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NOTE

Hydrogen Adsorption on Copper*†

Studies of Parahydrogen Conversion

It is well known that the chemisorption of hydrogen on copper is negligible when ordinary gas uptake methods are used for detection (*1*). A much more sensitive test for hydrogen chemisorption is the parahydrogen conversion reaction which has been used previously by many workers (*2–4*).

It is generally assumed that a partly empty *d* orbital is a necessary requirement for the chemisorption of hydrogen on a metal surface. Regardless of whether the bonding is with an atomic *d* orbital as suggested by Beeck (*5*) or with a hybrid metal orbital as suggested by Eley (*6*) the fact that the parahydrogen conversion reaction proceeds suggests the existence of these vacancies. Calculations by Weiss and DeMarco (*7*) from X-ray measurements of atomic scattering factors suggest that copper has an incomplete *d* band containing 9.8 *d* electrons. The possibility of promotion of a 3*d* electron to the 4*s* level exists for copper since it has been shown that the 3*d* and 4*s* bands of copper overlap and that the *d–s* optical promotional energy is only 3.0 eV (*8*).

The high-temperature chemical mechanism of conversion at the surface is not clearly understood. There are two proposed reaction mechanisms, the Bonhoeffer-Farkas (9) and Eley-Rideal (*10*) mechanisms. Various authors (*2, 9–11*) have argued for one mechanism or the other, however, there still is not a clear picture of the situation, although the discovery of weak reversible chemisorption at room temperature and below on some metals has removed earlier objections to the Bonhoeffer-Farkas mechanism.

The apparatus and experimental techniques have been described previously (*12*). The copper films were evaporated from wire supplied by Johnson, Matthey & Co. with a purity of 99.999 + %.

RESULTS AND DISCUSSION

The results were analyzed according to kinetic equations given previously (*12*). As found for copper (*3*) and other metals, the pressure dependency of the first order rate constant follows a Langmuir isotherm, as shown in Fig. 1.

From the temperature dependency of the ratio of the adsorption–desorption rate constants the heat of adsorption of hydrogen on copper was determined. Values of $(-\Delta H_a)$ of 7.97 ± 0.03 and 7.39 ± 0.03 kcal/mole were obtained, which may be compared with values of 8.0 kcal/mole (*3*) and, by calorimetric techniques, 9.0 (*13*) and 10.0 kcal/mole (*14*).

Determination of the equilibrium surface coverage of copper by chemisorbed hydrogen gives value of $\theta = 0.15$ and $\theta =$

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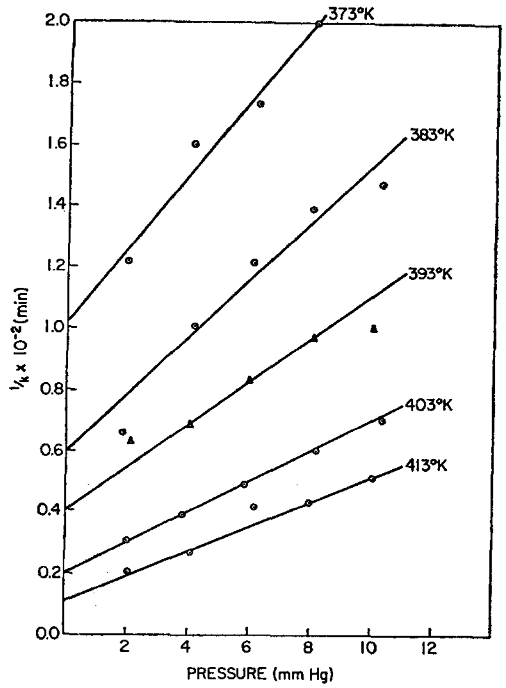

FIG. 1. Pressure dependency of the conversion.

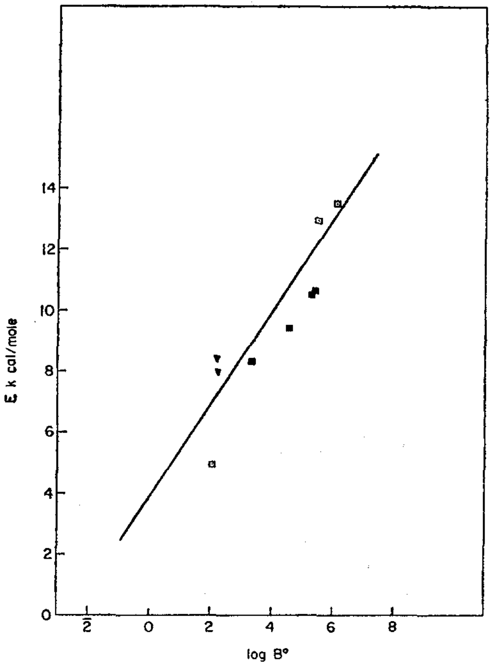

FIG. 2. Compensation effect for copper films: □, present work; ▽, calculated; ■, ref. *3*.

0.17 (*15*). By the calculation of entropy changes during the adsorption process, as shown earlier (*12*), the chemisorbed hydrogen film on copper may be shown to be mobile, as given in Table 1.

Figure 2 shows the activation energies and frequency factors obtained for the conversion reaction. The kinetic analysis of Eley (*12, 16*) enables values for the activation energies and frequency factors to be calculated. Table 2 shows the results obtained, the notation being the same as in ref. (*12*).

From Table 2 the activation energy was

TABLE 1

EXPERIMENTAL AND THEORETICAL ENTROPY CHANGES

Metal film	Surface standard state	Average temp (°K)	ΔS expt. (eu)	${}_3S_{trans} - {}_2S_{trans}$ (eu)	${}_3S_{trans} - S_{config}$ (eu)	State of adsorbed layer
Cu I	0.17	413	−21.0	−17.9	−33.2	Mobile
Cu II	0.17	393	−23.5	−24.0	−30.7	Mobile

TABLE 2

CALCULATION OF LOG $(k_0 + k_p)$ AS A FUNCTION OF TEMPERATURE FOR COPPER FILM II

T(°K)	$1/k_{p\to 0}$	$k_{p\to 0}$	b	$(k_0 + k_p)$	$\log (k_0 + k_p)$
413	11.07	0.0903	0.3521	5.803×10^{-3}	$\bar{3}.764$
403	20.00	0.0500	0.2466	4.673×10^{-3}	$\bar{3}.670$
393	40.66	0.0246	0.1726	3.367×10^{-3}	$\bar{3}.527$
383	59.79	0.0167	0.1561	2.594×10^{-3}	$\bar{3}.414$
373	101.78	0.0098	0.1206	2.023×10^{-3}	$\bar{3}.306$

determined as 8.1 kcal/mole and the logarithm of the frequency factor as 2.3. A similar calculation on another copper film yielded values of 8.2 kcal/mole and 2.3, respectively. These calculated points are also shown on Fig. 2. They fall on approximately the same compensation effect line as the experimental points, indicating that the calculated values represent the net conversion of parahydrogen molecules to orthohydrogen molecules.

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