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Abstract

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PHYSICAL CHEMISTRY

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HEATS OF CHEMISORPTION AND THE STRUCTURE OF SURFACE CHEMICAL COMPOUNDS ON METALS

(Presented by Academician A. A. Balandin on 27 X 1964)

Although a large amount of experimental material on the initial heats $(\Delta H)_{\theta=0}$ of chemical adsorption on comparatively clean metal surfaces has been accumulated in the literature (2,3), these data have not yet been sufficiently systematized.

It has been noted (4) that the heats of adsorption of hydrogen on metals at half coverage ($\theta = 0.5$) vary regularly in the periodic system of the elements. It has recently been shown (5) that the values of $(\Delta H)_{\theta=0}$ for a series of gases are linearly related to the standard heats of formation of the highest oxides, calculated per metal atom.

The latter correlation relation is of definite interest, but it is nevertheless a rough approximation. Thus, for example, $(\Delta H)_{\theta=0}$ for Cr and W are practically identical in the case of chemisorption of N_2, C_2H_4, whereas the corresponding heats of formation of the oxides differ by more than one and a half times. A similar picture is observed when comparing the heats of adsorption of hydrogen on Cr, Mo, W, and Ta. Moreover, with such an approach it is unclear how to consider different forms of chemisorption of an adsorbate on one and the same metal.

Since the initial heats of different adsorbates on one and the same metal apparently refer to adsorption centers of the same type (the most active ones), it is precisely for $(\Delta H)_{\theta=0}$ that one may expect comparatively simple regularities, independent of the nature of the heterogeneity of the active metal surface and, consequently, of the method of preparing the adsorbent. Therefore, only $(\Delta H)_{\theta=0}$ are considered below.

Chemical adsorption proceeds according to the equation:

$$\Pi\mathrm{Me} + \mathrm{A} \rightarrow (\mathrm{Me}_{\Pi} - \mathrm{A}) + (\Delta H)_{\theta=0}, \tag{1}$$

where A is an adsorbate molecule, Me is a surface atom of the metal, and Π is a stoichiometric coefficient*, which characterizes the structure (geometry) of the surface compound $(\mathrm{Me}_{\Pi} - \mathrm{A})$.

In a first approximation one may take:

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$$(\Delta H)_{\theta=0} = -\Pi\left({}^{1}/{}_{6}\Delta H_c\right), \qquad (2)$$

where ΔH_c is the heat of sublimation of the metal.

This relation is obtained if one assumes that, in the elementary act of adsorption, the overall energy balance $(\Delta H)_{\theta=0}$ corresponds to the liberation of the surface energy of Π metal atoms. It is significant here that, for a series of metals, the value of the surface energy is close to ${}^{1}/{}_{6}\Delta H_c$ (6).

It follows from (2) that the correlation (2) between $(\Delta H)_{\theta=0}$ and the heat of sublimation, or other characteristics of metals that are functions of the latter, may be partially satisfied. If it is taken into account that, in chemisorption of an adsorbate on a metal, the forces acting are chemical in nature, characterized by short-range action and the property of saturation, then the calculated values of Π from (2), as a rule, should be integral num—

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* Term proposed by Prof. M. I. Temkin.

···multiples of 0.5, or equal to 0.5. In complicated cases of chemisorption, when estimating P it is necessary to consider several adsorbate molecules.

Table 1

Initial heats and stoichiometric coefficients of chemisorption on metals

Metal	$\frac{1}{6}\Delta H_c$, kcal/mol	Values of $P/(-\Delta H)_{\theta=0}$, kcal/mol						
		H_2	O_2	C_2H_4	C_2H_2	N_2	CO	NH_3
Tl	18.7		13/236a					
Nb	28.6		7/208a					
Cr	15.8	3/45	12/174a	6/102				
Fe	16.5	2/34	8/136a	4/68		4/70g0.5/16	2/32	2.5 (3)/45
Co	16.9	1.5/24	6/100a					
Ni	16.8	1.5/25k	6/107a	3.5/58	4/67		2/35	2/37
Ta	31.1	1.5/45	7/212a	4.5/138		4.5/140		
Mo	26.2	1.5/40	6/172a					
W	33.4	1.5/48.5	6/194a	3/102		3/95	2/67v2/65/16	2/629v
Ru	24.3	1/26						
Ir	26.6	1/26						
Mn	11.1	1.5/17.1z	14/150a					
Rh	22	1.2/26	5/110	2.5/50				
Pt	22.5	1.2/280.5/16	3/67a					

