSITION METALS BY MEANS OF AN EMPIRICAL MODEL

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The adsorption heats of hydrogen on transition metals were approximated using a first order polynomial containing variables of basic physical importance, which were determined recently by means of the empirical method of pattern recognition: the heat of fusion, heat of vaporization, Pauling electronegativity, molar thermal conductivity, first and second ionization energies, electrical conductivity, Debye temperature and atomic volume of the metal. The agreement with experimental values is closer than that obtained with the Pauling relation. Values of adsorption heats are predicted for seven transition metals.

The energy values for the bonds between reactants and catalyst surface are important for prediction of effectiveness of a catalyst. The energy of these bonds cannot be measured directly and is estimated by means of the adsorption heats. A very illustrative situation exists for the hydrogen adsorption on metals, where a simple relation[1,2] between both quantities can be used:

$$E(\mathrm{M{-\!\!-}H}) = 0{\cdot}5[\mathrm{D(H{-\!\!-}H)} + Q(\mathrm{H}_2)]\,, \qquad (1)$$

where $E(\mathrm{M{-\!\!-}H})$ is the bond energy between hydrogen and metal surface, $D(\mathrm{H{-\!\!-}H})$ is the dissociation energy of the hydrogen molecule and $Q(\mathrm{H}_2)$ is the adsorption heat of hydrogen. The amount of information about the energy of the adsorption bond between hydrogen and the catalyst surface (the knowledge of which is important in technological processes, as *e.g.* in the Fischer–Tropsch synthesis) is, however, limited not only by the approximate character of the given expression but above all by a relatively large scatter of experimental values of the hydrogen adsorption heats with individual metals. For some metals no data are available at all. In a situation where no corresponding quantitative data can be obtained for this type of bond by purely theoretical methods[3], it is appropriate to apply empirical approaches. An application of these is illustrated in this paper by modelling of the hydrogen adsorption heats for a set of transition metals. The adsorption heats are approximated by a polynomial in which individual terms represent linearly independent quantities characteristic of the metal.

EXPERIMENTAL

Methods. The experimental values of adsorption heat of hydrogen on Ti, Cr, Mn, Fe, Co, Ni, Mo, Rh, Pd, W, Ir and Pt were taken from the review of Toyoshima and Somorjai[4] and the values for Nb from ref.[5], Re from ref.[6], Ru from ref.[7] and Cu from ref.[8], respectively. The nine, practically linearly independent variables in the polynomial were selected by means of the method of pattern recognition[9]. The coefficients in the polynomial equation were determined by means of least-square analysis and Simplex procedure[10]; the calculations were carried out on a Hewlett-Packard 9825 computer.

RESULTS AND DISCUSSION

The values of the adsorption heats (Table I) were calculated from a relation

$$Q'(H_2) = \sum_{i=1}^{N} a_i x_i + b \,, \tag{2}$$

TABLE I

The experimental and calculated adsorption heat values for hydrogen on transition metals (kcal/mol)

metal	$Q(H_2)$	$Q'(H_2)^a$	$(Q'(H_2)^b)$	metal	$Q(H_2)$	$Q'(H_2)^a$	$(Q'(H_2)^b)$
Cu^c	10	14	(15)	Mn^e	17	27	(28)
Ag^c	—	18	(13)	Re^d	31	34	(33)
Au^c	—	18	(18)	Fe^d	32	23	(21)
Ti^d	39	37	(35)	Ru^d	24	39	(27)
Zr^d	—	44	(46)	Os^d	—	33	(29)
Hf^d	—	37	(57)	Co^d	24	26	(21)
V^d	—	28	(32)	Rh^d	28	24	(23)
Nb^d	28	32	(42)	Ir^d	26	26	(28)
Ta^d	—	33	(47)	Ni^d	31	25	(21)
Cr^d	45	40	(27)	Pd^d	28	27	(16)
Mo^a	40	34	(30)	Pt^d	21	23	(23)
W^d	45	38	(41)				

[a] Calculated from equation (*2*); [b] calculated from equation (*3*), where the energy *E*(M—M) is approximated by one sixth of the heat of sublimation; [c] the metal is inactive towards chemisorption both according to experiment and calculation by means of the method of pattern-recognition;; [d] the metal is active, both according to experiment and calculation[9]; [e] the chemisorption activity of the metal towards hydrogen was predicted by means of the method of pattern-recognition.

where x_i are the linearly independent variables, N denotes their number ($N = 9$) and a_i and b are coefficients (Table II). Both methods of calculation yielded the same values for the coefficients. The agreement between the calculated $Q'(H_2)$ and experimental $Q(H_2)$ values is presented as a sum of the square of their differences $\sum_{j=1}^{M} [Q'(H_2) - Q(H_2)]^2 = 615$ ($M = 16$); this value corresponds approximately to a mean deviation ±6 kcal/mol. If a sum of the heat of fusion and heat of vaporization in equation (*2*) is approximated by the heat of sublimation, the results obtained for both cases are practically equal (±0·5 kcal/mol).

