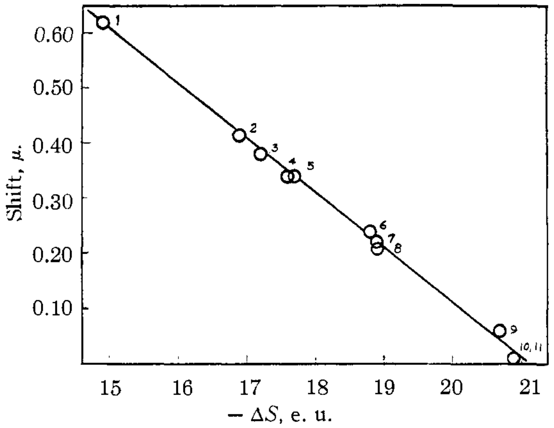


Fig. 1.—A plot of the shift of the 3.46μ absorption band of hydrogen chloride against its entropy of solution in: (1) diethyl ether, (2) β,β′-dichlorodiethyl ether, (3) *n*-butyl phenyl ether, (4) phenetole, (5) anisole, (6) *m*-nitrotoluene, (7) nitrobenzene, (8) diphenyl ether, (9) chlorobenzene, (10) bromobenzene and (11) benzene. The spectroscopic data are taken from the papers of Gordy[4] except those for chlorobenzene and bromobenzene [W. West and P. Arthur, *J. Chem. Phys.*, **2**, 215 (1934)] and for benzene [E. K. Plyler and D. Williams, *Phys. Rev.*, **49**, 215 (1936)]. The entropy values not presented in Table II were taken from the earlier papers.[3]

and the deviation of hydrogen chloride from the law of Raoult.[7] Differences in the heat of solution in the various solvents would lead to deviations from such a relationship. It is, of course, interesting that the increase in the partial molal entropy of the solute is greatest in the more basic solvents in which the infrared absorption band is shifted to the greatest extent.

Summary

1. The partial pressure of hydrogen chloride from its solutions in phenetole, *n*-butyl phenyl ether, diphenyl ether and *m*-nitrotoluene have been determined at two or more temperatures. From these data, the mole fraction solubilities at 1 atm., the partial molal heats and the partial molal entropies of solution of hydrogen chloride have been calculated.

2. A linear relationship between the entropy of solution and the shift of the 3.46 μ absorption band of hydrogen chloride reported previously is further substantiated by a comparison of the calculated entropies of solution with the spectroscopic data available in the literature.

(7) Compare W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940).

BOUND BROOK, NEW JERSEY
WASHINGTON SQUARE
NEW YORK, N. Y.

RECEIVED APRIL 20, 1949

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Importance of Interatomic Spacing in Catalysis. A Correlation between Hydrogen Overvoltage on Metals and the Distance between Atoms[1]

BY HENRY LEIDHEISER, JR.

Introduction

It is of great importance to the theories of surface phenomena to understand the importance of the distance between surface atoms in controlling the rates of reactions. A few studies indicate the importance of this distance in catalytic reactions.[2] Recent measurements of the hydrogen overvoltage offer a series of values which may be utilized to compare the relative catalytic activities of a number of metals under similar experimental conditions. Hydrogen overvoltage may be considered as a numerical value representing the ability relative to platinized platinum with which a material catalyzes the over-all reaction, $2H^+ + 2e = H_2(gas)$, in an acid solution. The greater the numerical value of the hydrogen overvoltage, the greater the difficulty with which the reaction occurs.

Correlations of the results of hydrogen overvoltage studies on different metals have been made previously with position in the periodic table, melting point, catalytic activity for the combination of hydrogen atoms, and thermionic work functions,[3] but no one has pointed out the interesting correlation between hydrogen overvoltage and the distance between atoms in the surface.

Results

In Fig. 1 values for the hydrogen overvoltage at 10^{-3} amp./sq. cm. are plotted *versus* the distance of closest approach of atoms for all the body-centered cubic and face-centered cubic metals for which reliable values are available. The values for nickel, copper, molybdenum, tantalum and columbium were taken from Bokris,[4] the values for lead, aluminum, silver, chromium (estimated from the value at 10^{-1} amp./sq. cm.), iron, tungsten, plati-

---

(1) This paper was written during the author's residence at the University of Virginia under a grant from the Research Corporation. Present address: Virginia Institute for Scientific Research, Richmond 20, Virginia.

(2) See for example: O. Beeck, *Revs. Modern Physics*, **17**, 61 (1945); J. Turkevich and R. K. Smith, *Nature*, **157**, 874 (1946); H. Leidheiser, Jr., and A. T. Gwathmey, THIS JOURNAL, **70**, 1200, 1206 (1948); H. Leidheiser, Jr., and R. Meelheim, *ibid.*, **71**, 1122 (1949).

(3) See J. O'M. Bokris, *Chem. Revs.*, **43**, 525 (1948), for a recent comprehensive discussion of the theories of hydrogen overvoltage and a critical evaluation of the data.

