TABLE II

CALCULATION OF EQUILIBRIUM OF CONSTANTS FROM COMPLEX CONCENTRATIONS

At each pH the values in the (a) series were solved at isosbestics by equations 10 and 11 while those in the (b) series were solved by determinants using equation 11 at 600, 640 and 700 mμ.

pH	$\frac{[en]}{[C_2O_4^{2-}]} \times 10^6$		X_{ox}	X_m	X_{en}	pK_p	pK_q	pK_s
6.85	183	(a)	0	0.177	0.823	4.41		
		(b)	0	.188	.812	4.38		
6.73	93.5	(a)	0	.253	.747	4.50		
		(b)	0	.271	.728	4.46		
6.66	74.1	(a)	0	.341	.659	4.42		
		(b)	0	.359	.641	4.38		
6.56	47.8	(a)	0	.408	.592	4.48		
		(b)	0	.437	.563	4.40		
6.47	33.8	(a)	0.014	.495	.491	4.47		
		(b)	.018	.490	.492	4.47		
6.37	22.8	(a)	.029	.600	.351	4.41		
		(b)	.035	.597	.371	4.44		
6.28	15.9	(a)	.082	.609	.310	4.51	5.67	1.16
		(b)	.075	.611	.308	4.50	5.71	1.24
6.19	11.0	(a)	.134	.632	.234	4.52	5.63	1.07
		(b)	.147	.614	.257	4.58	5.58	1.00
6.08	6.92	(a)	.244	.593	.137	4.53	5.54	1.02
		(b)	.262	.586	.163	4.60	5.51	.92
5.90	3.25	(a)	.388	.503	.109	4.82	5.60	.78
		(b)	.414	.513	.091	4.74	5.58	.85
5.81	2.33	(a)	.507	.423	.070	4.85	5.56	.71
		(b)	.478	.463	.035	4.51	5.62	1.11
5.72	1.32	(a)	.612	.365	.039		5.66	
		(b)	.589	.371	.032		5.68	
5.61	0.956	(a)	.685	.285	.022		5.64	
		(b)	.685	.285	.023		5.64	
5.50	.595	(a)	.819	.163	.018		5.53	
		(b)	.795	.186	0		5.60	
5.29	.227	(a)	.927	.073	0		5.54	
		(b)	.895	.095	0		5.67	
5.20	.140	(a)	.947	.053	0		5.58	
		(b)	.939	.059	0		5.62	
					Av. (a)	4.54	5.60	.95
					(b)	4.51	5.62	1.04

good agreement with the values obtained by two different slope intercept methods. On a statistical basis alone the concentration of the mixed complex should be twice that of either simple complex for equal concentrations of the latter two. Thus statistical considerations lead to a value of 0.60 for pK_s compared to the observed value of 1.0. A complete interpretation of the factors responsible for the remaining 0.40 must await further study of other mixed complexes. It is probably due to the absence of the electrical repulsion contribution obtained when two oxalate anions are associated for the effect is larger when the tetravalent pyrophosphate anion replaces the oxalate anion.[4] In the latter case pK_s has the value 1.70.

The values of pK_p and pK_q obtained from the individual data are also in good agreement with those obtained by the slope intercept treatments. In Table III are summarized the mean values of K_m calculated by eight different methods. The mean value of pK_m is -15.44 ± 0.14.

TABLE III

Method	Equations	pK_p	pK_q	pK_s	log K_m
Slope intercept	5	4.53			15.51
Slope intercept	7		5.88		15.58
Isosbestics	10, 2	4.54			15.50
Isosbestics	11, 4		5.60		15.30
Isosbestics	10, 11, 9			0.95	15.35
Determinants	13, 2	4.51			15.53
Determinants	13, 4		5.62		15.32
Determinants	13, 9			1.04	15.39
				Av.	15.44 ± 0.14

COLUMBUS, OHIO

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Hydrogen–Deuterium Exchange on Copper, Silver, Gold and Alloy Surfaces[1]

BY RICHARD J. MIKOVKSY, MICHEL BOUDART AND HUGH S. TAYLOR

RECEIVED FEBRUARY 11, 1954

The catalytic activity of copper, silver and gold foils, of a silver–lead (0.69 atom %) alloy foil and of several granular silver catalysts has been studied in the hydrogen–deuterium-exchange reaction. Observed activation energies and temperature ranges of activity of the catalysts have been measured. The data lead to observations on two possible mechanisms of the exchange reaction, to a suggested activation of copper by d-s promotion of the metal, and to a possible unification of "Brillouin zone" and d-band concepts in relation to catalysis.

