The most fundamental difference between B_2O_3 and SiO_2 and their liquid systems with M_2O lies in the coördination numbers of B and Si. Classically, this has been considered to be three, with an increasing degree of four coördination upon addition of M_2O. Conversely, Grojtheim and Krogh-Moe[11] and Berger[12] concluded that vitreous B_2O_3 was predominantly four coördinated, in equilibrium with the three coördinated form; whereas Fajans and Barber[13] suggested a molecular structure. More recently, the classical structure has been supported by X-ray and electron diffraction measurements of Silver and Bray.[14] Despuljols[15] and Milberg and Meller.[16] The latter authors have concluded that some degree of four coördination is not inconsistent with their measurements. In support of an increase of four coördination on addition of O ions to liquid B_2O_3, Bockris and Mellors[10] observed a decrease of the molar volume of $PbO-B_2O_3$ on addition of PbO to B_2O_3.

Were B_2O_3 entirely three coördinated in the liquid, the effect of temperature would be predominantly to expand the liquid lattice and hence to *increase* the compressibility with increase of temperature. The negative temperature coefficient indicates a temperature-dependent structural change upon compression. Let it be supposed that liquid B_2O_3 contains a significant amount of four-coördinated B.[16] Under pressure, an increase of the four-coördinated structural component would be favored because of the large compacting effect which would follow the formation of the four-coördinated form. Such a transition is consistent with the fact that the compressibility for B_2O_3 is about 10^2 times that for SiO_2 at the lowest temperature at which measurements are here recorded. With increase of temperature, the increasing thermal motion resists a tendency for the coördination to change from three to four upon compression, and hence the compressibility decreases with temperature increases. Such an effect, and the magnitude of the associated negative temperature coefficient of compressibility, will become less upon addition of Li_2O, because this causes an increasing quantity of three-coördinated B to become four-coördinated, so that less of the former material is present for the compacting effect of pressure supposed.

The decrease of β_s with the initial increase of Li_2O content (*cf.* Fig. 4) is consistent with increasing four coördination (*i.e.* the melt is becoming more compact, *cf.* the decrease of molar volume observed upon addition of PbO to B_2O_3[10]). However, this explanation is only consistent with the model of discrete borate ions[10] (or "icebergs"[17]) commencing at about 10% M_2O, up to this composition, or after that until the composition at which the change to four coördination upon addition of Li_2O is complete (33%). Fig. 4 shows a measurement for $Li_2O \cdot SiO_2$ which (therefore anomalously) indicates a β_s value less than that at 33%. Above the 1:1 composition, the structure of the borate melt would be analogous to that of the corresponding silicate, *e.g.*, both have one "single-bonded" O per network-forming cation. With increase of M_2O above 50 mole %, the compressibility would be expected to increase by a mechanism similar to that suggested in section 2.

Acknowledgments.—The authors are grateful to the support of this work by the Atomic Energy Commission, under Contract AT. 30-1-1769.

[11] K. Grojtheim and J. Krogh-Moe, *Naturwissenschaften*, **41**, 526 (1954). K. Grojtheim, *Kgl. Norske Vidensk. Selskab. Forh.*, **29**, 6 (1956).

[12] S. V. Berger, *Acta Chem. Scand.*, **7**, 611 (1953).

[13] K. Fajans and S. W. Barber, THIS JOURNAL, **74**, 2761 (1952).

[14] A. H. Silver and P. J. Bray, *J. Chem. Phys.*, **29**, 984 (1958).

[15] J. Despuljols, *J. phys. radium*, **19**, 612 (1958).

[16] M. Milberg and F. Meller, *J. Chem. Phys.*, **31**, 126 (1958).

[17] J. O'M. Bockris, J. W. Tomlinson and J. C. White, *Trans. Faraday Soc.*, **52**, 299 (1956).

