The Dehydrogenation of Isopropanol on Catalysts Prepared by Sodium Borohydride Reduction

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Nickel catalysts reduced with sodium borohydride have been found to be active for the liquid phase dehydrogenation of isopropanol. The activity, per unit weight of catalyst, is at least as high as that of Raney nickel. Promotion of the new catalysts with small amounts of chromium has been explained by an increase in surface area. Indeed, the activity per unit surface area of the unpromoted and promoted nickel catalysts is constant over a sevenfold range of surface area.

Recently, Brown and Schlesinger's technique (*1*) of preparing unsupported metal catalysts by means of sodium borohydride reduction has attracted considerable attention. When aqueous solutions of sodium borohydride are added to solutions of metal salts, the metals are reduced to finely divided powders. These porous powders have been shown to have high surface area, good catalytic activity, and stability. Beyond conventional catalytic applications, nickel catalysts prepared by this method are thought to hold promise as economical hydrogen-oxygen fuel cell electrodes (*2*).

The Brown technique is much simpler than the common Raney method in which approximately 50:50 alloys of the metal of interest with aluminum are prepared and the aluminum is then leached out with sodium hydroxide.

The formation of the catalyst is accompanied by the decomposition of the borohydride according to the reaction

$$BH_4^- + 2H_2O = BO_2^- + 4H_2$$

This reaction is highly exothermic [63.9 kcal./mole (*3*)] and proceeds vigorously. It is also catalyzed by the metals produced (*4*).

A number of metal salts have been reduced to the metallic state; with nickel and cobalt, boron-containing products were found. Chemical analysis (*1*, *5*) has shown that the nickel catalyst contained 7 wt. % boron, corresponding to a nickel–boron atom ratio of 2:1. Hence, it is commonly called nickel boride. In contrast to Raney nickel, the catalyst was reported to be neither pyrophoric nor ferromagnetic.

Both Soviet (*6*) and French (*7*) workers have investigated the catalyst structure by means of powder x-ray diffraction. The pattern obtained has diffuse peaks which may indicate very small basic crystallite size (of the order of 50 to 100 Å.) or an amorphous structure. Because of the diffuse nature of the peaks, the exact structure cannot be determined.

Paul et al. (*5*) appear to have been the first to investigate the catalytic activity of the nickel borides. They studied liquid phase hydrogenation of safrole, furfural, and benzonitrile at atmospheric pressure. Comparison of plots of hydrogen uptake vs. time showed the activity per gram to be as good or better than that of Raney nickel. It was discovered that the addition of small quantities of chromium, molybdenum, or tungsten salts before the reduction promoted the catalytic activity. Tverdovskii and Tupitsyn (*6*) also reported that nickel catalysts promoted with chromium were more active than the unpromoted catalysts for liquid phase hydrogenation of nitrobenzene. However, no explanation of this effect was offered in either work, and the kinetics of the hydrogenations were not studied.

Brown and Brown (*8*) in 1962 studied the liquid phase hydrogenation of a number of normal and cyclic olefins. The nickel catalyst was again found to be as active or more active on a weight basis than Raney nickel by comparison of times for reaching 50% conversion. A related study (*9*) showed that the sodium borohydride technique also produces highly active noble metal catalysts for the hydrogenation of octene-1.

In choosing a reaction for further studies of these interesting catalysts, one reasoned that liquid phase hydrogenation, at atmospheric pressure, is generally influenced by mass transfer of the reactant hydrogen. Hydrogen is only slightly soluble in common organic solvents, and its transport to the surface can easily become limiting.

From the extensive work of Jungers et al. (*10* to *12*), it appeared that the dehydrogenation of isopropyl alcohol to acetone

$$CH_3\text{—}CHOC\text{—}CH_3\ (\text{liquid}) \rightarrow$$
$$CH_3\text{—}CO\text{—}CH_3\ (\text{liquid}) + H_2\ (\text{g.})$$

might prove a clean test reaction. In these investigations, Raney nickel was used as a catalyst and at low temperature (< 100°C.) no evidence of side reactions such as dehydration was observed. At low temperatures, the reaction is thermodynamically unfavorable but may be carried out by operating in the liquid phase and continuously removing hydrogen. Here the low solubility of hydrogen is actually an advantage.

Rates may be obtained conveniently from the volume of hydrogen evolved with time. Since acetone and alcohol concentrations are stoichiometrically related to the amount of hydrogen evolved, time-consuming chemical analysis is eliminated. The rates are readily measurable at the boiling point of the alcohol, 82°C., and 1 atm. with a few grams of catalyst. These conditions permit the use of simple glass equipment. The apparatus of Jungers et al. essentially consisted of a round-bottom flask with a stir-bar and a reflux condenser in series with two gas burettes.

Jungers et al. have extensively studied the dehydrogenation of a series of secondary alcohols. They found that the reaction was strongly inhibited by the ketone products. Accordingly, the rate r was expressed in the form

$$r = \frac{k K_I (I)}{K_I (I) + K_A (A)} \qquad (1)$$

where k is a rate constant and also the rate in the absence of acetone. The concentrations of the secondary alcohol and ketone are denoted by (I) and (A), respectively, and K_I and K_A are adsorption equilibrium constants.

The rate expression was rearranged to the linearized form

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{k}\,\frac{K_A}{K_I}\,\frac{(A)}{(I)} \qquad (2)$$

which gave a good fit to the data. However, the dependence of the rate on alcohol concentration was not investigated. Pure alcohol was used and its concentration remained essentially constant during runs at low degrees of conversion.

A possible objection to this work of Jungers et al. was raised recently by Kiperman et al. (*13*), who repeated some of the Belgian studies. In experiments with propeller stirring and with shaking, they found that the reaction rate increased with agitation up to a certain intensity and then remained constant. With no mechanical agitation, the rate depended on intensity of boiling, which also provides agitation. The Soviet investigators intimated that the reaction could have been diffusion controlled under Jungers' conditions.

The present study undertook an examination of the dehydrogenation activity of nickel catalysts prepared by sodium borohydride reduction. The alcohol selected was isopropanol. It was necessary to study first the influence of mass transfer on the reaction to delineate conditions under which its influence could be eliminated. A more detailed study of the kinetics was also desirable.

EXPERIMENTAL

Fresh catalyst batches were prepared for each run or series of runs in a simple reduction apparatus shown in Figure 1.

A standard procedure was used to minimize variations in activity. Three hundred cc. of an aqueous 4 wt. % solution of nickel acetate (Matheson reagent grade) was charged to the magnetically stirred flask. The solution and flask were previously swept with nitrogen for 20 min. to remove dissolved oxygen. The reduction was accomplished by adding 120 cc. of an aqueous 10 wt. % solution of sodium borohydride over a period of 20 to 30 min. to the nickel acetate solution. Hydrogen was vigorously liberated when the black, voluminous precipitate appeared. At the end of the reaction the temperature had risen to about 50°C. and the *p*H to about 10.