Introduction

Copper has occupied an anomalous position in the history of hydrogenation catalysts in that while its activity in certain reactions has been studied for many years it has been known that, for the hydrogenation of benzene, it was ineffective in comparison with such catalysts as nickel.[2] It did not conform to the Balandin multiplet hypothesis relating catalytic action to lattice parameter.[3] Latterly, the relative inactivity of copper and of silver and gold has been related to the complete d-bands in their crystals[4] with the possibility that activity in chemisorption is related to d-s promotion.[5] The white color of silver suggests that the d-s promotion energy is greater than in the case of the colored metals copper and gold. That evaporated films of copper are unable to chemisorb N_2 and H_2 in the region 0 to −183° has recently been recorded by Allen and Mitchell.[6] By contrast, in the early literature, chemisorption of hydrogen by reduced copper

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[1] This article is based on a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree in Princeton by R. J. Mikovsky in September, 1951.

[2] J. H. Long, J. C. W. Frazer and E. J. Ott, THIS JOURNAL, **56**, 1101 (1934); V. N. Ipatieff, B. B. Corson and J. D. Kurbatov, *J. Phys. Chem.*, **43**, 589 (1939).

[3] P. H. Emmett and N. Skau, THIS JOURNAL, **65**, 1029 (1943).

[4] D. A. Dowden, *Research*, **1**, 239 (1948); *J. Chem. Soc.*, 242 (1950).

[5] (a) M. Boudart, A.C.S. meeting, New York, September, 1951; (b) THIS JOURNAL, **74**, 1534 (1952); (c) R. J. Mikovsky, Thesis, Princeton, 1951; (d) B. M. W. Trapnell, *Proc. Roy. Soc. (London)*, **A218**, 566 (1953).

[6] J. A. Allen and J. W. Mitchell, *Discs. Faraday Soc.*, 361 (1950).

catalysts has been abundantly recorded.[7] The heat of chemisorption of hydrogen by reduced copper at 0° was one of the earliest of such measurements made.[8]

Correlation between electronic structure and catalytic activity has been extended by studies not only on these single metals but also on alloy systems of which they were one component, notably by Schwab[9] and by Rienäcker.[10] Schwab, in studying the dehydrogenation of formic acid on such surfaces, reached the conclusion that the chemisorption of hydrogen from the molecule was a significant step in the decomposition and that this could be influenced by the addition to the metal catalyst of alloying elements with further correlation with the electronic structure of the alloy systems. These several considerations led to the following studies of the metal-alloy systems on the chemisorption of molecular hydrogen, by measurement of the rates and activation energies of hydrogen-deuterium exchange on such surfaces.

Experimental

Experimental Procedure.—The reaction was followed by means of a Nier mass spectrometer which gave a reading indicative of the mass 3(HD) to mass 2(H_2) ratio. The particular instrument used possessed two collectors and a feed-back amplifier which enabled a part of the mass 2 signal to be used to cancel the potential setup by the mass 3 ion current. This null point arrangement made the instrument essentially independent of the pressure behind the leak, the ion current, and, within limits, the filament current and the accelerating voltage. Permanent magnets produced the magnetic field.

The instrument could be calibrated to read the percentage of HD in the samples. This was unnecessary, however, since the relative spectrometer readings could be used to calculate the percentage of conversion for a measure of the extent of reaction. Zero per cent. conversion was represented by the spectrometer reading for a sample of gas used for the subsequent passage over the catalyst being studied and 100% reaction by the spectrometer reading for the gas stream after passage over an equilibrating catalyst. This catalyst was an efficient platinum-charcoal catalyst, active even at low temperatures. Mass action calculations show that this equilibration, for all practical purposes, results in complete exchange when the concentration of deuterium in the initial gas stream is of the magnitude used, *i.e.*, approximately 1.5%.

Apparatus.—The schematic diagram of Fig. 1 shows the essential parts of the experimental apparatus. The electrolytic cell used for hydrogen generation contained 25% KOH solution and the deuterium cell held heavy water (99.8% D_2O) into which sodium had been introduced and reacted with the water. The cells were set in parallel to adjust for variation in the direct current, thus maintaining a constant ratio of deuterium to hydrogen electrolyzed. The current through the deuterium cell was always set at 1.5% of that through the hydrogen cell. When a flow system was used, the total current passing through the two cells was taken as a measure of the flow rate. The amperages used corresponded to flows varying between 1.36 and 2.78 liters per hour at room temperature.