[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND]

The Activity of Raney Nickel as a Function of Hydrogen Content

BY R. J. KOKES AND P. H. EMMETT

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The surface area of Raney nickel and its activity for ethylene hydrogenation and parahydrogen conversion were studied as a function of hydrogen content. These data were interpreted on the assumption that Raney nickel is a substitutional solid solution of nickel, aluminum and hydrogen promoted with alumina. It was tentatively concluded on the basis of comparison of these results with those reported for the copper-nickel system that the number of valence electrons per unit cell added by dissolved hydrogen, copper or other alloying components is an important consideration in comparison of such alloy systems. The activity of nickel at first decreases and then increases with an increase in the number of added electrons per unit cell.

It has been recognized for some time that Raney nickel catalysts which are prepared by leaching a nickel-aluminum alloy with alkali[1] usually contain not only nickel but also free aluminum and some alumina.[2] Moreover, the catalyst contains sufficient hydrogen[3] to lead some investigators to suggest that it is a compound of nickel and hydrogen.[4] It has also been shown that the activity of these catalysts for the hydrogenation of benzene is a function of the hydrogen content.[3] The role this hydrogen plays in catalysis is not clear, but recent evidence[5] suggests that the metallic phase of the catalyst is an atomic, substitutional, nickel-aluminum-hydrogen alloy wherein the hydrogen func-

[1] E. Lieber and F. L. Morritz, *Advances in Catalysis*, **5**, 417 (1953).

[2] V. N. Ipatieff and H. Pines, THIS JOURNAL, **72**, 5320 (1950).

[3] H. A. Smith, A. J. Chadwell and S. S. Kirdis, *J. Phys. Chem.*, **59**, 820 (1955).

[4] M. Raney, *Ind. Eng. Chem.*, **32**, 1199 (1940).

[5] R. J. Kokes and P. H. Emmett, THIS JOURNAL, **81**, 5032 (1959).

tions as copper in a copper-nickel alloy and contributes one electron per atom to the d-band of the nickel. Removal of the hydrogen from the catalyst by controlled heat treatment creates a defective lattice with vacancies at sites formerly occupied by hydrogen atoms. (The existence of a defect structure was suggested earlier by Taylor and Weiss.[6])

Of late, there have been many catalytic studies on alloys systems[7-9] which facilitate controlled variation of solid state properties and thereby permit testing of the qualitative theories first put forth by Dowden. Raney nickel catalysts should be ideal for such studies; with appropriate heat treatment the hydrogen content of a single sample can be varied with little or no collapse in structure or fall off in surface area.

In the present study we have investigated the activity of a Raney nickel catalyst at −78° as a function of hydrogen content. The reactions studied were ethylene hydrogenation and parahydrogen conversion. The purpose of the study was to check the effect of the hydrogen content of Raney nickel on its activity and to study thereby the effect of a controlled variation in solid state properties on catalytic activity.

Experimental

The Raney nickel used in the present studies was prepared from a 50–50 Ni–Al alloy. The procedure was the W-6 procedure of Adkins and Billica[10] as modified by Smith, *et al.*[3] The catalyst is the same as that described in an earlier paper.[5] The degassed catalyst contained 0.3% acid insoluble material (HCl), 77.3% nickel and 13.2% Al. It was assumed that the catalyst contained only Ni, Al and Al_2O_3 and the following composition was deduced: 77.3% Ni, 19.8% Al_2O_3 and 3.0% Al. These values are in fair-agreement with the data reported by Ipatieff and Pines.[2,11] Prior to use, the catalyst was stored under distilled water.

The surface area of this catalyst was determined on a BET system as a function of hydrogen content, with the latter determined as described earlier.[5] Nitrogen chemisorption was no problem in these surface area measurements.

The activity of the catalyst was measured at −78° as a function of hydrogen content both for the hydrogenation of ethylene and the parahydrogen conversion. The reactants (60–40 hydrogen:ethylene) for the hydrogenation tests were obtained in a single tank from the Mathieson Chemical Company. Chromatographic analysis showed the gas contained not only hydrogen and ethylene but also small quantities of ethane (about 1%) and about 0.1% of a noncondensable gas other than hydrogen. This mixture was purified by passage over a glass wool-sodium trap described by Storch,[12] and since no noticeable poisoning of the catalyst occurred on exposure to the reactant gases, this purification scheme was deemed adequate. The hydrogen was purified by passage through a trap at −195° which contained 150 to 200 cc. of activated charcoal.