Washing and handling were carried out under a flowing nitrogen atmosphere to prevent any deactivation by exposure to air. The supernatant clear liquid was decanted through the stopcock, and 200 cc. of oxygen-free distilled water was added. The catalyst was stirred for 10 min. and again allowed to settle. Three washings with water and three with isopropyl alcohol were performed in this manner. The catalysts were stored under isopropyl alcohol.

The 3:1 molar ratio of sodium borohydride to nickel acetate was used to insure complete reduction. Stirring at higher speeds, with an egg-shaped stirring bar driven by a Mag-stir mixer, gave little change in catalyst properties or activity.

Promoted catalysts were prepared by adding small aliquots of chromium chloride solution (Baker and Adamson reagent grade) to the nickel acetate solution before reduction. For 1 wt. % chromium with respect to nickel, 2.5 cc. of an aqueous solution containing 1.2 wt. % chromium were added to the standard solution. Catalysts containing 0.5 to 5 wt. % chromium were prepared.

Surface areas of the catalysts were determined by the fatty acid adsorption method of Smith and Fuzek (*14*). Adsorption isotherms of lauric acid on Raney nickel exhibited a pronounced saturation that corresponded to the formation of an oriented monolayer on the surface. The specific surface area was calculated from the amount adsorbed and the weight of sample with a cross-sectional area of 21.5 sq. Å/molecule.

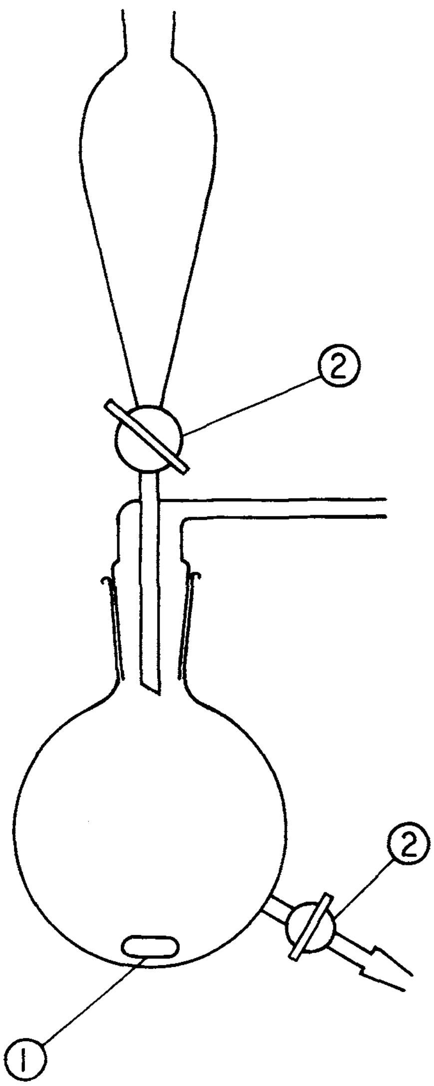

Fig. 1. Catalyst reduction apparatus. 1. Stirbar. 2. Teflon stopcocks.

The lauric acid surface area for our nickel boride catalyst was compared with the nitrogen B.E.T. surface area determined by a Perkin-Elmer Shell Sorptometer (*15*). This instrument is essentially a chromatograph in which the sample replaces the column and physically adsorbs nitrogen from a helium carrier stream. For a typical unpromoted catalyst, a value of 11.8 sq. meter/g. was obtained, which agrees well with the lauric acid result of 12.0 sq. meter/g. Smith and Fuzek also found good agreement between lauric acid and B.E.T. surface areas for Raney nickel catalysts with areas of about 50 sq. meter/g.

Average particle diameters of promoted and unpromoted catalysts were determined by optical microscopy. A 120-power microscope with a filar micrometer eyepiece (*16*) was used. The boron content of the unpromoted catalysts was determined by a standard alkali titration (*17*) in the presence of mannitol to be 7.0 wt. % in agreement with the results of Paul et al. (*5*).

The dehydrogenation apparatus is shown in Figure 2. The reaction was carried out in a Morton type of baffled glass reactor (*18*). The high-speed propeller was driven by magnetic coupling to eliminate shaft sealing problems. The propeller blades had a diameter of 3 cm. and were arranged to give an upward flow. Indented baffles prevented vortex formation. A small neck not shown was provided for a ground joint thermometer. All ground-glass joints were fitted with Teflon sleeves to prevent any poisoning from stopcock grease dissolving in the alcohol.

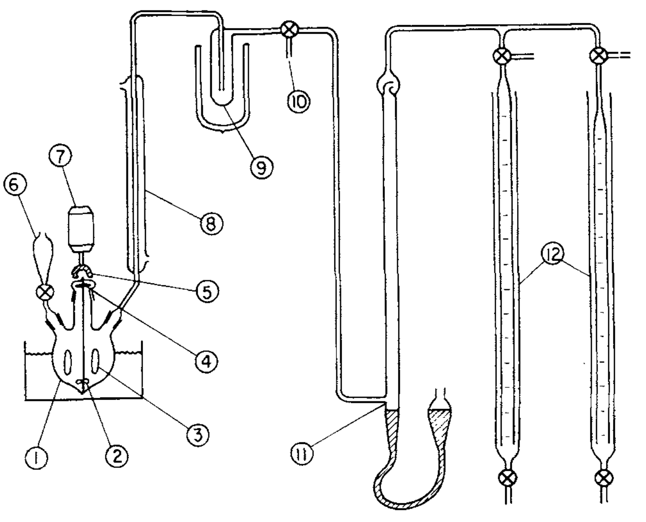

Fig. 2. Apparatus for dehydrogenation of isopropanol. *1.* Reactor. *2.* Propeller. *3.* Baffle. *4.* Glass-enclosed steel bar. *5.* Drive magnet. *6.* Addition funnel. *7.* Motor. *8.* Reflux condenser. *9,* —78°C. cold trap. *10.* To vacuum. *11.* Mercury valve. *12.* Gas burets.

A small motor, regulated by a Powerstat, drove a U-shaped Alnico 5 magnet mounted just above the cap of the flask. Constant speed was achieved by using a voltage regulator to eliminate line voltage fluctuations. After careful balancing, the propeller could be driven at speeds up to 4,000 rev./min. Propeller rev./min. was measured by a Cenco stroboscope which was periodically calibrated by means of a vibrating reed with a frequency of 3,600 min.$^{-1}$.