The reproducibility of this means of generating a gas mixture was excellent, usually amounting to well within one per cent. as evidenced by the mass spectrometer analyses.

The gas streams passed through purification trains which consisted of copper at ~350°, calcium chloride, ascarite and magnesium perchlorate.

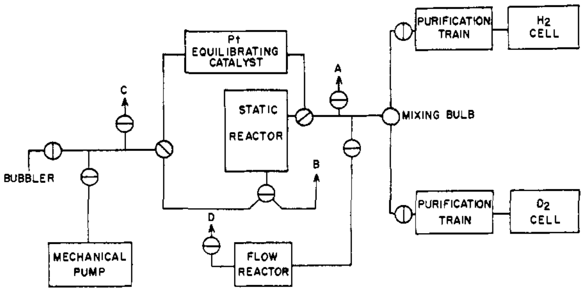

Fig. 1.—Schematic diagram of apparatus.

Mixing was effected and an inlet sample (zero per cent. exchange) could be taken at point A. The equilibrated sample was taken at point C, the gas stream could be diverted to pass through any of the reactors.

Each of the reactors was enclosed in an air jacket wrapped with heating elements and lagged. The air jackets served as thermoregulator units which allowed a temperature control to within 0.5° for an indefinitely long period.

The static reactor was used in studying the foil catalysts. Its volume was somewhat less than 300 cc. The metallic foils were wound around a thermocouple well. The H_2-D_2 mixture was introduced and time allowed for complete flushing to take place. The foil catalysts were relatively inactive and, as a result, the inlet sample could be taken at point B simultaneously with the flushing or by means of the regular sampling procedure.

Samples were extracted from the reactor by expansion into a sample tube attached at point B after its evacuation by means of the mechanical pump. The total amount of gas taken in the sampling was about 10% of the volume of the reactor.

The granular catalysts were studied in the flow reactor. The reactor possessed a pre-heating coil and samples were taken at point D. Here the experimental procedure consisted in changing the temperature at a constant flow rate (electrolysis current).

Catalysts.—The preparations of the various catalysts were carried out as follows.

1. Pure silver foil: pure silver wire was cold rolled into a foil ~0.1 mm. thick. The total area was 55.4 cm.^{2}.
2. Pure gold foil: foil of 0.001 in. thickness with a total area of 143.6 cm.^{2} was used.
3. Silver-0.69 atom % lead alloy: the appropriate amounts of silver wire and C.P. lead were melted together under borax. The melt was stirred and cooled slowly. The resultant bead of alloy was gradually cold rolled into a foil and a strip of 49.8 cm.^{2} total area was used in the experiments. We followed Schwab[9] in this choice to yield a homogeneous solid solution, the so-called α-phase, crystallizing in the face-centered cubic lattice of Ag.
4. Pure copper foil: a high purity copper foil was prepared by electroplating. Spectroscopically pure copper (<0.0005% Ni) was dissolved in nitric acid and converted to the sulfate by successive fuming procedures with sulfuric acid and diluted to an approximately 0.8 molar acid solution. The copper was planted on to a stainless steel cathode at a current density of 5 amp./dm.^{2}. The copper foil (60 μ thick) was peeled from the cathode and 117 cm.^{2} of it was inserted in the static reactor.
5. Precipitated silver: this granular catalyst was prepared by the precipitation of silver oxide from silver nitrate solution by the addition of potassium hydroxide. After washing and drying subsequent decomposition yielded the free metal. The temperature necessary for decomposition was 340°, significantly higher than that suggested by the available literature on the dissociation pressure of silver oxide. The flow reactor was charged with 28.6 g. of the pure metal.
6. Silver-0.64% calcium-0.025% nickel alloy: this was a commercial oxidation catalyst prepared by leaching out the calcium from a melt of the component metals. The amount inserted in the reactor was 12.9 g.
7. Silver (1 mole %)-magnesia: seven grams of this catalyst, made up in accordance with the directions of Matsumura,[11] by heating magnesia impregnated with silver nitrate solution to 1000° for 30 minutes and so used. This

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(7) R. M. Burns and H. S. Taylor, THIS JOURNAL, **43**, 1273 (1921); R. N. Pease, *ibid.*, **45**, 1196 (1923); W. A. Dew and H. S. Taylor, *J. Phys. Chem.*, **31**, 277 (1927).

(8) R. A. Beebe and H. S. Taylor, THIS JOURNAL, **46**, 51 (1924).