At the flow rates used the effluent hydrogen contained para and orthohydrogen in a 1:1 ratio corresponding to equilibrium at −195°. Chromatographic analyses of the ethylene–ethane product with hydrogen as a carrying gas were precise to about ±0.2%. The conductivity cell used as a detector was also used to analyze the effluent hydrogen for parahydrogen.

A single sample of W_6 catalyst weighing about 6 g. was the source of the catalyst used for the activity measurements. Pretreatments were carried out in a special tube which readily permitted transfer in an atmosphere of helium to a reactor tube.

With a conventional flow system the activity of the catalyst was so great that the heat released by the hydrogenation reaction caused it to "run away". For this reason the activity for ethylene conversion was studied using a microcatalytic technique[7,13] in which a slug of reactant gas (about 11.6 cc.) was passed over the catalyst diluted 50:1 with Vycor at an entering flow rate of 40 cc./min. With this procedure the specific hydrogenation rates of different duplicate samples of catalyst (3 to 20 mg.) were the same to ± 10%.

The amounts of catalysts weighing more than 10 mg. were determined by weighing and those weighing less than 10 mg. by analyzing, the sample plus Vycor, for nickel at the completion of the experiment. In the worst cases the sample weight was known to within ±10%.

The ortho–parahydrogen conversion was followed by conventional flow techniques. The apparent first order rate constant k_p was calculated according to the equation

$$\ln \frac{P_0 - P_e}{P_t - P_e} = wk_p t_c$$

where P_0, P_t and P_e are the inlet, exit and equilibrium parahydrogen pressures, respectively, w is the weight of the catalyst and t_c is the contact time. Tests with a single sample of catalyst at different flow rates demonstrated that the above equation provided an accurate description of the data up to 50% conversion. The equation was also tested by measurements of $k_p t_c$ at the same flow on three different samples of catalyst having the same pretreatment. Although the weights differed by a factor of almost 5 the value of $k_p t_c$ was found to be 24 ± 2 (Table I).

TABLE I

RATE OF PARAHYDROGEN CONVERSION AND HYDROGENATION OF ETHYLENE OVER RANEY NICKEL AS A FUNCTION OF THE AMOUNT OF HYDROGEN REMOVED FROM THE CATALYST

Run no.	Catalyst wt., mg.	Hydrogen removed, cc./g.	Ethylene converted, cc./catalyst, g.	$k_e t_c$[a]	$k_p t_c$[b]	k_e/k_p
3	20	18.0	32	4.75	21	0.23
4	11.2	18.0	42	6.11	25	.24
6	3.2	18.0	31	4.41	..[g]	
8	4.4	18.0	36	5.27	26	.20
9	4.5	22.6	25	3.56	25	.14
10	9.4	34.7	16	2.31	15	.15
11	14	49.7	12	1.75	10	.18
12A	26	60.4	10	1.44	11	.13
12B	26	..[c]	13[c]	1.87	(19)[c]	(.10)[c]
12C	26	..[d]	58[d]	8.69	55[d]	.16
13A	27	66.9	13	1.89	71	.03
13B	27	..[f]	27[f]	3.97	60[f]	.07[f]
16	27	72.4	31	4.59	117	.04

[a] This is the reaction velocity constant for ethylene hydrogenation multiplied by the contact time for the inlet flow; the rate of hydrogenation is assumed to be first order with respect to hydrogen and zero order with respect to ethylene. The entering flow rate was 40 cc./min. [b] This is the first order constant for the parahydrogen conversion mutliplied by contact time. The flow rate was 40 cc./min. [c] This sample was exposed to hydrogen at 1 atm. at -78" for 20 minutes. The value of $k_p t_c$ is approximate. [d] This sample was exposed to hydrogen at 1 atm. at 25° for 240 hr. [f] This sample was exposed to hydrogen at 1 atm. at 25° for 20 hr. [g] The value of $k_p t_c$ was not determined.