The reactor was submerged in a silicone oil bath heated by an immersion heater. The bath temperature was controlled by a thermostat set at 30° above the boiling point of the alcohol. The oil bath was agitated by a magnetic stir-plate beneath it which could be lowered to halt the reaction. Maintaining the alcohol at the boiling point resulted in reasonably good temperature control. During the course of a run the temperature dropped about 1° due to the increasing acetone concentration. Variation of the boiling temperature with changing atmospheric pressure was less than 0.2°C.

Hydrogen evolved in the reactor passed through the reflux condenser and a —78°C. cold trap which isolated the reactor from water and mercury vapor present downstream. The mercury valve could be raised to increase the pressure and thus raise the boiling point in the reactor. The Volmer types of hydrogen burettes had capacities of 100 and 250 cc.

The reactor was first evacuated by a mechanical pump and swept with nitrogen at atmospheric pressure for 5 min. About 200 to 250 cc. of isopropanol were added and brought to the boiling point. The reaction was started by adding the catalyst under isopropanol to the flask. The volume of hydrogen evolved was measured at 30- to 120-sec. intervals in the gas burettes. The acetone product accumulated in the flask. Runs were generally stopped after 2 liters of hydrogen were evolved (about 2% conversion). The liquid volume was then measured and the catalyst was transferred to a weighed flask. The liquid was evacuated by a mechanical pump and the catalyst weight determined.

Rates were obtained by graphical differentiation of the smooth volume-time curves. The stoichiometric relation of acetone concentration to volume of hydrogen evolved was checked at the end of a number of runs. Samples were titrated for acetone by a standard procedure (*19*) with hydroxylamine hydrochloride.

To study the effect of mass transfer under completely different hydrodynamic conditions, shaking experiments were also conducted. A horizontal cylindrical reactor, 21 cm. by 5.5 cm. I.D., was mounted on an Eberbach shaker with a 4-cm. stroke. The shaking was adjustable between frequencies of 130 and 450 min.$^{-1}$ by means of an adjustable pitch pulley.

Some runs were also made with normal alkane solvents to change the initial alcohol concentration. Matheson spectroquality *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane were used to give 25 and 50% alcohol concentrations. Since the solvents also changed the boiling point of the mixture, it was possible to examine the variation of rate parameters with temperature. The oil bath temperature was set at 20° to 30°C. above the boiling temperature to maintain an equivalent amount of refluxing.

RESULTS

One of the first observations of this study was that nickel catalysts prepared by sodium borohydride reduction are very active for isopropanol dehydrogenation. Since previous workers studied hydrogenations, this represents a new application for these catalysts.

For the early studies, a provisional rate expression similar to that used by Jungers et al. [see Equation (1)] was used.

$$r = \frac{k_w}{1 + \beta(A)} \qquad (3)$$

This expression was linearized

$$1/r = 1/k_w + 1/k_w\,\beta(A) \qquad (4)$$

and rate data were plotted as 1/*r* vs. A. Straight-line plots were obtained, the intercept of which gave the rate constant k_w, while the inhibition coefficient β (in liters/mole) was obtained from the slopes.

To study the influence of mixing and external diffusion effects, a series of runs with increasing propeller speed was performed. The effect of completely different hydrodynamics was also investigated in a series of shaking experiments with increasing frequencies. Several typical runs at different stirring and shaking intensities are shown in Figure 3. Equation (4) is seen to fit the data of individual runs well. A small random variation in the intercept giving the rate constant can be noticed. However, a marked decrease in the slope and thus in the value of β is apparent with increasing agitation. The same conclu-

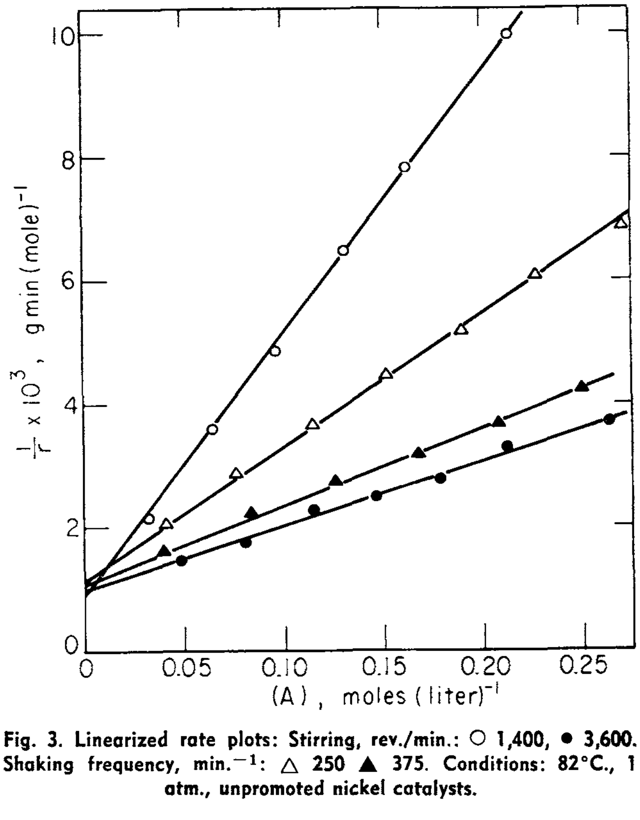

Fig. 3. Linearized rate plots: Stirring, rev./min.: ○ 1,400, ● 3,600. Shaking frequency, min.$^{-1}$: △ 250 ▲ 375. Conditions: 82°C., 1 atm., unpromoted nickel catalysts.

TABLE 1. SUMMARY OF RUNS WITH VARYING AGITATION INTENSITY

Reactors: Stirred flask or horizontal cylindrical shaker

Conditions: Initially pure isopropanol, 82°C., 1 atm.

Run	Wt. % Cr	Agitation	rev./min. or frequency, min.$^{-1}$	$k_w \times 10^3$, mole/(g.)(min.)	β, liter/mole	S, sq. meter/g.	$k_s \times 10^5$, mole/(sq. meter)(min.)
26	0	stir	2200	1.07	11.5	12	8.9
27	0	stir	2600	1.10	10.8	15	7.4
29	0	stir	1400	1.27	43	15	7.4
30	0	stir	3600	1.03	9.2	13	7.9
31	0	stir	3600	0.99	8.9	12	8.3
42	0	shake	250	0.83	15.5	11	7.6
43	0	shake	250	0.79	20	11	7.1
44	0	shake	375	0.84	8.9	11	7.6
45	0	shake	194	0.63	32	12	5.3
46	0	shake	450	0.83	8.3	11	7.8
53	3	stir	3600	6.2	9.2	85	7.2
54	3	stir	1400	5.5	15.7	85	6.5
55	3	stir	2400	5.9	11.1	85	7.0
56	3	stir	2600	6.2	9.2	85	7.3

sions were drawn from the other runs in this series and are summarized in Table 1.