(9) G. M. Schwab, *Trans. Faraday Soc.*, **42**, 689 (1936).

(10) (a) G. Rienäcker and B. Sarry, *Z. anorg. Chem.*, **257**, 41 (1948); (b) G. Rienäcker and H. Bade, *ibid.*, **248**, 45 (1941).

(11) G. Matsumura, THIS JOURNAL, **73**, 2375 (1951).

gives a catalyst which, after extraction with dilute acetic acid to remove magnesia, filtration and dialysis, has been shown by Matsumura to yield a gray-pink colloidal solution of metallic silver contaminated with a trace of magnesium.

8. Magnesia blank: pure magnesia was put through a blank procedure similar to that used for the silver (1 mole %)-magnesia catalyst. The amount charged (6.8 g.) corresponded to the weight of magnesia in the charge of the silver-magnesia catalyst.

Experimental Results

The types of data obtained are illustrated in Figs. 2 and 3. Here the percentage of exchange is shown *versus* the temperature for various contact times in the case of the gold foil and the granular silver. These exemplify the two types of catalysts studied. Plots of the type shown in Fig. 2 for the foils were obtained by the inversion of the isothermal rate curves.

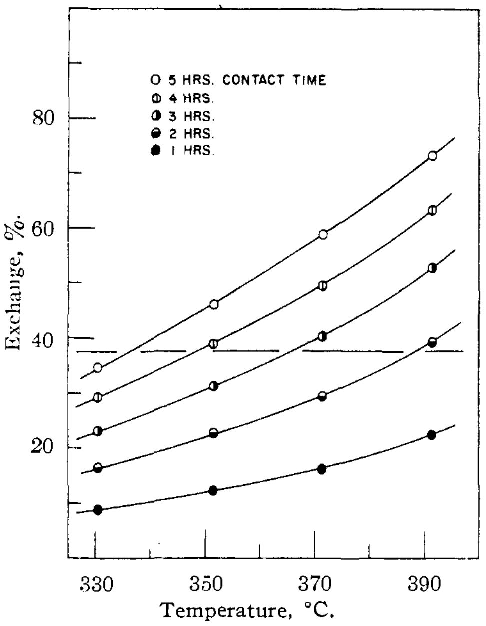

Fig. 2.—H_2–D_2 exchange on pure gold foil.

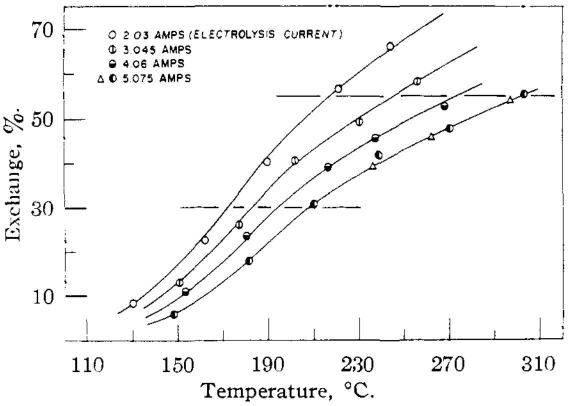

Fig. 3.—H_2–D_2 exchange on pure granular silver.

The curves of Figs. 2 and 3 determine the activation energies for the exchange on the gold foil and granular silver. The activation energy plots for all the systems studied are shown in Figs. 4–7. The numerical results are gathered in Tables I and II and compared with data obtained in other reactions.

Table I

Catalyst	E_{act}, kcal./mole $HCOOH \rightarrow H_2 + CO_2$	E_{act}, kcal./mole $H_2 + D_2 \rightarrow 2HD$	Temp. range, °C.	Reference
Ag foil	..	16.5	400–460	This work
	17.6	..	200–500	9
	30.8	..	180–250	*a*
Ag-Pb (0.69 atom%)	..	29.2	370–450	This work
	35.0	..	300–450	9
Au foil	..	13.9	330–400	This work
	12.5	..	200–500	9
Cu foil	..	23.1	310–350	This work
	22.3	..	120–200	10*b*
Glass	..	17.0	370–450	This work
	28.0	..	180	*a*

[a] These data are from H. C. Tingey and C. N. Hinshelwood, *J. Chem. Soc.*, 121, 1668 (1922); C. N. Hinshelwood and B. Topley, *ibid.*, **123**, 1014 (1923). They were obtained in static systems.

