Research on Activation Energy. III. On Activation Energy for the Adsorption of Hydrogen on Reduced Copper

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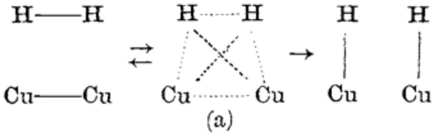
Introduction

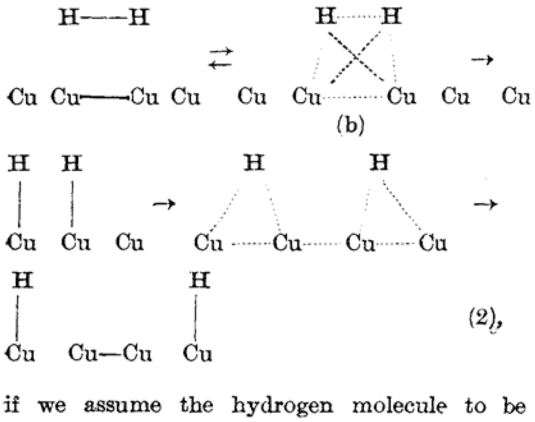
Because of experimental difficulties most of the hitherto observed values of the activation energy for the adsorption of hydrogen on metals are not fully reliable. T. Kwan⁽¹⁾ has recently obtained, however, the reliable value for the activation energy of the adsorption of hydrogen on reduced copper, since in this case the velocity of adsorption has a moderate value. So we intend to calculate the activation energy for this process by means of the empirical rule which we have previously proposed,⁽²⁾ as a typical example of the heterogeneous reaction.

In order to calculate the activation energy for a reaction we must have clear knowledge of the mechanism of the given reaction. Since the velocity of the adsorption of hydrogen on reduced copper was found by the experiment of Kwan⁽¹⁾ to be the first order with respect to hydrogen, the mechanism of the reaction must be either



(1)

or



(2),

if we assume the hydrogen molecule to be adsorbed dissociatively.⁽³⁾ So long as no information is given on the adsorption isotherm, it is not possible to decide which of the above given mechanisms is the correct one. But if it is assumed that the configuration of the activated complex (a) of the mechanism (1) and that (b) of the mechanism (2) are the same, the activation energy must be the same for both mechanisms. The activation energy for the reaction has been calculated under this assumption, and compared with the observed value of Kwan.

Calculation of Activation Energy

The method of the calculation refers to the previous paper.⁽²⁾ The fundamental data used for the calculation are given in Table 1, where

Table 1

Fundamental Data Used for the Calculation

Bond	D_e(kcal./mole)	r_e(Å.)	ω_e(cm.$^{-1}$)
H—H	109.2⁽⁴⁾	0.75⁽⁴⁾	4276⁽⁴⁾
Cu—H	62.2⁽⁵⁾	1.46⁽⁴⁾	1940.1⁽⁴⁾

D_e is the equlibrium dissociation energy, r_e the internuclear distance and ω_e the frequency of the vibration of the given bond.

If we calculate the activated distance r^*, the distance between two atoms in the actived state, for H-H and Cu-H from the data given in Table 1 by the use of the equations⁽²⁾

$$r^* = r_e + 1/a$$

$$a = 9.28\times10^{-3}\omega_e\sqrt{\mu/D_e},$$

we obtain $r^*=1.12$ Å. and $a=2.68$ Å.$^{-1}$ for H-H and $r^*=1.90$ Å. and $a=2.27$ Å.$^{-1}$ for Cu-H. But since the activated distance has a fixed

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(1) T. Kwan, *J. Research Inst. Catalysis* (*Hokkaido Univ.*), **1**, 95(1949); T. Kwan, This Bulletin, **23**, 73 (1950).

(2) K. Otozai, This Bulletin, **24**, 218(1951); K. Otozai, *Collected Papers from the Faculty of Science, Osaka Univ.*, No. 20; S. Kume and K. Otozai, This Bulletin, **24**, 257(1951).

(3) G. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Company, New York and London, 1941, p. 356.

(4) H. Sponer, "Molekülspektren und ihre Anwendungen auf chemische Probleme," Julius Springer, Berlin, 1935. D_e (109.2 kcal.) is sum of the ordinary dissociation energy (103 kcal.) and the zero point energy (6.2 kcal.).