(4) J. O'M. Bokris, *Trans. Faraday Soc.*, **43**, 417 (1947).

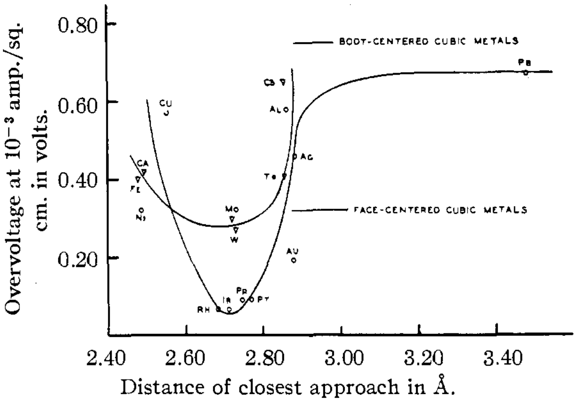


Fig. 1.—The relation between the hydrogen overvoltage at 10^{-3} amp./sq. cm. and the distance of closest approach of atoms for sixteen metals of the body-centered cubic and face-centered cubic structures.

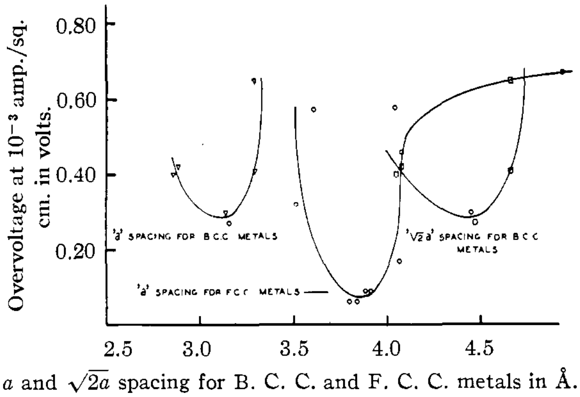


Fig. 2.—The relation between the hydrogen overvoltage at 10^{-3} amp./sq. cm. and the a and $\sqrt{2a}$ spacings for sixteen metals of the body-centered cubic and face-centered cubic structures.

num, gold and rhodium from Hickling and Salt,[5] and values comparative to these were estimated for palladium and iridium from the combined data of Newbery,[6] Volmer and Wick,[7] and Frumkin and Aladzhalova.[8] It should be pointed out that Bokris and Hickling and Salt obtained similar values for the hydrogen overvoltage using different methods for nickel, copper and lead, the only metals that were studied in common. The choice of values obtained at 10^{-3} amp./sq. cm. for plotting is purely arbitrary but curves of comparable shape would be obtained if the hydrogen overvoltage at 10^{-2} or 10^{-1} amp./sq. cm. were plotted. These three current densities are the only ones that have been extensively studied with a number of different metals.

With the exception of vanadium and barium, for which no data are available, and the alkali metals, which cannot be studied in aqueous solution because of their reactivity, all the metals of body-centered cubic structure that are stable at room temperature are included. In the case of the face-centered cubic metals ten different metals are included. It can be seen that the interatomic spacing of approximately 2.7 Å. in the case of both body-centered cubic and face-centered cubic metals corresponds to the minimum overvoltage. The hydrogen overvoltage values for the hexagonal close-packed metals are not complete enough to prepare a similar plot for metals of this structure. However, the values at 10^{-3} amp./sq. cm. for beryllium, cadmium and thallium, the only hexagonal close-packed metals for which reliable values are available, are not inconsistent with a plot of the same general shape as those for the body-centered cubic and face-centered cubic metals.

As shown in Fig. 2 equally good curves can be drawn for the a spacing of the face-centered cubic metals and for the a and $\sqrt{2a}$[9] spacing of the body-centered cubic metals. However, as can readily be seen from Fig. 2 the minimum overvoltage does not occur at the same spacing for these two different metallic structures when plotted in this manner. It is felt that the approximate coincidence of the minima for both types of structure at 2.7 Å. is evidence that this spacing is the important one in hydrogen overvoltage phenomena.

The exact manner in which the curves are drawn in Figs. 1 and 2 is subject to considerable latitude. In the case of the body-centered cubic metals it is impossible to decide on the exact position of the minimum. The reason for this is the small number of body-centered cubic metals which are stable at room temperature. In the case of the face-centered cubic metals the exact position of the minimum depends on a more critical determination of the relative values for the hydrogen overvoltage of rhodium, iridium, palladium and platinum. However, the presence of minima at approximately 2.7 Å. is very definite. Two points occur to the left of the minimum and two occur to the right of the minimum for the body-centered cubic metals. For the face-centered cubic metals two points occur to the left of the minimum and 4 points occur to the right of the minimum. The fact that all of the 16 points plotted are consistent with minima at the 2.7 Å. spacing is strong statistical evidence that the effect is a valid one.