Table II

Catalyst	E_{act}, kcal./mole	Temp. range, °C.
Ag Foil	16.5	400–460
Ag (Granular)	10.8 and 6.0	130–300
Ag-Ca(0.64%)-Ni(trace)	11.0	70–220
MgO-Ag(1 mole %)	18.3	70–100
MgO blank	19.4	100–125

The glass blank was necessary only in the case of the silver-lead alloy and to a much smaller extent in the case of gold. The correction varied up to ~50% of the measured exchange for the silver-lead catalyst and was practically negligible for the gold foil.

The preliminary runs on copper showed a deactivation taking place. This was attributed to the elimination of water from the surface and also that occluded during the electrodeposition. An activation then appeared which persisted for approximately 750 hr. at temperatures between 350 and 400°. This slow activation was finally completed by five successive oxidation-reduction procedures *in situ*. These procedures enhanced the surface area enough to lower the time necessary to obtain suitable exchange from 40 to 6 hr. and also to lower the temperature necessary to values which made the blank unnecessary. The subsequent runs were made with the reactor at temperature a minimum length of time, thereby making any activation negligible.

The granular silver catalyst showed a slow activation in contrast to the lack of one in the silver-calcium alloy. This behavior continued through about eight runs at a constant flow rate. The runs then became reproducible and the curves of Fig. 3 were obtained. The existence of two activation energies is to be noted. The measurements are entirely reproducible as shown in the two sets of points at the highest flow rate. Figure 6 shows these two activation energy plots corresponding to 10.8 and 6.0 kcal./mole.

The numerical magnitudes of the activation energies of the granular silver, alloy and colloidal silver catalysts are shown in Table II, in comparison with silver foil.

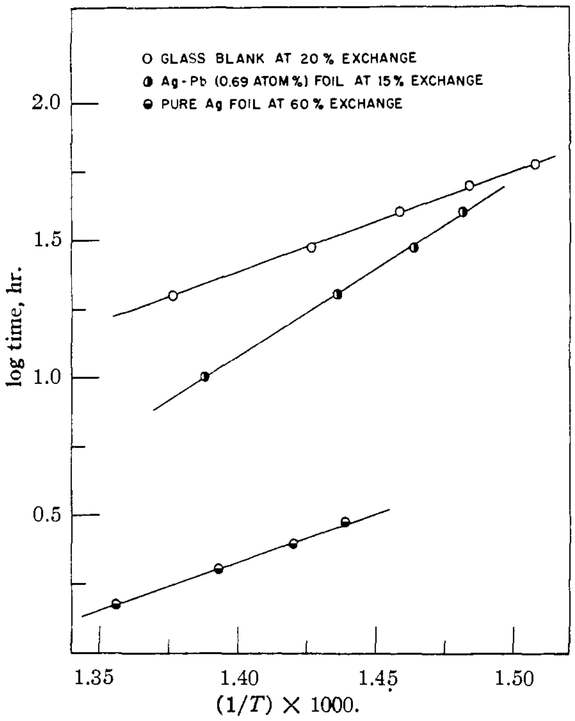

Fig. 4.—Activation energy plot.

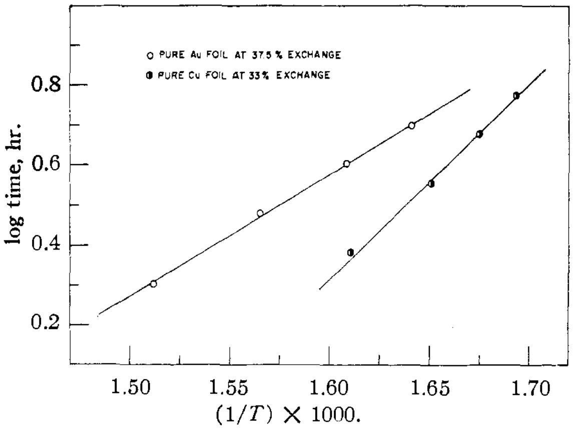

Fig. 5.—Activation energy plot: ○, pure Au foil at 37.5% exchange; ◑, pure Cu foil at 33% exchange.

