[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

The Surface Area and Catalytic Activity of Aluminum Oxide[1]

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The ability of a solid catalyst to promote a gaseous reaction depends upon the amount of surface which the solid possesses as well as upon the specific activity of the surface. Methods of surface area measurement, such as that based on the theory of Brunauer, Emmett and Teller,[3] afford a means of distinguishing between changes in quality and in extent of a catalyst surface. Aluminum oxide is known to undergo changes on thermal treatment, and the purpose of this investigation was the determination of how the resulting variations in its effectiveness as a catalyst for the dehydration of ethanol are related to the two aspects of surface alteration.

Experimental

Alumina catalysts were prepared from $^8/_{14}$ mesh Alorco Activated Alumina by heating at temperatures between 500 and 1000°, both in vacuum and in the presence of water vapor. Surface areas of the catalysts before use were measured by the BET method using nitrogen,[3] following outgassing of the samples at 400°.

The catalytic reaction was carried out at 350 and 400° in an electrically heated, vertical tube, of 25 mm. inside diameter. The 200-proof ethanol was pumped at constant rate into an electrically heated evaporator and then passed as vapor into the reactor. The upper part of the reactor tube contained a preheater section packed with quartz chips and provided with manual temperature control; the middle section of the tube contained the catalyst bed of 49 cc. volume, and the temperature of this part was controlled to about ±1° by means of a Micromax potentiometer controller. The liquid products of the reaction were condensed in receivers cooled in ice and in dry ice and were analyzed by distillation. The uncondensed gas was measured in a wet-test meter and analyzed for ethylene by absorption in $HgSO_4$-H_2SO_4 solution.[4] Before the reaction was begun the catalyst tube was brought up to temperature under vacuum and then filled with nitrogen; the first portion of the products was discarded while the system was reaching a steady state.

Results and Discussion

Surface Areas.—Catalysts prepared by evacuation at 600 to 900° show an approximately linear decrease of area with increasing temperature (Table I). The areas of aluminas treated with water vapor are always lower than are those of the aluminas vacuum-treated at corresponding temperatures; the magnitude of the difference depends somewhat upon the pressure of water vapor as well as upon the duration of vapor treatment.

All materials prepared by heating at temperatures between 500 and 900°, either in vacuum or in the presence of water vapor, were shown by X-ray diffraction powder photographs to consist of gamma alumina. Increasing treatment temperature, as well as the presence of water, caused the sharpening of the gamma alumina lines, indicating growth of the crystallites composing the solid. A parallel increase in particle size[5] would, of course, explain the reduction in area. Between 900 and 1000° a sharp decrease in area was found as the result of both methods of treatment; the diffraction patterns indicated that the 1000° samples had been partially converted to corundum.

The surface area values here cited may be compared with the measurements made earlier in this laboratory on portions of the same large quantity of alumina.[6] For samples outgassed between 400 and 500°, the present area values are about 15% larger than the previous results, while areas of samples evacuated at 600° and above are closely coincident in the two sets of measurements. We interpret these facts as evidence that interaction with water took place during the intervening period in a manner so that removal of water by heating disrupted the crystal; this effect was eliminated by higher evacuation temperatures at which crystallite growth and sintering occurred, and where, in the absence of water vapor, the area is a function of temperature of preparation only.

Changes of Catalyst Activity with Use.—Runs employing one catalyst under similar conditions in general gave results which were in satisfactory agreement; ethylene conversion at a reaction temperature of 400° was reproducible within 3%. For certain catalysts, however, there was a consistent trend in activity with use for the first few runs: catalysts heated in vacuum at 800 and 900° became more active, while those heated at 600° in vacuum or in steam were deactivated.

That these changes were not due to changes in surface area is evidenced by the complete restoration, after use, of the activity of catalyst D, originally steam-treated at 600°, by heating in vacuum at 525°, and by the observed lack of increase in area with use of catalyst K, originally heated in vacuum at 900°. Rather, they are associated with the existence of an optimum surface water content for the reaction, and with the slow activated adsorption of water by the catalyst during use. The 600° catalysts thus have at the outset a water content in excess of the optimum; as they are used, adsorption of more water reduces activity. The 800 and 900° vacuum-treated catalysts have initially less than the optimum water

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[1] Based on the thesis of Wallace S. Brey, Jr., presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: St. Joseph's College, Philadelphia, Pa.