Discussion

The results reported herein furnish evidence that the spacing between atoms in the surface is an important consideration in the rates of catalytic reactions. An interesting observation which shows up in Fig. 1 is the fact that not only is spacing important but also the crystal structure in which the metal crystallizes. The face-centered

---

[5] A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, **36**, 1226 (1940).

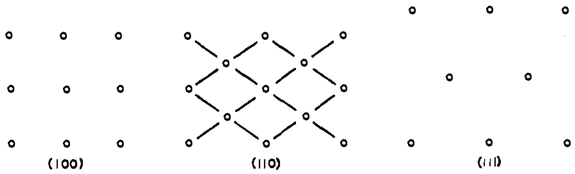
[6] E. Newbery, *J. Chem. Soc.*, **109**, 1051, 1107 (1916).

[7] M. Volmer and H. Wick, *Z. physik. Chem.*, **172**, 429 (1935).

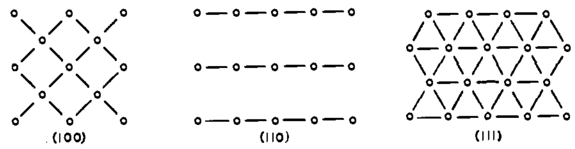
[8] A. Frumkin and N. Aladzhalova, *Acta Physicochim. U. R. S. S.*, **19**, 1 (1944).

[9] The a spacing refers to the distance along the cube edge and the $\sqrt{2a}$ spacing refers to the distance along the diagonal of the cube face.

cubic metals and body-centered cubic metals fall in two distinct classes. Although the data are incomplete for the hexagonal close-packed metals it also appears that these metals fall into a third class. The structure can play a part in the geometry of the surface and in the frequency with which a certain type of spacing occurs in the surface. It is impossible at present to decide between the relative importance of these two possibilities. Figure 3 represents a schematic drawing of the arrangement of atoms on the 3 major faces, (100), (110) and (111), of the body-centered and face-centered cubic metals. The solid lines represent the distance of closest approach of the atoms. It will be noticed that the arrangement of atoms, or geometry, is different on each of these 6 faces and that the distance of closest approach occurs more often in the face-centered cubic structure than in the body-centered cubic structure.



BODY-CENTERED CUBIC METALS .



Face-centered cubic metals.

Fig. 3.—The arrangement of atoms and the frequency with which the distance of closest approach of atoms occurs on the major faces of the body-centered cubic and face-centered cubic metals. The solid lines represent the distance of closest approach.

It is of interest in terms of the correlation between hydrogen overvoltage and thermionic work function[4] that there is no relation similar to that of Fig. 1 for thermionic work function and interatomic distances. Thermionic work function is very roughly a linear function of interatomic distance in the case of the high-melting body-centered cubic metals, the low-melting body-centered cubic metals, and the face-centered cubic metals (the linear relation here is very poor—platinum is a bad exception).

Weeks[10] has previously pointed out the qualitative correlation between hydrogen overvoltage and the melting point of metals. As shown in Fig. 4 there is also a correlation between melting point and the distance of closest approach of atoms in the case of the face-centered cubic and body-centered cubic metals. A comparison of Figs. 1 and 4 indicates that the maximum in melting point and the minimum in hydrogen overvoltage occur at approximately 2.7 Å. Although the shapes of the curves are drawn slightly differently in Figs. 1 and 4, it can be seen that there is a semi-quantitative similarity of the relative positions of the metals in both figures.

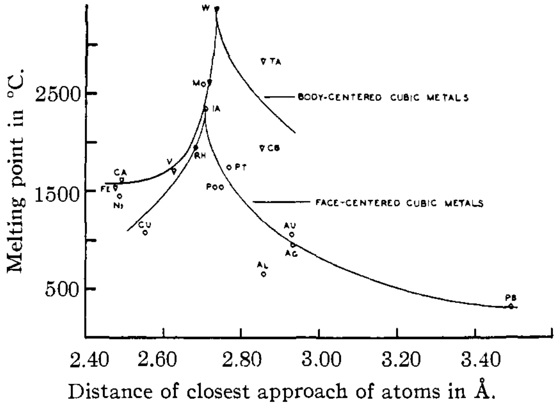


Fig. 4.—The relation between the melting point and the distance of closest approach of atoms for seventeen metals of the body-centered cubic and face-centered cubic structures.

The correlation between hydrogen overvoltage and the spacing between atoms in the surface as reported in this paper does not in itself enable one to choose between the numerous theories developed to account for the phenomenon of hydrogen overvoltage. It is hoped, however, that these results will stimulate theoretical investigations of the significance of the 2.7 Å. spacing in hydrogen overvoltage.

Summary

Evidence was presented which indicated that the spacing between atoms is an important factor in catalysis. Values of the hydrogen overvoltage were shown to be a minimum at a distance of closest approach of atoms of approximately 2.7 Å. for both the body-centered cubic and face-centered cubic metals.

CHARLOTTESVILLE, VA. RECEIVED MAY 12, 1949

---

(10) E. J. Weeks, *Chem. News*, **129**, 17 (1924).