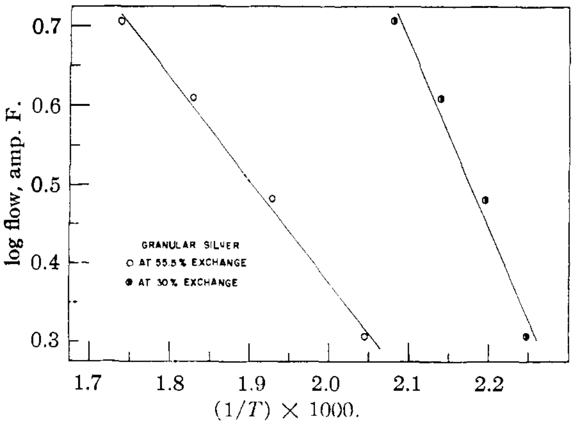

Fig. 6.—Activation energy plot for granular silver: ○, at 55.5%; ◑, at 30% exchange.

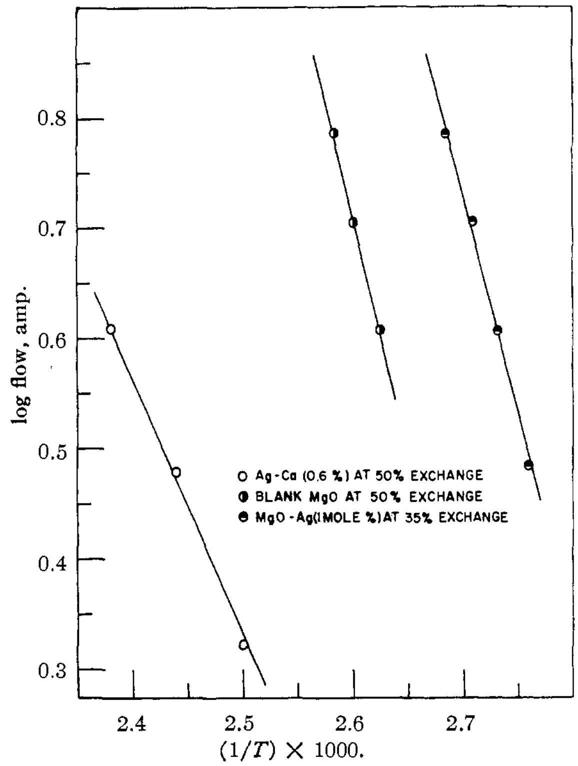

Fig. 7.—Activation energy plot.

Discussion

Two obvious conclusions immediately emerge from the experimental data. There is a close parallelism between our findings on the activation energies of exchange on the Cu, Ag, Au and Ag–Pb (0.69 atom %) alloy and those obtained by Schwab and by Rienäcker on similar systems with the dehydrogenation of formic acid. The second observation is that in each case the dehydrogenation occurs, in the case of formic acid, at temperatures 100–200° lower than those required for the hydrogen isotope exchange reaction. In addition, granular silver in contrast to the foil possesses a noticeably lower activation energy of exchange and a conspicuously lower reaction temperature for a given amount of reaction. The same is true for reduced copper catalyst powders as evidenced from unpublished work in this Laboratory and in many other researches elsewhere.

Every mechanism proposed for the hydrogen-deuterium exchange involves chemisorption of at least one of the reactants. For this reason we conclude that whereas neither copper, silver nor gold show chemisorption of hydrogen on the evaporated metal films in the temperature range 20 to −180°, as recently found by Trapnell,[5d] the present data show that chemisorption of hydrogen by these elements does occur in higher ranges of temperature.

To compare the surface chemistry of various surfaces, the hydrogen–deuterium exchange is an advantageous test reaction because of the absence of surface contamination by reaction products. Thus, with the formic acid hydrogenation, one may reasonably fear the effect of water produced by a small simultaneous dehydration of the acid. Nevertheless, the H_2–D_2 exchange is not an unequivocal index of surface activity especially in the absence of complete rate data including surface area determinations.

Indeed, two reaction paths with quite different implications are conceivable and have been repeatedly discussed in the literature.

The first path, known as the Bonhoeffer–Farkas (B.F.) mechanism proceeds *via* a surface recombination of adsorbed atoms (subscript a)

$$H_2 \text{ (or } D_2) \longrightarrow 2H_a \text{ (or } 2D_a) \qquad (1)$$

$$H_a + D_a \longrightarrow HD \qquad (2)$$

The second path, the so-called Rideal–Eley (R.E.) mechanism, postulates a chain process, with initiation and termination steps corresponding to adsorption and desorption, respectively, the chain propagating step being a switch reaction

$$H_a \text{ (or } D_a) + D_2 \text{ (or } H_2) \longrightarrow HD + D_a \text{ (or } H_a) \qquad (3)$$

With a B.F. mechanism, the rate r_I of the exchange is equal to the rate of desorption (2)

$$r_I = k_2\theta_{H_a}\cdot\theta_{D_a} \qquad (4)$$

which is of course equal to the rate of adsorption since the exchange proceeds under conditions of hydrogen adsorption equilibrium if one neglects a small correction due to the isotope effect.