For the unpromoted catalysts, a striking increase in β is evident at lower intensities. Below 2,000 rev./min. or 250 min.$^{-1}$, the alcohol-catalyst mixture appeared transparent with scattered lumps of suspended catalyst and appreciable clumping on the bottom of the reactor.

A catalyst promoted with 3 wt. % chromium was then run. This catalyst had an average particle diameter of 50 μ, almost three times smaller than that of the unpromoted catalyst, namely, 145 μ. This catalyst was found to be much easier to suspend at low propeller speed, and the increase in β was much less pronounced as shown in Table 1. At high agitation, complete dispersion was achieved for both catalysts and the solution appeared uniformly opaque. The same limiting value of β was approached at higher speeds, and all further experiments were performed at a rate of agitation sufficient to yield these limiting values of β.

The promotion effect of small amounts of chromium on the catalyst activity was then investigated. The information obtained is summarized in Table 2.

A large increase in k_w, the rate constant per gram, was observed with increasing small amounts of chromium (see Table 2). The inhibition coefficient remained essentially constant at a value of 8.6 ± 0.6 liter/mole. The large increase in activity is particularly interesting, since chromium alone was reduced to a colloidal green material which was inactive.

TABLE 2. SUMMARY OF RUNS WITH PROMOTED AND UNPROMOTED CATALYSTS AT HIGH STIRRER SPEED

Conditions: 3,600 rev./min., 82°C, 1 atm.

Run	Wt. % Cr	$k_w \times 10^3$, mole/(g.) (min.)	β, liter/ mole	S, sq. meter/g.	$k_s \times 10^5$, mole/(sq. meter)(min.)
30	0	1.03	9.2	13	7.9
31	0	0.99	8.9	12	8.3
33	2	6.0	8.3	73	8.3
35	1	5.2	7.8	63	8.2
47	0	1.1	8.6	—	—
50	0.5	1.9	8.3	26	7.3
51	0.5	2.2	8.0	26	8.4
53	3	6.2	9.3	85	7.2
63	5	6.8	8.5	116	5.9
65	1	4.9	8.5	61	8.0
66	4	6.5	8.9	104	6.2
67*	1	5.1	8.6	—	—
68*	2	6.2	9.3	83	7.5

* Reduced under more intense agitation conditions.

Lauric acid surface areas S are collected in Table 2 vs. the amount of chromium in the catalyst. It is striking that the surface area increased tenfold over the small range of chromium addition. These surface areas are much larger than could be accounted for by the external area of the particles. Thus the catalysts are highly porous with large internal surface area. This conclusion is also supported by the low apparent catalyst densities of 1.1 g./cc. for an unpromoted catalyst and 0.74 g./cc. for a catalyst with 4 wt. % chromium. No change in surface area during a run was found.

The rate constant per unit weight k_w, shown in Table 2, remained directly proportional to surface area over most of the range. The rate constant per unit surface area k_s, also shown in Table 2, is seen to remain approximately constant over the tenfold change in surface area.

Since the runs previously described were carried out in pure alcohol to 2% conversion, the alcohol concentration remained essentially constant. To investigate whether the rate constant depended on alcohol concentration, runs were also made in which the initial alcohol concentration was lowered by using normal alkane solvents. The work of Kiperman et al. (20) showed that these solvents have negligible adsorption on nickel in this temperature range and should not interfere with the reaction. Since the solvent in most cases changed the boiling temperature, information was also obtained on the temperature dependence of the rate expression parameters. The concentrations, temperatures, and rate parameters from these runs are given in Table 3.

An Arrhenius plot is shown in Figure 4 for the rate constant k_s obtained at different alcohol concentrations. The activation energy is 20.5 kcal./mole and the pre-exponential factor is 2.8×10^8 mole/(sq. meter) (min.).

A van't Hoff plot for the inhibition coefficient is also shown in Figure 4 for the values of β obtained in pure alcohol, as well as for those obtained in solvents with varying concentrations.

Finally, it should be noted that in a number of runs the initial rates were somewhat higher than k_w [see Equation (3)], which is an extrapolated initial rate. This deviation is believed to be due to an initial poisoning of more active sites. An initial deactivation was also observed in one of Kiperman's runs in which the acetone

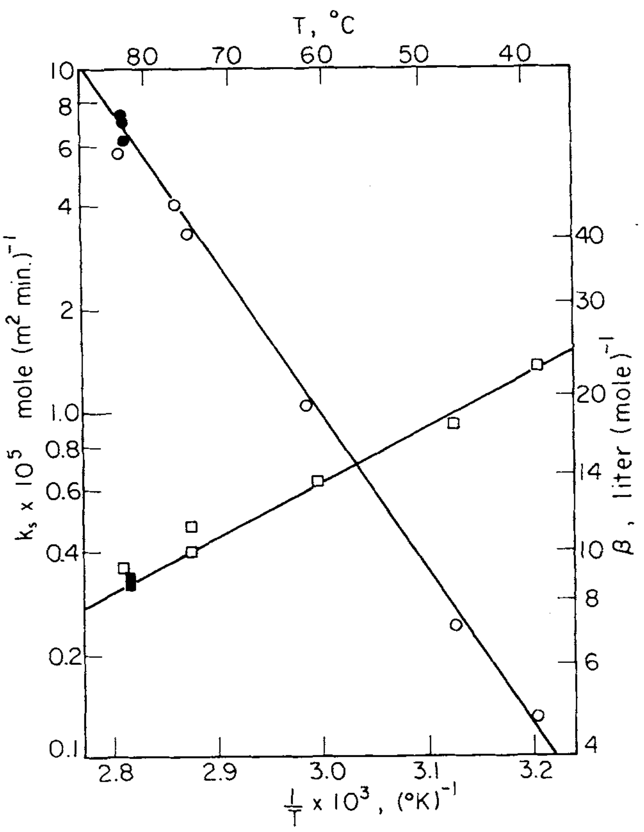

Fig. 4. Variation of rare parameters with temperature. Circles, rate constant. Squares, inhibition coefficient. Filled symbols, runs with initially pure alcohol. Closed symbols, runs with varying alcohol concentration in normal alkane solvents (see Table 3).

product was continuously removed. After an initial drop, the rate remained constant thereafter.