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Metal	$\frac{1}{6}\Delta H_c$, kcal/mol	Values of $P/(-\Delta H)_{\theta=0}$, kcal/mol						
Pd	15.1	2/27	4/64a					
Cu	13.5	2/28		1.5/18.2b	1.5/19b		0.7/9.3b	
Au	14.6			1.5/20.8b	1.5/21b		0.6/8.7b	
Ag	11.3			0.8/8.5b	0.8/9.3b			
C	28.3	2/50	3.5/97					0.5/17
		Ba	Sr	Na	Cs	Ag		Cl_2
W	33.4	2.5/83k	2.5/79k	1/32	2/64			
Mo	26.2					1.5/43.8e	2/36.8e	
Ni	16.8				4/67.3d			
C	28.3				2/61d			1/31
Re	30.9				2.5/70d			
Zr	24.1				3/74d			

References to the literature: a—(15), b—(14), v—(13), g—(16), d—(17), e—(9), zh —(11), z—(12), i—(10), k—(8), l—(18).

What has been said is confirmed by the results of calculations (Table 1), in which the most reliable values of $(\Delta H)_{\theta=0}$, taken from monographs ([2],[3]) and from other sources, were used. The given values of P for the most part reproduce, within 10%, the experimental heats of adsorption and, in a number of cases, agree with chemisorption data and with results from IR spectra on the structure of surface compounds.

An important consequence of equation (2) is the multiplicity in the ratio of the highest heats of adsorption of different gases on one metal with an unfilled *d*-shell (see Table 1). For example, $(\Delta H)_{H_2} = \frac{1}{4}(\Delta H)_{O_2}$, $(\Delta H)_{H_2} = \frac{1}{2}(\Delta H)_{N_2, C_2H_4}$. It should be noted that for metals with a filled *d*-shell and a partially filled outer *s*-shell (Ag, Au, Cu, Pd, etc.), equations of an analogous type differ substantially in quantitative terms. It is interesting that the multiplicity is also preserved for the heats of adsorption of vapors of alkali and alkaline-earth metals, and of a series of gases (H_2, O_2, Cl_2, NH_3)—on graphite.

Since for transition elements with an unfilled *d*-shell (with the possible exception of manganese) there are general relationships for $(\Delta H)_{\theta=0}$ of different adsorbates, according to chemisorption ability—the highest heats—the metals of the indicated group are arranged in a single series (Fig. 1):

$$\begin{array}{cccccccccccc} \text{Co} & \text{Rh} & \text{Ir} & \text{Ru} & \text{Ni} & \text{Fe} & \text{Mo} & \text{Cr} & \text{W} & \text{Nb} & \text{Ta} & \text{Ti} \\ 0.51 & 0.55 & 0.55 & 0.55 & 0.55 & 0.71 & 0.88 & 0.95 & 1 & \sim 1.07 & \sim 1.1 & \sim 1.22, \end{array}$$

where $(\Delta H)_{\theta=0}$ for all metals are compared with the heats of adsorption on tungsten, as the most thoroughly studied metal. As can be seen from Fig. 1, with an accuracy of up to 10% the experimental values of $(\Delta H)_{\theta=0}$ for most metals are satisfactorily represented by linear dependences; the greatest scatter of the data is observed for tantalum.

(Figure: Fig. 1. Correlation of initial heats of adsorption on transition metals with an unfilled d-shell: a–H_2, –CO, –NH_3, –N_2, –O_2, e–C_2H_4.)

Fig. 1. Correlation of initial heats of adsorption on transition metals with an unfilled *d*-shell: a–H_2, –CO, –NH_3, –N_2, –O_2, e–C_2H_4.

In accordance with (2), one may expect that the heats for different forms of chemisorption of an adsorbate on the same metal will also be related by a multiple ratio. The latter is satisfactorily confirmed, for example, by data on the heats of adsorption of CO on tungsten.

The regularities considered make it possible to systematize, and also to carry out comparative calculations of, $(\Delta H)_{\theta=0}$ for unstudied systems.

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