The rate of the exchange for the R.E. case is, on the other hand

$$r_{II} = k_3[\theta_{H_a}p_{D_2} + \theta_{D_a}p_{H_2}] \qquad (5)$$

The chain mechanism was originally introduced in order to explain the ortho–parahydrogen conversion on tungsten because it was felt that the rate of adsorption was too slow to account for the observed rate of the catalytic reaction. While this argument has been invalidated by more recent adsorption data on tungsten, the chain mechanism remains an attractive possibility in other cases where the condition for which it was invented prevails, namely, a slow rate of adsorption. Indeed, if the activation energy for adsorption E_a is substantially larger than the activation energy for the switch reaction E_S, r_{II} becomes larger than r_I. As remarked by Laidler[12] E_S must be larger than 7 kcal./mole, the activation energy for the gas phase exchange $H + H_2 \rightarrow H_2 + H$. This situation seems to explain why the R.E. mechanism is unlikely on transition metals of the 8th group which are characterized by a low value of E_a.

As a matter of fact, the low values of E_a for hydrogen recorded on a variety of clean metal surfaces have cast some doubt on the reality of activated adsorption as originally postulated by Taylor. The case of copper now gives considerable support to the concept of activated adsorption. The inability of copper films to chemisorb hydrogen up to room temperature was first observed by Leypunsky[13] and has been amply confirmed by more recent work.[6] This fact and the contrasting behavior of inadequately reduced copper powders led Kwan[14] to a careful study of the rate of hydrogen adsorption on copper powders reduced carefully at 400°. While no adsorption of hydrogen could be detected on this sintered copper adsorbent below 300°, the rate was measured at 300, 350 and 400°. The adsorption follows a first order law and the activation energy calculated from first-order rate constants is 20 kcal./mole.

The results of Kwan are essentially confirmed by the present study: the rate of the exchange was measurable on the copper foil above 300° and the activation energy is 23 kcal./mole. A B.F. mechanism immediately suggests itself, the exchange rate being the rate of activated adsorption.

It seems of interest to speculate at this stage on the nature of this activated adsorption. The inactivity of Cu, Ag, Au with respect to hydrogen adsorption, as compared to the activity of Ni, Pd, Pt, respectively, can be attributed to the filling of the d-band that takes place when one passes from the 8th group to the 1st B subgroup and that explains a number of properties in metal and alloy physics. Let us consider copper first. While no d-orbitals are normally available in copper for surface bond formation, vacant d-orbitals may be created by promoting a d-electron to the top of the s-band with relatively little expenditure of energy.[5] The edge of the absorption band of copper in the visible suggests that the promotional energy for this internal photoelectric effect is about 2.1 e.v. As is well known, the corresponding thermal energy might be substantially less than that required by a light quantum, as a consequence of the Franck–Condon principle.[15] Furthermore, visible light penetrates into the metal to a depth of the order of 10^{-3} cm. and it seems natural that the promotional energy be less at the surface because of its unsaturated valences than in the layer beneath. It is tempting therefore to identify the activation energy for adsorption or the exchange with the d-s promotional energy in copper. It must be emphasized that this type of reasoning has been successfully used in the chemistry of complexes of transition metals[16]: when the bonding energy gained as a result of promotion is sufficient the latter tends to take place. Here, an "excited" or "active" copper atom would resemble nickel and thus be able to adsorb hydrogen with sufficient strength.[17]

If this reasoning is correct, the activation energies for the exchange on gold and especially silver foils ought to be larger than on copper insofar as the promotional energies are higher for these metals. Thus for Ag and Au, the absorption edges indicate an internal photoelectric effect corresponding to energies equal to 4 and 2.3 e.v., respectively.[18] The data show that the opposite is observed: the activation energies are lower than in the case of copper. However, two other details are quite revealing. First, the activation energy on glass is the same as on silver, *viz.*, 17 kcal./mole. Second, the

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(12) K. J. Laidler, *J. Phys. Chem.*, **57**, 321 (1953).

(13) O. Leypunsky, *Acta Physicochim. U.R.S.S.*, **5**, 271 (1936).

(14) T. Kwan, *J. Res. Inst. Catalysis*, **1**, 95 (1949).

(15) F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 458.

(16) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell Univ. Press, Ithaca, N. Y., p. 250.