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(6) A. Taylor and J. Weiss, *Nature*, **141**, 1055 (1938).

(7) W. K. Hall and P. H. Emmett, *J. Phys. Chem.*, **63**, 1102 (1959).

(8) D. A. Dowden and P. W. Reynolds, *Discussions Faraday Soc.*, **8**, 172 (1950).

(9) R. H. Best and W. W. Russell, THIS JOURNAL, **76**, 838 (1954).

(10) H. Adkins and H. R. Billica, *ibid.*, **70**, 695 (1948).

(11) These analyses are different from those suggested by Watt and Parker (G. W. Watt and S. G. Parker, *ibid.*, **74**, 1103 (1952)). For reasons given earlier[5] we do not agree with their interpretation of the analytical results.

(12) H. H. Storch, *ibid.*, **56**, 374 (1934).

(13) R. J. Kokes, H. Tobin and P. H. Emmett, *ibid.*, **77**, 5860 (1955).

Results

Figure 1 shows the hydrogen evolution from this sample of catalyst as a function of temperature. At each of the indicated temperatures the catalyst was degassed for roughly thirty minutes.

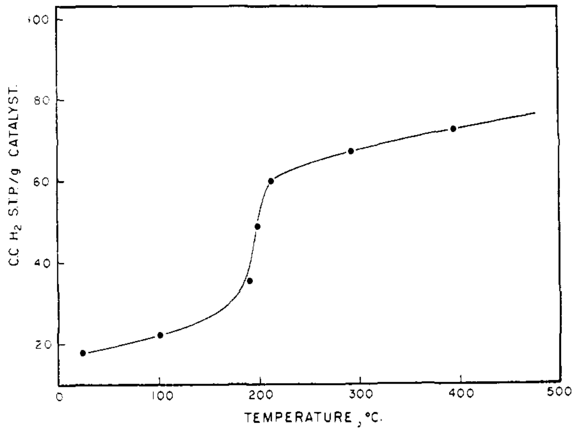

Fig. 1.—Hydrogen evolution from W-6 Raney nickel.

The variation of the surface area as a function of hydrogen content for a different sample of the same catalyst is given in the plot in Fig. 2. These results clearly indicate that the surface area of these catalysts remain essentially constant until about 85 to 95% of the hydrogen is removed which corresponds to a temperature of 300 to 400°; at higher temperatures the surface area falls off rapidly.

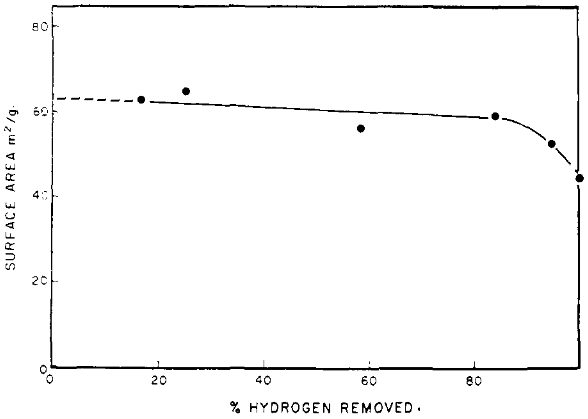

Fig. 2.—Surface area of W-6 Raney nickel.

The activity data for the catalyst as a function of hydrogen content are summarized in Fig. 3 and Table I. The data express the ethylene hydrogenation activity in terms of cc. STP of ethylene converted per gram of catalyst at a standard rate of flow corresponding to a contact time of approximately one second. These data and those in Fig. 2 indicate that the specific activity of these catalysts varies from about 0.2 up to 0.8 cc. of ethylene converted per square meter of catalyst per second.

Table I and Fig. 3 also summarize the activity data for the parahydrogen conversion. All studies of the parahydrogen conversion were carried out at the same fixed flow and the value of $k_{p}t_{c}$ was evaluated using the formula given in the Experimental section.