DISCUSSION

The promotion by chromium of nickel catalysts reduced with sodium borohydride previously was an unexplained phenomenon. The present work shows that the addition of chromium greatly increases the surface area of the catalyst. For both promoted and unpromoted nickel catalysts, the rate constant per gram was found to be directly proportional to the area per gram over a large range. It appears that chromium acts as an unusual type of structural promoter, simply increasing the specific area of the active nickel component. For amounts of chromium greater than 3 wt. %, it is believed that the inactive chromium in some oxidation state may start to gather at the surface. This would lead to the deviations observed in Table 2 at high amounts of chromium.

The finding of direct proportionality of activity to surface area is not only interesting in itself, but it also provides strong evidence against the importance of mass transfer limitations under the conditions of high agitation intensity used in this work. Indeed, both the rate constant per unit surface area and the inhibition coefficient remained essentially constant over a sevenfold variation in specific surface area. It seems highly unlikely that this constancy of both parameters could be achieved if internal and external diffusion limitations were occurring under these conditions.

In the study of Kiperman et al. (*13, 20*), the reaction on Raney nickel was investigated at high agitation intensity, and the results were also interpreted to be in the kinetic regime. Hindrance from internal diffusion effects was deemed insignificant, because essentially the same rates per unit surface area were found (*21*) on 3 μ particles, fifty times smaller than their standard Raney nickel. Their reported values of 3.1 to 3.8 cc. hydrogen/(sq. meter) (min.) are surprisingly close to the values we find for nickel boride catalysts. Our rate constant k_s converted to their units is 2.0 to 2.5.

However, it appears from Figure 3 that at conditions of low agitation intensity, diffusion limitations are present which require explanation. One consideration in the choice of the test reaction was the belief that it should be free from hydrogen mass transfer limitations frequently encountered when hydrogen is a reactant. That this condition is satisfied is easily shown by comparison of the rate of alcohol dehydrogenation with the rate of hydrogen evolution during the catalyst preparation. In the catalyst reduction, even at moderate temperatures and mild stirring conditions, the rates of evolution per gram were three to four times higher than the maximum rates found for isopropanol dehydrogenation. Hence, hydrogen mass transfer should not be responsible for the observed rate limitations at low agitation conditions, and acetone or alcohol may be the offenders in mass transfer.

Agglomeration of suspended particles and clumping on the bottom were observed at low agitation intensities. Harriott (22), in a study of mixing intensity and mass transfer to fine acid exchange beads, found that a sharp decrease in the external mass transfer coefficient resulted when clumping was first observed on the bottom. The critical intensity at which this occurs depends on the particular mixer geometry, but the effect on the mass transfer coefficient should be similar in our case.

As a result of agglomeration and clumping, internal (and to a certain extent external) diffusion limitations develop which reduce the rate except at zero time when the concentration gradients have not yet arisen. It is an interesting but unexplained observation that the form of the rate expression is maintained under diffusion-influenced conditions, as shown by the good fit of the data at low agitation in Figure 3. Because transport processes have their primary effect on β, the rate expression used in this work is a versatile tool for diagnosing the activity of metal catalysts. The sequence of steps leading to such a rate expression will now be discussed.

Comparison of initial rates and inhibition behavior indicates close similarity between nickel boride and the Raney nickel catalysts used by the Belgian and Russian workers. For two different Raney nickel catalysts, Jungers et al. found initial rates of 6.1 and 9.2 × 10^{-4} mole/(g.) (min.) (*12*). Our value on unpromoted nickel catalysts is 1.0 × 10^{-3} mole/(g.)(min.). The surface area of Jungers' catalysts was not reported, so comparison on a per unit surface area basis is precluded. By comparing Equations (2) and (4) we estimate that the ratios of adsorption equilibrium constants obtained by his group correspond to inhibition coefficients β of about 10 and 16 liters/mole. These values may be somewhat high compared to ours because of diffusion limitations. Kiperman's data show similar inhibition as well as initial rates per unit area that are very close to ours. Accordingly, other studies performed on nickel, which are of interest in establishing the sequence of elementary steps, may reasonably be applicable for our catalysts.

Kemball and Stoddart (*23, 24*) studied the deuteration and exchange of acetone on evaporated nickel films at 0°C. and analyzed the products with an adjoining mass spectrometer. They found that the primary act of deuteration involves simply the addition of two deuterium atoms to the carbonyl group of the acetone molecule. From the initial distribution of deuterium in the exchanged molecules, it was inferred that multiple exchange occurs primarily in one methyl group rather than in both. The exchange results indicated a long residence time for acetone with strong adsorption via opening of the double bond. The acetone, although strongly adsorbed, will not cover the surface completely because of steric blocking of sites surrounding each molecule. The vacant sites between the molecules are thus available for adsorption of hydrogen atoms. We will accordingly assume that the hydrogen atoms will not compete with acetone for sites.

Kemball et al. also investigated the deuterium exchange of isopropanol on nickel films at 0°C. and below. It was concluded that exchange of the hydroxyl hydrogen atom occurred instantaneously on nickel films above −23°C. The rate of secondary hydrogen exchange occurred much more rapidly than that of hydrogen in the methyl groups. These exchange experiments suggest that dissociative chemisorption of the alcohol is involved.

The work on deuteration and exchange is compatible with the following sequence of elementary steps which is essentially that proposed by Kemball et al.:

$$S + I_p \rightleftarrows I_a + H_a \qquad (1)$$

$$I_a \rightleftarrows A_a + H_a \qquad (2)$$

$$A_a \rightleftarrows A + S \qquad (3)$$

$$2H_a \rightleftarrows H_2 \qquad (4)$$

In the first step, an alcohol molecule I_p, in a physically adsorbed layer, chemisorbs on a site S which is unoccupied by chemisorbed species (subscript a). This step is assumed to occur with dissociation of the hydrogen atom from the secondary carbon of the molecule. The second step is then dissociation of the hydroxyl hydrogen atom to yield an adsorbed acetone molecule A_a. The latter desorbs into the liquid phase in step 3. The final step is desorption of molecular hydrogen.

It should be realized that this is not the only path by which the reaction can take place. Newham and Burwell (*25*) have indicated that the above scheme taken alone was not sufficient to explain their results for racemization of optically active 2-butanol-2-*d* on copper catalysts at 135° and 155°C. A parallel path involving a symmetrically adsorbed acetone molecule may be important for racemization.

If adsorption of acetone were rate determining in the work of Kemball et al., the deuteration of acetone should proceed at a slower rate than the exchange of the secondary hydrogen atom in isopropanol, a process which would occur by step 1 followed by its reverse. But it was found that the rates of the two processes were closely comparable and that they had roughly the same activation energy. This suggested that the rate-determining step for each process was the same, namely, the addition of a deuterium atom to the secondary carbon atom. Hence, we assume that step 1 is the rate-determining step in this sequence.