[3] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

[4] Francis and Lukasiewicz, *Ind. Eng. Chem., Anal. Ed.*, **17**, 703 (1945).

[5] Jellinek and Fankuchen, *Ind. Eng. Chem.*, **37**, 158 (1945).

[6] Krieger, THIS JOURNAL, **63**, 2712 (1941).

TABLE I

AREAS AND RATE CONSTANTS OF ALUMINA CATALYSTS

Batch	Treatment Method	Treatment Temp., °C.	Treatment Time, hr.	Area, millimoles N_2/g.	Ignited wt., g.	Reaction temp. 400° k_1	Reaction temp. 400° k_1'	Reaction temp. 350° k_1	Reaction temp. 350° k_1'	$100k_1$ at 400°/total area of batch
A	Vacuum	500	19	2.49	33.1	0.55	2.0	0.052	1.0	0.67
A-2	[a]			1.86	33.1	.37[f]				.60
B	Steam[b]	500	5	1.30	33.4	.25	1.6	.025	0.9	.58
C	Vacuum	600	19	2.29	33.7	.45	2.1	.040[f]		.58
D	Steam[c]	600	6	1.32	34.5	.27	1.3	.0241	0.46	.59
D-2	Vacuum[d]	525	3		34.5	.35[f]				
E	Vacuum	700	9	1.82	35.9	.32[f]				.49
F	Vacuum	700	20	1.87	34.0	.31	1.7	.030[f]		.48
G	Steam[b]	700	5	0.80	34.7	.12[f]				.43
H	Vacuum	800	19	1.49	34.4	.25	1.6	.0221	0.7	.49
J	Steam[c]	800	8	0.75	33.0	.067	0.8	.008[f]		.27
K	Vacuum	900	19	1.24	34.7	.13	2.0	.0122	1.9	.30
L	Steam[c]	900	5	0.87	36.0	.10[f]				.32
M	Steam[c]	900	5	0.83	[e]					
N	Vacuum	1000	5	0.64	[e]					
O	Steam[c]	1000	5	0.48	35.8	.04[f]				.23

[a] Following several runs in which it was used with aqueous feed, catalyst batch A was designated A-2; the area cited for A-2 was determined after use. [b] In flowing stream of water vapor at 1 atm. pressure. [c] Water vapor pressure about 25 mm. [d] Catalyst D, after use, was evacuated to produce this batch. [e] Activity not determined. [f] Estimated from relatively few runs.

content; adsorption of more water causes the surface to become more efficient as a catalyst.[7]

Reaction Products and Mechanism.—In Figs. 1 and 2 are plotted representative conversion curves for the formation of ether and ethylene in runs using several of the catalysts. The reaction rate is given by the slope of these curves.[8] The trend of the curves with increasing extent of reaction is similar to the results of earlier workers.[9] For every catalyst studied at a reaction temperature of 400° and for the more active catalysts at 350° the ether conversion passes through a maximum while the ethylene conversion steadily increases. For the less active catalysts at 350° the alcohol feed rate was not in all cases sufficiently reduced for the ether maximum to be reached but there seems no doubt that it could have been observed.

In order to evaluate quantitatively the catalyst activity, it is necessary to relate the observed rates of ethylene formation to a velocity constant of the rate-determining step in the reaction. Diffusion is not rate-controlling, in view of the large temperature coefficient of the reaction and the dependence of rate upon surface area. The problem of establishing the rate constant is thus that of the choice of the direct precursor or precursors of ethylene.

If alcohol is assumed to be the sole immediate source of ethylene, then, since ether is produced initially quite rapidly and subsequently disappears, the ether must be formed from alcohol and then reconverted to alcohol to maintain equilibrium with the latter as it is converted to ethylene

$$\begin{tikzcd} C_2H_5OH \arrow[r] \arrow[d, shift left] & CH_2{=}CH_2 + H_2O \\ H_2O + C_2H_5OC_2H_5 \arrow[u, shift left] & \end{tikzcd}$$