(5) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, London, 1947. In the calculation of D_e the zero point energy was neglected in view of the uncertainty of the spetroscopic value itself.

value for the respective sort of bond, the maximum possible distance between Cu-Cu for which the dissociative adsorption of hydrogen can occur, must be equal to the total length, *i. e.*, 4.92 Å., of the linear or stretched form of the activated complex:

$$\begin{array}{c} 1.90\quad 1.12\quad 1.90 \\ \mathrm{Cu}\cdots\cdot\mathrm{H}\cdots\cdot\mathrm{H}\cdots\cdot\mathrm{Cu} \\ \longleftarrow 4.92 \longrightarrow \end{array}$$

On the other hand there are seven possible inter-atomic distances between the adjacent atoms on the surfaces of the copper crystal as is shown in Fig. 1, because copper crystallizes in a face-centered cubic lattice having a lattice constant $a=3.609$ Å. But since, as pointed above, no dissociative adsorption of hydrogen can occur on a pair of copper atoms, whose inter-atomic distance is larger than 4.92 Å., only three sorts of inter-atomic distances I, II and III need to be considered for the calculation of the activation energy for the adsorption. Furthermore, the adsorption of hydrogen on copper is clearly an exothermic process.⁽⁶⁾ Then the energy of activation in question can readily be calculated by means of our empirical rule, according to which the activated complex must have a symmetrical form as shown in Fig. 2 for the present case, and the sum of the energies of the two diagonal Cu-H bonds which appear only in the activated complex and hence have been called the "*activated bonds*," represents the energy of the activation for the reaction. For instance, when hydrogen is adsorbed on the pair of copper atoms, whose mutual distance is equal to 2.56 Å., the length of the two activated bonds becomes 2.55 Å. as is shown in Fig. 2. Hence, the energy of each activated bond has been calculated as 18.3 kcal. by putting $r=2.55$ Å. in Rydberg's equation⁽²⁾ and twice this value, *i. e.*, 36.6 kcal./mole represents the activation energy for the given adsorption.

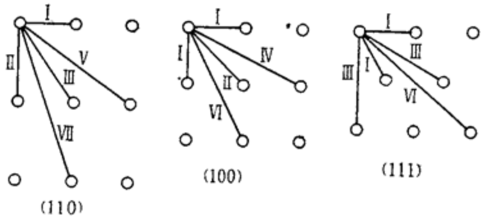

Fig. 1.—Inter-atomic distances on the surface of copper crystal: I $=\sqrt{1/2}\,a=2.56$ Å.; II $=a=3.61$ Å.; III $=\sqrt{3/2}\,a=4.42$ Å.; IV $=\sqrt{5/2}\,a=5.71$ Å.; V $=\sqrt{3}\,a=6.25$ Å.; VI $=\sqrt{7/2}\,a=6.74$ Å.; VII $=\sqrt{9/2}\,a=7.65$ Å.

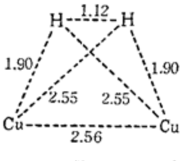

Fig. 2.—The activated complex for the adsorption on the Cu-Cu distance of 2.56 Å.

Similar calculations have been made for the other two Cu-Cu distances and the results are presented in Table 2 and Fig. 3.

Table 2

The Activation Energies of Adsorption of H_2 on Cu

Cu-Cu distance, Å.		Activation energy, kcal./mole
I:	2.56	36.6
II:	3.61	25.4
III:	4.42	19.4

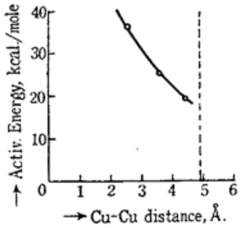

Fig. 3.—The activation energies of adsorption of H_2 on Cu.

Discussion

As will be seen from Table 2 and Fig. 3, the energy of activation for the adsorption of hydrogen on copper decreases considerably as the Cu-Cu distance increases. Hence, if the copper metal in question contains no amorphous parts and the rate of adsorption on various parts of the copper surface is mainly determined by the magnitude of the activation energy, the surfaces (110) and (111), which contain the largest Cu-Cu distance III (*cf.* Fig. 1), will be adsorped preferentially by hydrogen and the surface (100), which contains only I and II distances, may be ignored. The activation energy, which will be observed, will thus be equal to 19.4 kcal. corresponding to the adsorption at the largest Cu-Cu distance III. This value agrees, however, very well with the observed value 20 kcal./mole of Kwan, although this agreement may be to some extent an accidental one, when it is taken into consideration that the general accuracy of the present

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(6) The heat of adsorption was computed by Kwan as larger than 35 kcal./mole.

rule is ± 3 kcal. and the estimation of the fundamental data may contain some errors. The above obtained conclusion that hydrogen can be adsorbed more easily on the surfaces (110) and (111) than (100) of copper crystal has not yet been experimentally ascertained. But it may be worth pointing out the fact that according to the experiment of Leidheiser and Gwathmey⁽⁷⁾ the catalytic reaction between hydrogen and oxygen takes place more quickly on the surface (111) than on the surface (100) of copper.

Summary

The activation energy for the activated adsorption of hydrogen on copper metal has been calculated by the use of the empirical rule previously proposed. The calculated value 19.4 kcal./mole agrees very well with the observed value 20 kcal./mole of T. Kwan. It has been concluded that hydrogen will be adsorbed more quickly on the surfaces (110) and (111) than on the surface (100) of copper crystal.

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(7) H. Leidheiser, Jr., and A. T. Gwathmey, *J. Am. Chem., Soc.*, **70**, 1200, 1206 (1948); H. Leidheiser, Jr., and A. R. Meelheim, *ibid.*, **71**, 1122 (1949).