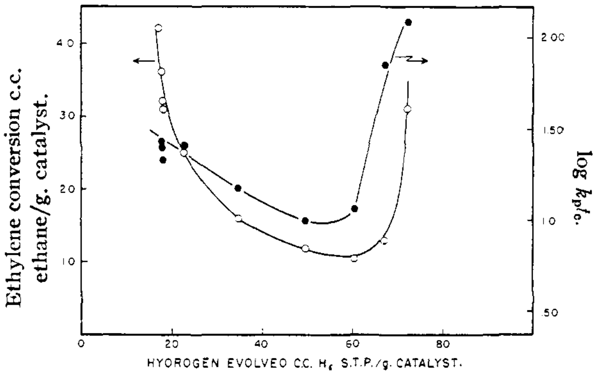

Fig. 3.—Activity of W-6 Raney nickel ethylene hydrogenation and parahydrogen conversion.

For both the hydrogenation and parahydrogen conversion there is a decline in activity during the initial stages of hydrogen removal followed by a sudden increase in the activity as the final amounts of hydrogen are removed. This increase in activity after the removal of small amounts of hydrogen at high temperatures could conceivably be due to the reaction of hydrogen with traces of oxygen present as a poison on the metallic surface. Data on the weight loss during this latter stage of the degassing reveal no weight loss ascribable to oxygen removal. On the basis of the experimental error in these measurements, it appears that the maximum amount of oxygen poison that could be removed by reaction with hydrogen would be ~0.2 cc. STP./g. catalyst, *i.e.*, enough to cover about 1% of the total surface or 5% of the metallic surface.

Except for run 12 the activity data in Fig. 3 were based on the average of two or more successive runs carried out on the same sample of catalyst at about 20 minute intervals; hence, if hydrogen was being resorbed by the catalyst from the carrier gas, it was immeasurably slow (or fast) compared to the time required for a run. In the run 12 series the second run (12B) showed an activity higher than the first run by some 30% (see Table I), and the estimated value of $k_{p}t_{c}$ was 70% higher than the value obtained in the first run. Both of these measurements were repeated after the catalyst had been stored in hydrogen for 240 hr. at room temperature. The effect of this pretreatment was profound; the activity for both reactions increased five- or sixfold. In run 13 no such effect was noted for successive runs but prolonged exposure to hydrogen (13B) resulted again in a significant increase in the ethylene activity although in this case the value of $k_{p}t_{c}$ decreased.

Discussion

No attempt was made to determine the equations which describe the kinetics of ethylene hydrogenation over this catalyst. For the purposes of this discussion we will assume that the kinetics are identical to those on pure nickel catalysts. The rate of hydrogenation of ethylene with nickel catalysts is usually first order in hydrogen pressure and zero order in ethylene which is often interpreted to mean that the surface is saturated with ethylene and either gas phase or physically adsorbed hydrogen reacts with the adsorbed olefin.[14] With this interpretation the ability of the catalyst itself to activate hydrogen should not necessarily parallel the activity of the catalyst for ethylene hydrogenation. The parallelisms that we observe for the parahydrogen conversion and the ethylene hydrogenation are to be expected, however, if we accept the mechanism suggested by Beeck[15] and Jenkins and Rideal[16] who propose that gas phase ethylene reacts with hydrogen chemisorbed on that part of the catalyst not covered with acetylenic complexes. In the further discussion we shall assume that the latter mechanism[15,16] is correct even though at this time its validity may be questionable.[17]

This interpretation suggests that the apparent poisoning of the conversion[18] during ethylene hydrogenation arises from two sources; (a) the formation of strongly adsorbed ethylene (acetylenic complex) which renders that part of the surface inactive for hydrogen activation, and (b) the reaction of gas phase ethylene with activated hydrogen which apparently is so rapid that very little of the activated hydrogen can recombine and thereby accomplish a parahydrogen conversion. Thus, in cases like nickel where the conversion is severely poisoned,[14] it is reasonable to equate the ethylene hydrogenation rate with the hydrogen activation rate on that portion of the surface not covered with complexes. Therefore, the ratio of the rate constant for ethylene conversion to the rate constant for parahydrogen conversion on a clean surface should serve as a rough index[19] of the fraction of the surface not covered by adsorbed ethylene or its complexes.