This mechanism, with the assumptions that the surface reaction is rate-determining, that ethanol and water are strongly adsorbed while ethylene and ether are not, that only one active site is involved in the reaction and that the reverse reaction may be neglected because of the magnitude of the equilibrium constant, leads to the equation

$$22{,}400R = \frac{kLK_aP_a}{K_aP_a + K_wP_w} = \frac{k_1P_a}{P_a + k_1'P_w} \qquad (1)$$

where R is the rate in moles ethylene formed per cc. of catalyst bed per sec., k is the rate constant, L is the number of active sites per cc., the K's are adsorption equilibrium constants, the P's are partial pressures, and the subscripts a and w refer to alcohol and water, respectively.[8] Equation (1) fits the experimental data, while similar equations for the cases in which adsorption or desorption are rate-determining do not. The curves of conversion to ethylene in Figs. 1 and 2 have been calculated from equation (1), employing the values of the constants shown in Table I, while the points shown represent experimental results. The constants in equation (1) were evaluated by the method described in reference (8), pages 958–959.

If, on the other hand, ether is formed from alcohol and is the sole source of ethylene, the initial

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(7) (a) Eucken and Wicke, *Naturwissenschaften*, **32**, 161 (1945); (b) Munro and co-workers, *Can. J. Research*, **10**, 321 (1934); **12**, 707 (1935); **21B**, 21 (1943).

(8) Hougen and Watson, "Chemical Process Principles," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1947.

(9) (a) Engelder, *J. Phys. Chem.*, **21**, 676 (1917); (b) Pease and Yung, THIS JOURNAL, **46**, 390, 2397 (1924); (c) Clark, Graham and Winter, *ibid.*, **47**, 2748 (1925); (d) Alvarado, *ibid.*, **50**, 790 (1928); (e) Parravano, *Mem. accad. Italia, Classe sci. fis. mat. e. nat.*, **1**, *Chim.* No. 1, 1 (1930); (f) Kearby and Swann, *Ind. Eng. Chem.*, **32**, 1607 (1940).

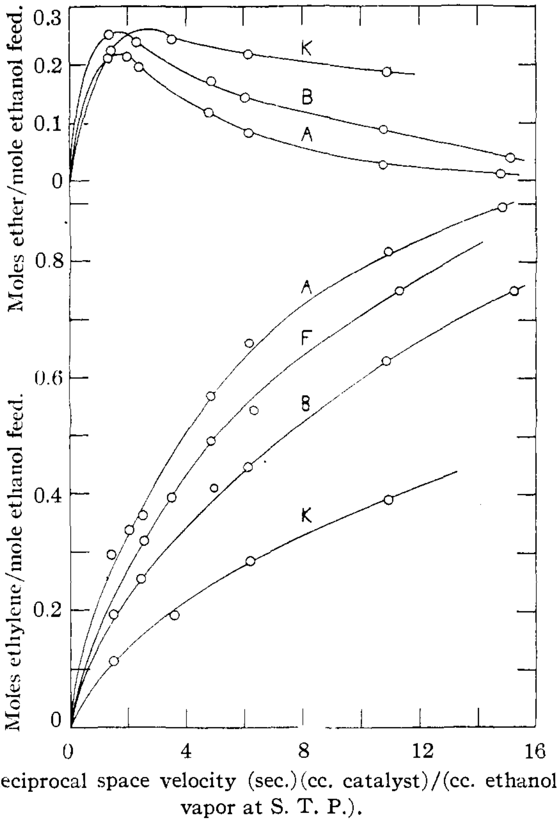


Fig. 1.—Conversion of ethanol to ethylene and ether at 400° reaction temperature for representative catalyst batches.

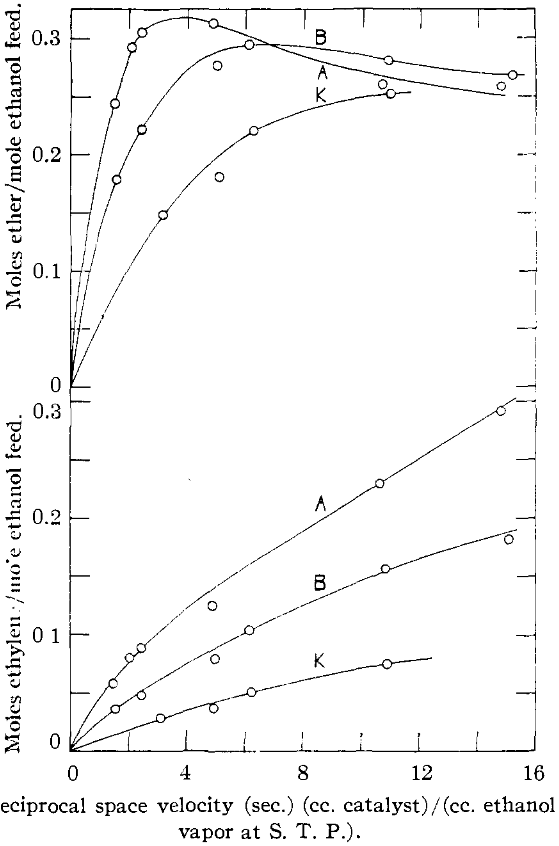
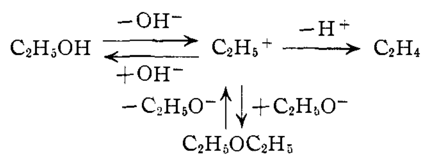