(17) Since according to this scheme the activation energy becomes related to the color of metallic copper, it is of interest to note that common experience of catalyst preparation teaches that an efficient copper catalyst must not look like copper. If the characteristic color of copper appears, say after excessive reduction, the catalyst is dead.

(18) J. Friedel, *Proc. Phys. Soc. (London)*, **65B**, 769 (1952).

temperature ranges for measurable exchange rates are substantially higher in the case of gold, silver and glass than for copper. This last circumstance may be attributed to a particularly small frequency factor in the rate expression, especially considering that the apparent activation energies are smaller than on copper. It is important to realize that the surface areas are in all cases of the same order of magnitude. Small frequency factors, lack of specificity (glass behaves like silver) and relatively small apparent activation energies indicate that here conditions may be fulfilled for a R.E. chain mechanism. The activation energy for adsorption is probably quite large, as predicted by the considerations above and the fraction θ of surface covered with hydrogen atoms is quite small. These are factors against a B.F. surface recombination mechanism but in favor of a chain mechanism. Now, from equation 4, it follows that the apparent activation energy E of the exchange reaction for small coverage θ is now, as follows from (5)

$$E = E_s + \frac{u}{2} - \frac{q}{2} \text{ kcal./mole}$$

where q is the heat of adsorption and u is the promotional energy as explained above. The lack of specificity of various surfaces then becomes understandable since the activation energy E_s for the switch reaction should increase with q. Although it is not possible from the data to calculate E_s, u and q from E, reasonable values for those three unknown quantities give E values of the right order of magnitude. Thus for illustration, if for silver $E_s = 15$, $u = 30$ and $q = 25$, one would have $E = 17.5$. For gold, one might assume the same values for E_s and thus, for q, put $u = 22$ in agreement with the optical evidence which suggests that gold has a promotion energy intermediate between those of copper and silver. For glass, the mechanism is obviously different: $u = 0$ but hydrogen is presumably chemisorbed with formation of strong OH bonds; reasonable values might be $E_s = 35$, $q = 34$ leading to a value of E of the right order of magnitude.

Additional evidence in support of the scheme here advanced are the exchange data on silver–lead alloy foils. Here again, optical properties of, for instance, copper–zinc alloys, show that the promotional energy of a metal of group IB increases when metals of higher valencies are alloyed to it. This is due to the fact that additional valence electrons of the alloying element fill up the s-band of the noble metal. The present work shows that this effect finds its counterpart in the characteristics of the exchange reaction. Thus 0.6 atom % Pb in silver increases the apparent activation energy from 17 to 29 kcal./mole, while the temperature range of the observation remains the same. In our scheme this means that E_s and thus q remain essentially unchanged but u increases rather strongly.

The concept of promotional energy introduced here in accordance with known metallic properties and the importance of d-orbitals in chemisorption of hydrogen, corresponds to the idea of thermally induced active centers first proposed by Volkenshtein[19] and discussed elsewhere by us.[20] The idea of Schwab relating electron concentration of Hume-Rothery alloys with their catalytic activity for the dehydrogenation of formic acid are not essentially different from those exposed in this paper. Schwab shows that the apparent activation energy for this reaction increases with the filling up of the Brillouin zone of a given alloy. We have attempted to provide a reason for this in terms of availability of d-orbitals. Table I contains the data of Schwab for the metals studied in this work. The agreement between apparent activation energies for the two types of reaction is surprising. Only further work on the mechanism of both reactions can establish the true significance of this correlation.

As to the data collected in Table II and contrasting the behavior of silver "catalysts" as opposed to silver foils, they illustrate sharply for this metal what has been known for a long time to be the case for copper, namely, that "dirty" metallic surfaces are not necessarily less active catalytically than clean metal films. Thus, the heat treatment of the silver granular catalyst (at 340°) while sufficient for the decomposition of bulk silver oxide is certainly incapable of removing surface oxygen. Indeed, Buttner, Funk and Udin[21] have shown that at 932°, an adsorbed oxygen film on a silver wire would start evaporating only if the partial pressure of oxygen is less than 10^{-5} atm., whereas the decomposition pressure of solid silver oxide at the same temperature is 1.7×10^4 atm. The contrast between these catalysts and the metal foils also suggests that the latter were reasonably clean, as we have implicitly assumed all along. It is our opinion that surface contamination, which cannot be ruled out positively in the present experiments on foils, must be invoked only *in extremis* if alternative explanations fail to systematize all the facts observed.

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