The remaining steps are assumed to be in quasiequilibrium. For step 4 there is independent evidence in support of this view in the work of Hartog et al. (*26*). They found the hydrogen-deuterium exchange reaction on Raney nickel was too rapid to measure at room temperature and were forced to work in the range −80° to −20°C.

We write, in particular, for a uniform surface

$$(A_a) = K_3(A)(S) \qquad (5)$$

where K_3 is the equilibrium constant for adsorption of acetone. The surface coverage by chemisorbed alcohol I_a is assumed to be small in comparison to that by the strongly adsorbed acetone A_a. With this approximation (L), the total concentration of surface sites, is given by

$$(L) \approx (S) + (A_a) = (S) + K_3(A)(S) \qquad (6)$$

and solving for (S)

$$(S) = \frac{(L)}{1 + K_3(A)} \qquad (7)$$

At the steady state, the reaction rate r is given by the rate of the first step

$$r = r_1 = k_1(I_p)(S) \qquad (8)$$

In the present case, the reverse reaction can be neglected due to the low hydrogen pressure above the boiling liquid and the low acetone concentration. Substituting Equation (7) into (8), we obtain

$$r = \frac{k_1(L)(I_p)}{1 + K_3(A)} \qquad (9)$$

The unknown value of (L) can be absorbed into the rate constant k_1 without loss of generality. This is also true for (I_p), as can be shown by the following argument.

Kiperman et al. (*20*) performed experiments to determine the adsorption of iso-octane on Raney nickel. One gram of catalyst was placed in an ampoule suspended on a sensitive spring and immersed in 90 cc. of iso-octane. The solvent was brought to 93°C. and 1 cc. of isopropanol was added. A weight increase of 44 mg. was found, which is equivalent to 4.4×10^{20} molecules taken up. Using their surface area of 34 sq. meter/g. and a site density of 1.5×10^{15}/sq. cm., we estimate that 5×10^{20} sites were available. The molecular weight of iso-octane is twice that of alcohol. If iso-octane were adsorbed initially and the alcohol replaced it, a negative weight change would be expected. Thus Kiperman et al. concluded that the iso-octane solvent is not appreciably adsorbed on Raney nickel under the conditions also used in our work.

It seems reasonable to assume that isopropanol will be preferentially adsorbed from mixtures of alcohol and alkanes. Thus the mole fraction of alcohol in the physically adsorbed layer adjacent to the surface will remain near 1, irrespective of its concentration in the solutions used in the present work. Hence the concentration (I_p) can be taken as a constant and be absorbed into the rate constant k_1. The rate expression simplifies to

$$r = \frac{k_1}{1 + K_3(A)} \qquad (10)$$

This rate expression is identical to Equation (3) used in this work and quite similar to Equation (1), which can be rearranged to the form

$$r = \frac{k}{1 + \dfrac{K_A(A)}{K_I(I)}} \qquad (11)$$

In some experiments of Jungers et al. initially pure alcohol was used, and the boiling temperature was raised by increasing the pressure. During the course of the runs, the alcohol concentration remained essentially constant. Therefore, in their work, Jungers et al. could have used our rate expression, Equation (10). But the reverse does not appear to be true.

Indeed, in our experiments in which the alcohol concentration was varied, the ratio K_A/K_I of Equation (11) appeared to be concentration dependent and did not vary exponentially with temperature as seen in Table 3. For example, with pure alcohol at 82°C., a ratio K_A/K_I of 113 was found, while in 40% alcohol in *n*-octane at 83°C. a ratio of 49 was obtained. It is possible that if good activity coefficients were available to correct concentrations to activities, more meaningful values of K_A/K_I might be obtained. As it stands, our constant K_3 was well behaved as shown in Figure 4. It may be noted at this point that

TABLE 3. SUMMARY OF RUNS WITH NORMAL ALKANE SOLVENTS

Conditions: Nickel + 2 wt. % chromium catalysts, 3,600 rev./min., 1 atm.

Run	Solvent	T, °C.	(I), mole/liter	$k_w \times 10^3$, mole/(g.) (min.)	S, sq. meter/g.	$k_s \times 10^5$, mole/ (sq. meter) (min.)	β, liter/mole	K_A/K_I
68	None	82	12.2	6.2	84	7.3	9.0	110
69	Heptane	76	4.9	3.9	84	4.0	11.6	57
70	Octane	83	5.5	3.4	59	5.7	9.3	51
76	None	82	12.2	4.8	79	6.1	8.8	118
77	Pentane	39	6.4	0.11	79	0.13	22.6	115
78	Hexane	62	6.3	0.80	79	0.80	13.5	75
79	Heptane	75	6.1	2.6	79	3.3	9.8	61
82	None	82	12.2	5.7	80	7.1	9.2	112
83	Pentane and hexane*	47	3.1	0.19	80	0.24	17	53

* Equimolar mixture.

acetone can be treated as a solute with an activity coefficient of unity since the acetone concentration remained low enough in this work and in that of Jungers et al. so that no correction for nonideality appears necessary.

Rate expression *(10)* is based on a postulated rate-determining step that also accounts for the deuteration and exchange studies which have become available since the work of Jungers et al.

The activation energy of 20.5 kcal./mole for the rate constant k_1 on our catalysts over a 43°C. range compares with the value of 17.5 kcal./mole found by Jungers over a 15°C. range. The pre-exponential factor, in units of molecules/(sq.cm.)(sec.), is 3.2×10^{27}. From transition state theory, an order-of-magnitude estimate for the pre-exponential factor with an entropy of activation of zero is given by

$$\frac{kT}{h}(L) = (10^{13})(10^{15}) = 10^{28} \text{ molecules/(sq.cm.)(sec.)}$$

where k is the Boltzmann constant, h is Planck's constant, and (L) is an upper estimate of the site density on nickel, on the assumption that every surface site is active.

In examining the validity of adsorption equilibrium constants, researchers have often been satisfied if the heat of adsorption q is positive (or ΔH_a° is negative, since $q = -\Delta H_a^\circ$). From the van't Hoff plot in Figure 4, a heat of adsorption $q = +5.0$ kcal./mole was found, which satisfies this criterion.

Standard entropy changes ΔS_a° for adsorption are seldom examined. Everett *(27)* has given a statistical thermodynamic derivation of the Langmuir adsorption isotherm for gases with the usual assumptions of localized adsorption on equivalent sites and a constant heat of adsorption. He showed that $\Delta S_a^\circ = S_a^\circ - S_g^\circ$, where S_g°, the standard entropy of the gas, is referred to the unit pressure used, and S_a°, the entropy of the adsorbed molecule, is equal to the thermal entropy of vibration and rotation of the adsorbed molecule. S_a° is referred to surface coverage $\theta = 1/2$ and thus does not include configurational entropy. At least for nondissociative adsorption, S_a° will be less than S_g°, since S_g° includes translational entropy in addition to entropy for internal modes. Hence, for nondissociative adsorption, ΔS_a° should be negative.