Fig. 2.—Conversion of ethanol to ethylene and ether at 350° reaction temperature.

rate of ethylene production should be zero, since the initial ether concentration is zero. There is no indication of this in the present work or in the results reported by others, except in those of Alvarado.[9d]

It is possible that ethylene is produced by parallel paths, with a fraction coming directly from alcohol and the remainder from ether. In fact, ethylene is formed quite rapidly when ether is passed over the catalyst. From 0.52 mole of ether fed during sixty minutes, 0.39 mole of ethylene and 0.05 mole of alcohol were obtained, at a reaction temperature of 400°. This is roughly 50% more ethylene than would have been obtained from one mole of alcohol under the same conditions. However, the circumstance that the rate of ethylene formation is given satisfactorily by equation (1) and seems, on examination of the conversion curves, not to be directly affected by the changing ether pressure during the course of the reaction, indicates that if ethylene is produced by two paths, the effect of the presence of ether is not exerted independently of the alcohol concentration.

To account for this situation, it seems necessary to assume that a common intermediate such as a carbonium ion may be formed from either alcohol or ether and can then react to form either ethylene or ether



$$C_2H_5OH \underset{+OH^-}{\overset{-OH^-}{\rightleftarrows}} C_2H_5^+ \xrightarrow{-H^+} C_2H_4$$

$$-C_2H_5O^- \uparrow\downarrow +C_2H_5O^-$$

$$C_2H_5OC_2H_5$$

The appearance of this type of intermediate is indicated by the products formed when higher alcohols are dehydrated over alumina.[10] This mechanism also explains the important role of a water molecule in the reaction as the result of its ability to supply a hydrogen atom to form a hydrogen bridge between the catalyst and an alcohol or ether oxygen atom, thus weakening a carbon to oxygen bond in the organic molecule and creating a favorable situation for carbonium ion formation.[7a] If the carbonium ion concentration is proportional to the surface concentration of alcohol, and the rate-determining step is the conversion of the ion to ethylene, then the rate of ethylene production is proportional to the surface concentration of alcohol and the use of equation (1) is justified.

Specific Activity of the Catalyst.—In Table I are given the values of k_1 and k_1', from equation (1), for the reaction temperatures of 350° and 400°, as well as the ratio of k_1 at 400° to the total

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[10] Henne and Matuszak, THIS JOURNAL, **66**, 1649 (1944).

surface area of the catalyst batch. This ratio represents the activity of unit area of surface. For catalysts for which activity changed with use, the values are for the final, stable level of activity.

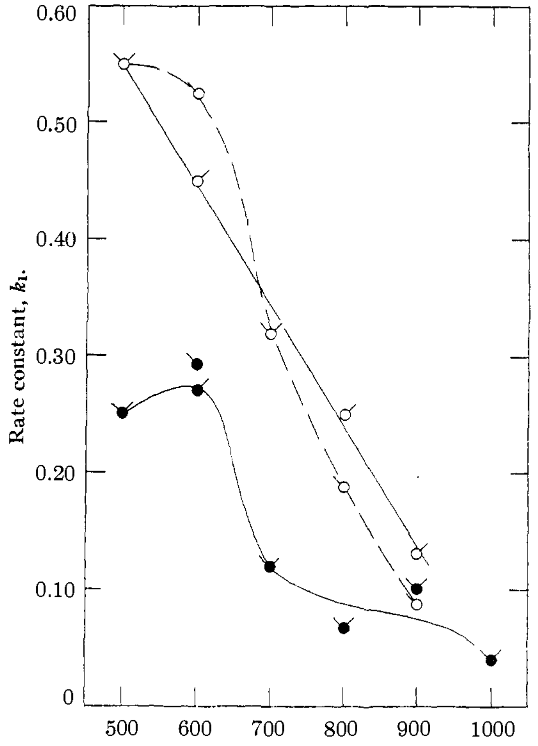

Fig. 3.—Rate constants at 400°: ○, initial activity of vacuum-treated alumina; ○, stable (final) activity, vacuum-treated; ●, initial activity, steam-treated; ●, stable (final) activity, steam-treated.