In Table I we have listed the values of $k_e t_c$ calculated from the formula

$$wk_e t_c^0 = \frac{V_0 - C_2}{V_0} \ln \frac{C_2}{C_2 - \alpha} + \frac{\alpha}{V_0}$$

where V_0 and C_2 are the initial volumes of total reactants and hydrogen, respectively, α is the volume of ethane produced and t^0_c is the reciprocal of the entering space velocity. This equation was derived on the assumption that the reaction was first order in hydrogen pressure in a constant pressure flow system. Values of the ratio of k_e/k_p are given in the last column of Table I. It appears that the fraction of the surface covered with acetylenic complex steadily increases as hydrogen is removed from the catalyst. This fact would tend to strongly decrease the ethylene hydrogenating ability of the catalyst except for the fact that the intrinsic ability of the catalyst to activate hydrogen increased. For example, in runs 3, 4 and 8 it would appear that effectively 75% of the catalyst is inactive due to adsorbed ethylene, whereas in run 16, 96% of the catalyst is inactive. In these two sets of runs, however, the catalysts show about the same activity for ethylene hydrogenation. This presumably is due to the more efficient hydrogen activation by the catalyst in run 16.

The promoting effect of resorbed hydrogen for ethylene hydrogenation already noted in runs 12 and 13 appears to be due in part to a decrease in the amount of acetylenic complex present as evidenced by the ratio in the last column; this promotion (run 12c) is further accentuated by a simultaneous increase in the intrinsic ability of the catalyst to activate hydrogen.

Previous investigations on this catalyst have suggested that the metallic phase of the W-6 catalyst is essentially a substitutional alloy of nickel (and aluminum) with hydrogen.[5] Many of the solid state properties of alloys such as magnetic characteristics, stability of crystalline phases, etc., are to a large degree controlled by the number of electrons per unit cell rather than the type of solute atoms.[20] In view of this we will attempt to carry out our discussion of activity as a function of hydrogen content on this basis. To do so effectively we must recognize that the determined aluminum content (*i.e.* 3% by weight) was computed by difference and is subject to an error of about ±1%, whereas measurements of the aluminum content by magnetic measurements[5] ($\sim$2%) might be more accurate. If we accept the latter and use the density data reported for this catalyst in a previous paper,[5] we can compute the number of added electrons per unit cell[21] as a function of composition on the basis of an assumption that each hydrogen atom contributes one and each aluminum atom three electrons.[20] The ethylene activity as a function of added electrons per unit cell is shown in Fig. 4.

If it is indeed the number of added electrons per unit cell which is the dominant factor in determining catalytic activity, it should be interesting to compare the results of this study with those reported by Hall and Emmett[7] for copper-nickel alloys. Such a comparison is relatively simple since these authors used the microcatalytic technique at the same flow and worked in the same temperature region as used in the present work. Three points for the copper-nickel system are shown in Fig. 4 as triangles.[22]

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(14) G. H. Twigg, *Discussions Faraday Soc.*, **8**, 152 (1950).

(15) O. Beeck, *Advances in Catalysis*, **2**, 151 (1950).

(16) G. I. Jenkins and E. K. Rideal, *J. Chem. Soc.*, 2490 (1955).

(17) D. D. Eley, "Catalysis," Vol. III, Ed. P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1955.

(18) A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A146**, 630 (1934).

(19) We do not intend to suggest that this ratio should be regarded as a quantitative measure of surface coverages but rather as a gauge for comparing relative surface coverages in the series of catalysts studied. This index would be quantitatively equatable to surface coverage if the Jenkins–Rideal mechanism were true and, in addition, the rate of hydrogen absorption were rate controlling for both conversion and hydrogenation.