This criterion is also applicable for adsorption from the liquid phase. Following Everett's derivation, standard states of 1 mole/liter for acetone in the liquid phase and surface coverage of $\theta = 1/2$ for adsorbed acetone are required in our case. The entropy change between these standard states is related to the standard enthalpy change by the expression:

$$\ln K_3 = \frac{\Delta S_a^\circ}{R} - \frac{\Delta H_a^\circ}{RT} \tag{12}$$

An entropy change of −10.0 cal./(mole)(°C.) is found which satisfies the criterion of a negative entropy change.

A more quantitative check was desired, however, and was found in a correlation between standard entropy and enthalpy changes for physical adsorption as advanced by Everett *(28)*. Everett compiled these changes for a wide variety of compounds on charcoal for adsorption in a monolayer or less. A linear relation was reported

$$\Delta S_a^\circ = -25.5 + 0.0014\,\Delta H_a^\circ \tag{13}$$

in which ΔS_a° at 25°C. is given in cal./(mole)(°C.) and referred to standard states of gas at 1 torr and surface coverage $\theta = 1/2$. The standard enthalpy change was expressed in cal./mole.

The reasoning behind this relationship is that a molecule with a higher heat of adsorption will be bound more tightly and hence be more restricted. This leads to a smaller entropy of the adsorbed molecule and thus a larger entropy change. We believe that this correlation should also be valid for the standard entropy and enthalpy of adsorption equilibrium constants obtained from kinetic studies at similar temperatures. While Everett's relation, Equation (13), was derived for physisorption, it is not unreasonable to expect it to hold for chemisorption, provided that adsorption takes place without dissociation.

Referred to Everett's standard states, our entropy and enthalpy changes are, respectively, −40 cal./(mole)(°C.) and −12.1 kcal./mole (see Appendix). Everett's correlation predicts an entropy change of −42.7 cal./(mole)(°C.) for $\Delta H_a^\circ = -12{,}100$ cal./mole. This agreement of the experimental entropy change with his correlation gives us some confidence in interpreting the limiting value of β as an adsorption equilibrium constant and not just an empirical fitting parameter. Furthermore, this means of examining the validity of adsorption equilibrium constants should serve as a tool for other investigators if further work confirms this usefulness.

Assuming moderate coverage by acetone and that desorption of acetone is rate determining, Kiperman et al. *(20)* derived another rate expression for dehydrogenation on a nonuniform surface. But, they did not analyze their data or those of Jungers et al. in terms of that rate expression. As noted above, desorption of acetone does not seem to be rate determining in the extensive work of Kemball et al.

In conclusion, we have shown that liquid phase dehydrogenation of isopropanol can be used readily for characterizing catalyst activity. Reduction by sodium borohydride produces active catalysts for this reaction. The activity of these unsupported catalysts, promoted or unpromoted, is proportional to their surface areas. Finally, these studies provide a basis for applying the reaction to other transition metals in order to investigate further the theoretical foundations of catalyst specificity.

ACKNOWLEDGMENT

This work was supported by National Science Foundation Grant GP-2305.

NOTATION

h = Planck's constant, 6.62×10^{-27}, erg/sec.
k = Boltzmann's constant, 1.38×10^{-16} erg/°K.
k = rate constant
k_s = rate constant per unit surface, g.-mole/(sq. meter) (min.)
k_w = rate constant per unit weight, g.-mole/(g.) (min.)
K = adsorption equilibrium constant, liter/g.-mole
L = total number of sites
(M) = concentration (surface or bulk) of species M
q = heat of adsorption
r = reaction rate, g.-mole/(g.) (min.)
R = gas constant, 1.98 g.-cal/(g.-mole) (°C.)
S = number of free sites
S = specific surface area, sq. meter/g.
T = temperature, °K. or °C.
x = mole fraction
ΔH = enthalpy change, g.-cal./g.-mole
ΔS = entropy change, g.-cal./(g.-mole) (°C.)
β = inhibition constant, liter/g.-mole

Superscript

o = standard

Subscripts

a = chemisorbed
f = final
g = gas
i = initial
p = physisorbed
A = acetone
I = isopropyl alcohol

LITERATURE CITED

1. Schlesinger, H. I., and H. C. Brown, U. S. Patent 2,461,661 (January 9, 1945).
2. Jasinski, R. J., *Advan. Chem. Ser.*, **47**, 95 (1965).
3. Davis, W. D., L. S. Mason, and G. Stegeman, *J. Am. Chem. Soc.*, **71**, 2775 (1949).
4. Brown, H. C., and C. A. Brown, *ibid.*, **84**, 1493 (1962).
5. Paul, R., and P. Buisson, and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952).
6. Tverdovskii, I. P., and I. F. Tupitsyn, *Akad. Nauk SSSR, Inst. Fiz. Khim., Soveshsch. Moscow*, **9**, 86 (1956).
7. Thonnart, P., P. Lenfant, and C. Legras, *Compt. Rend.*, **258**, (1964).
8. Brown, H. C., and C. A. Brown, *J. Am. Chem. Soc.*, **85**, 1003 (1963).
9. *Ibid.*, **84**, 2827 (1962).
10. Thonon, C., and J. C. Jungers, *Bull. Soc. Chim. Belges*, **58**, 331 (1949).
11. *Ibid.*, **59**, 604 (1950).
12. Claes, F., and J. C. Jungers, *Bull. Soc. Chim. France*, Ser. 5, **25**, 1167 (1958).
13. Davydova, I. R., S. L. Kiperman, and N. V. Nikolaeva, *Kinetika i Kataliz*, **4**, 605 (1963).
14. Smith, H. A., and J. F. Fuzek, *J. Am. Chem. Soc.*, **68**, 229 (1946).
15. Nelsen, F. M., and F. T. Eggertsen, *Anal. Chem.*, **30**, 1387 (1958).
16. Orr, C., Jr. and J. M. Dallavalle, "Fine Particle Measurement," p. 14, Macmillan, New York (1959).
17. Scott, W. W., "Standard Methods of Chemical Analysis," N. H. Furman, ed., 5 ed., Vol. I, p. 168, Van Nostrand, New York (1939).
18. Morton, A. A., *Ind. Eng. Chem., Anal. Ed.*, **11**, 170 (1939).
19. Bryant, W. M. D., and D. M. Smith, *J. Am. Chem. Soc.*, **57**, 57 (1935).
20. Kiperman, S. L., N. V. Nikolaeva, and I. R. Davydova, *Kinetika i Kataliz*, **4**, 723 (1963).
21. Kiperman, S. L., A. A. Balandin, and I. R. Davydova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, No. 12, 1482 (1957).
22. Harriott, Peter, *A.I.Ch.E. J.*, **8**, 93 (1962).
23. Stoddart, C. T. H., and C. Kemball, *J. Colloid Sci.*, **11**, 532 (1956).
24. Kemball, C., and C. T. H. Stoddart, *Proc. Roy. Soc. (London)*, **A241**, 208 (1957).
25. Newham, J., and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **86**, 1180 (1964).
26. Hartog, F., J. H. Tebben, and P. Zwietering, "Actes Deuxième Congr. Int. de Catalyse," p. 1229, Editions Technip, Paris (1961).
27. Everett, D. H., *Trans. Faraday Soc.*, **46**, 945 (1950).
28. *Ibid.*, 963.
29. Schumann, S. C., and J. G. Aston, *J. Chem. Phys.*, **6**, 485 (1938).
30. Black, C., *Ind. Eng. Chem.*, **51**, 211 (1959). The Van Laar constants are on p. 19 of the complete manuscript, available from *Ind. Eng. Chem.*