The obtained agreement is satisfactory when the large scatter of experimental data for the adsorption heats[4] is taken into account. The incoherence of the experimental data is above all caused by their dependence on the individual methods of measurement as well as on the selected form of the metal. In order to restrict the influence of the latter two effects, the calorimetric data obtained on metal films, at 273 K or room temperature, were used preferentially in the calculation.

The relation (*2*) used in this paper gives a better agreement with the measured data than the known Pauling equation for the adsorption heat of hydrogen on metals[11]:

$$Q'(H)_2 = E(M{-}M) + 46{\cdot}12(\varepsilon_M - \varepsilon_H)^2 , \qquad (3)$$

TABLE II

The linearly independent variables[9] and coefficients in equation (*2*)

i	Variable x_i	Coefficient a_i^a
1	molar heat capacity	$-1{\cdot}562 \,.\, 10^1$
2	2^{nd} ionization energy	$9{\cdot}021 \,.\, 10^{-2}$
3	electrical conductivity	$-3{\cdot}531 \,.\, 10^1$
4	heat of fusion^b	$1{\cdot}159$
5	Debye temperature	$3{\cdot}016 \,.\, 10^{-2}$
6	1^{st} ionization energy	$-8{\cdot}147 \,.\, 10^{-2}$
7	atomic volume	$2{\cdot}727$
8	Pauling electronegativity^{b,c}	$1{\cdot}665 \,.\, 10^1$
9	heat of vaporization^b	$-9{\cdot}257 \,.\, 10^{-3}$

[a] Coefficient $b = 65{\cdot}63$; [b] variables in the approximate equation (*3*); [c] for comparison with equation (*3*), electronegativity of the metal is used in the form of the square of its difference from the electronegativity of hydrogen $(\varepsilon_M - \varepsilon_H)^2$.

where $E(\mathrm{M—M})$ denotes the energy of interatomic metal bond, usually approximated as one sixth of the heat of sublimation and ε_M and ε_H are the electronegativities of metal and hydrogen atoms, respectively. If the adsorption heat values are calculated directly by means of Pauling relation (*3*), then $\sum_{j=1}^{M} [Q'(H_2) - Q(H_2)]^2 = 1\,235$ – which is twice as much than found by means of the approximation using relation (*2*). If the heat of sublimation is approximated by a sum of the melting heat and heat of vaporization, this value equals 1 403.

The values of the hydrogen adsorption heats, obtained for the transition metals show no marked regularity with respect to the periodic table of elements. The detection of the tendency of the adsorption heats to decrease in the table from left to right is complicated by the lack of data for metals of the fourth and fifth transition groups. Nevertheless, the adsorption heats seem to show a maximum for metals of the sixth transition group, while the thermal effect connected with dissolution of the adsorbed hydrogen in the lattice is experimentally not separated from the true adsorption heat. Within individual groups (*i.e.* with respect to individual periods), no remarkable trends are noticed. In group 7, the markedly low experimental value for manganese is probably connected with the contradicting information in the literature[3] on whether hydrogen is chemisorbed on this metal or not.

The calculated values support the above mentioned trend[12] in the periodic table, predicting the highest values for elements of the fourth group (Zr, Hf) and the lowest values for the group of copper; the metals of the sixth transition group exhibit a secondary maximum. The value of the adsorption heat calculated for manganese is comparable with the values of the adjacent groups of iron, cobalt and nickel (Table I).

The application of the given set of nine linearly independent variables (Table II) led to a substantially improved agreement with experiment, as can be expected from the result of the analysis of hydrogen chemisorption by means of the empirical method of pattern recognition. The predicted high adsorption heat values for zirconium and hafnium and the very low values for silver and gold are in agreement with chemical experience whereas the values predicted for the remaining metals – vanadium, tantalum and osmium – fall within the range of data of the respective transition groups.

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