(20) W. Hume-Rothery, "Atomic Theory for Students of Metallurgy," Institute of Metals, London, 1946. Since this paper was submitted for publication, P. Mars, J. J. F. Scholten and P. Zwietering (private communication) have objected to the tentative conclusions in ref. 5 regarding the origin of the hydrogen evolved when Raney nickel catalysts are degassed. They have evidence that part of this hydrogen can be formed by the oxidation of residual aluminum with residual water and suggest that none of the hydrogen, outside of that adsorbed on the nickel, is specially bound, *e.g.*, alloyed with the catalyst. Since their data are not wholly consistent with those of ref. 5, the issue is still unresolved. For the purposes of the present interpretation, it makes little difference whether the evolution of hydrogen comes about due to reaction with dissolved aluminum or due to decomposition of a hydrogen-nickel alloy; in either case, there is essentially the same decrease in the number of electrons in the d-band of the alloy.

(21) N. Lipson and A. Taylor, *Proc. Roy. Soc.* (*London*), **A173**, 232 (1939).

(22) In their plot of the catalyst activity *vs.* alloy composition Hall and Emmett[7] ignored the value obtained for the catalyst containing about 15% copper. As a result the activity of the helium treated catalyst showed a monotonic decrease in activity with the concentration of copper. If this point is accepted as correct, the plot shows a minimum in the nickel rich region as indicated in our Fig. 4. Unpublished results of G. Pass and P. H. Emmett dealing with the activity of these nickel rich catalysts confirms the existence of a minimum

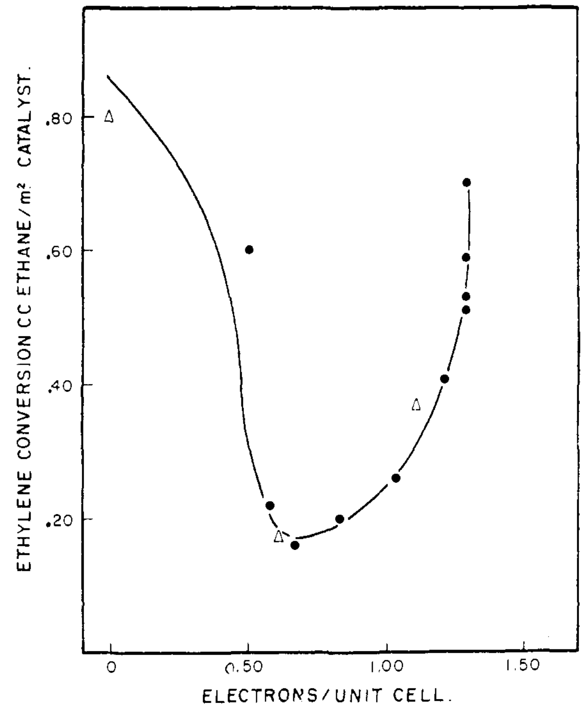

Fig. 4.—Activity of W-6 Raney nickel and copper-nickel alloys.

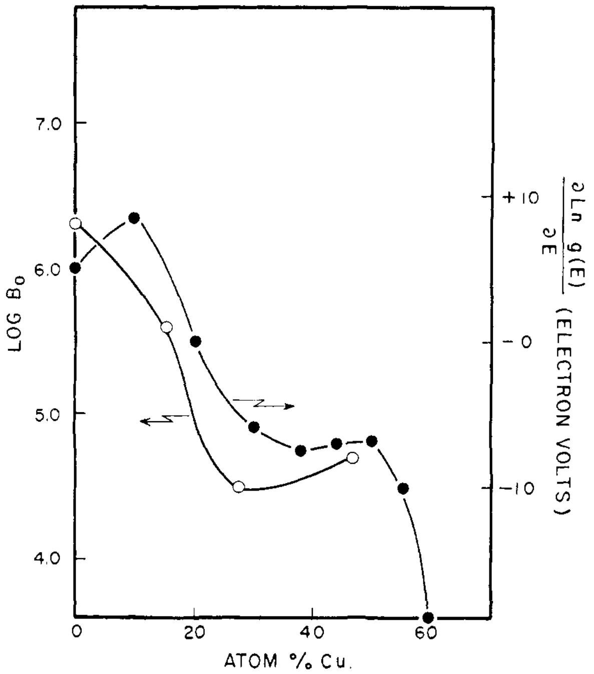

Fig. 5.—Entropy factor in ethylene hydrogenation.