APPENDIX. THERMODYNAMIC CALCULATIONS

The standard entropy change for acetone adsorption calculated from Equation (12) was referred to a standard state of acetone at a concentration of 1 mole/liter and to surface coverage of one half. To convert the standard entropy change to a standard state of 1 torr pressure, we consider a three-step process. This process is conveniently carried out at 56°C., which is the boiling point of acetone and is close to the midpoint of the temperature range used.

The entropy change for the first step, converting from 1 mole/liter ($x_i = 0.0775$) to pure acetone ($x_f = 1.00$), is given by the partial molar entropy of mixing

$$\Delta S_{\mathrm{mix}} = -R \ln \frac{x_f}{x_i} = -4.57 \log \frac{1}{0.0775} = -5.07 \frac{\text{cal.}}{(\text{mole})(\text{deg.})}$$

The effect of liquid phase nonideality is neglected but will be considered below.

The second step is vaporization of acetone at atmospheric pressure with an entropy change of +21.55 cal./(mole)(°C) (*29*). The final step is isothermal expansion from 760 torr to 1 torr. With the neglection of vapor phase nonideality, the entropy change is

$$\Delta S_{\mathrm{expan}} = -R \ln \frac{p_f}{p_i} = -4.57\,\mathrm{lo}\sigma \frac{1}{760} = +13.2 \frac{\text{cal.}}{(\text{mole})(^\circ\text{C})}$$

The entropy change of adsorption referred to a standard state of acetone at 1 torr is then given by

$$\Delta S^{o}_{a,\,1\ \mathrm{torr}} = \Delta S^{o}_{a,\,\frac{1\ \mathrm{mole}}{\mathrm{liter}}} - \Delta S_{\mathrm{mix}} - \Delta S_{\mathrm{vap}} - \Delta S_{\mathrm{expan}}$$

$$= 10.0 + 5.1 - 21.6 - 13.2$$

$$= -39.7 \text{ cal./(mole)(°C)}$$

Calculations which took into account the effect of liquid phase nonideality on ΔS_{mix} were also made. Activity coefficients were calculated with the Van Laar constants given by Black (*30*). The value for ΔS_{mix} obtained was −4.20

cal./(mole)(°C). This only slightly raises the value of $\Delta S_a{}^\circ$ to -40.6 cal./(mole)(°C).

The standard enthalpy of adsorption can be converted to the reference state of 1 torr by going through a similar three-step process. Neglecting liquid and gas phase nonideality, one must consider only the enthalpy of vaporization $+7.09$ kcal./mole (*29*). Hence, the standard enthalpy change becomes

$$\Delta H_{a,\,1\,\text{torr}} = \Delta H_{a,\,\frac{1\,\text{mole}}{\text{liter}}} - \Delta H_{\text{vap}} = -5{,}000 - 7{,}100$$

$$= -12{,}100\ \text{cal./mole}$$

Manuscript received July 22, 1965; revision received September 24, 1965; paper accepted September 27, 1965.

Accessibility of Surface to Gases Diffusing Inside Macroporous Media

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A method for measuring flow porosity with values from 35 to 100% of the open porosity measured is described. The accuracy of electrical conductivity measurements to obtain net diffusibilities was verified for media containing at least 75% of pore volume with radii greater than five mean free paths. It is pointed out that long dead-end pores feeding into larger diameter flow pores can contribute to the effective diffusion coefficient inside porous media, and methods of estimating their length and maximum possible contribution to diffusion are described.

The purpose of this work was to develop new techniques of predicting the accessibility of catalyst surface inside macroporous catalysts to diffusing gases. Internal diffusion rates retard many chemical reaction processes that use porous catalysts (*1*), and they can also strongly affect the product composition (*2*). The amount of retardation is expressed by the effectiveness factor, the ratio between the actual rate of a chemical reaction on a heterogeneous catalyst and the rate one would obtain if diffusional effects within the pellet did not retard the reaction. It is a function of a modulus m_T (*3*).

$$m_T = \frac{D_p}{2}\sqrt{\frac{k}{D_{eff}}} \tag{1}$$

D_p and k can be measured directly, but no methods of measuring D_{eff} which take into account the presence of dead-end pores have been previously described. In this work, a method of estimating limiting values of D_{eff} based on porosity, porosimeter, and either electrical conductivity or gas diffusion measurements is proposed. Once m_T has been calculated from D_{eff}, D_p, and k, the effectiveness factor can be read graphically (*1*).

Wheeler (*2*) pictured porous media as being "piles of boulders between which the continuous, interconnecting pores of irregular cross section run in random direction." Based upon this model, diffusion of two gases in opposite directions *through* a porous medium, herein known as net diffusion, is slower than that which would occur in free space because: diffusion occurs at a noticeable rate only through the pores, not through the solid; some of the pores are dead-end; the pores have constrictions and irregularities in them which retard diffusion; and the pores do not go straight through the medium, increasing the distance that the gases must diffuse. The increased distance for diffusion due to randomness of pore direction has been estimated as being 1.41 times the medium thickness (*2*).

Pores can be classified according to their accessibility. Pore spaces having at least one passage to the exterior are called open pores. Those with only one passage are known as dead-end pores; pores with more than one passage are called flow pores. Only the flow pores are active in electrical conduction (pores filled by conducting liquid) or in simple diffusion of nonreacting gases; how-

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