When one considers that Raney nickel is a porous promoted catalyst and that only one-fifth of the surface is metallic nickel,[5] it seems clear that the quantitative agreement indicated in Fig. 4 is fortuitous. Nonetheless, in view of the qualitative agreement, it would appear that the number of added electrons per unit cell is an important factor in determining the activity of these catalysts.

Any attempt to interpret activity data of the type given here or that reported by Hall and Emmett in terms of the structure of the catalyst must be formulated on the assumption that the mechanism does not change as the number of electrons per unit cell is varied. This cannot be the case over the whole concentration range of copper-nickel alloys. The activity of nickel is first order in hydrogen pressure,[14] whereas with copper it is first order in hydrogen and inversely proportional to the pressure of ethylene.[23] Thus, interpretation of the activity data for this system would be difficult unless we restrict ourselves to the nickel-rich region where it is more likely that the former kinetic expression is operating.

Hall and Emmett[7] found that as copper was added to nickel there was no significant change in activaion energy until about 85% copper was added. Thus, the observed variations in the nickel-rich region are due to changes in the frequency factor, *i.e.*, the entropy of activation. The entropy of the electrons in the metal or alloys $\bar{S}_e$ should contribute to the entropy of activation.[24] This term is given by $(\pi k)^2 T/3\ (\partial \ln g(E)/\partial E)_{E_f}$ where $g(E)$ is the density of states in the electron band, E is the energy, k is Boltzman's constant and T is absolute temperature. The differential in the expression is evaluated at the Fermi level E_f. It seems a reasonable approximation to assume that the copper contributes electrons to the nickel without materially distorting the band structure. Thus, we can calculate this factor from the data of Fletcher[25] for the head of the d-band in nickel. In Fig. 5 we have plotted the values of the log of the frequency factor and the value of $(\partial \ln g\ (E)/\partial\ E)_{E_f}$ as a function of the atom % copper. It is quite clear that these factors parallel each other. The variation in B_0, however, is about fiftyfold whereas the variation in B_0 predicted by $(\pi k)^2\ T/3\ (\partial \ln g\ (E)/\partial E)_{E_f}$ would be about threefold since $\ln B_0 = (\Delta\bar{S} + \bar{S}_e/R)$ and the variation in $\bar{S}_e$ is small compared to $\Delta S/R$. Thus, it is apparent that while the entropy of the electrons for the pure metal alloy is a factor in the variation of B_0, either it is not the controlling factor, or the way in which it enters into the rate expression is not as simple as postulated by Dowden.[24]

In summary, the results included here are consistent with the suggestion that Raney nickel is promoted with alumina and the metallic phase is a substitutional solid solution of nickel hydrogen atoms and aluminum. It appears that an important factor in determining the activity of alloy catalysts is the number of electrons per unit cell. This is substantiated by the fact that on the basis of electrons per unit cell the activity for the copper-nickel and the nickel-hydrogen-aluminum system are similar.

Acknowledgments.—The authors wish to express their appreciation to the W. R. Grace Chemical Company for financial support of this investigation and to Leeds and Northrup for furnishing the recorder used in the chromatographic equipment.

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in the plot of activity *vs.* copper concentration. Although these later results do not agree quantitatively with the results of Hall and Emmett, they are in complete agreement qualitatively.

[23] R. N. Fease, THIS JOURNAL, **45**, 1196, 2297 (1923).

[24] D. A. Dowden, *J. Chem. Soc.*, 242 (1950).

[25] G. C. Fletcher, *Proc. Phys. Soc.* (*London*), **A65**, 192 (1952).