In Fig 3 are plotted the values of k_1 at 400°, along with estimates of the original activities for the catalysts showing changing activity. It is clear from Fig. 3 that the effect of steam treatment is markedly to reduce total activity below that resulting from vacuum activation at the same temperature, except perhaps at the highest temperatures where all catalysts show very small activities. That this decrease in activity is not, however, a matter of quality, but only of quantity of surface is illustrated in the plot of specific activity presented in Fig. 4, which demonstrates that the activity per unit area of remaining surface is substantially independent of method of treatment except at 800°, where the vacuum activated surface is distinguished by ability to improve its activity upon use. Further evidence that the effect of water vapor is exercised largely through a change in surface area is given by the data in Table I for catalyst A. Following reaction runs with pure alcohol, this catalyst was employed several times with a feed containing approximately 75 mole per cent. water, at a temperature of 350°. When the catalyst was then again used with pure alcohol feed, the total activity had been reduced, during the runs with high water content, by 33%, while the specific activity had decreased only 10%.

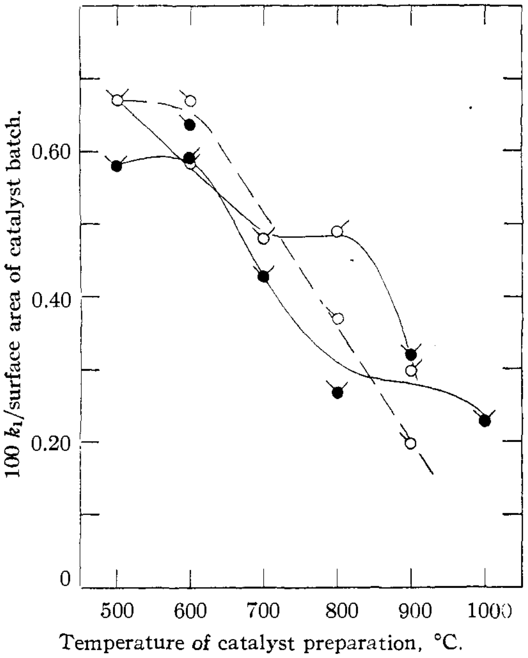

Fig. 4.—Specific activity of catalysts for 400° reaction temperature: ○, initial activity, vacuum-treated; ○, stable activity, vacuum-treated; ●, initial activity, steam-treated; ●, stable activity, steam-treated.

The specific activity of the catalyst decreases as the temperature of preparation is increased above 600°. This is probably a consequence of increased perfection of the crystal lattice, leading to a decrease in the number of sites at which there exist unsatisfied valence forces. However, it appears from the values of k_1 for 350° and for 400° in Table I that the temperature coefficient of the reaction is very nearly constant, within the experimental error, for all the catalysts studied, and consequently the active sites have approximately the same nature in all the materials.

Summary

1. The catalytic activity of samples of aluminum oxide prepared by heating in vacuum and in water vapor at temperatures between 500 and 1000° has been measured for the dehydration of ethanol at reaction temperatures of 350 and 400°.

2. Both total activity and specific activity decrease as the preparation temperature increases above 600°. Heating with water vapor induces an additional loss of area and activity as compared with heating in vacuum, but the specific activity of the surface is nearly independent of the presence of water.

3. Crystallite growth is a concomitant of the reduction in area produced by high temperatures

and by the presence of water vapor; under the more severe conditions of treatment, this change is accompanied by a decrease in the number of catalytic centers without substantial change in their nature.

4. Some possible mechanisms for the formation of ethylene have been considered in the light of the reaction kinetics, and the ether intermediate theory in its simplest form has been shown to be inapplicable.

5. Changes of activity with use have been explained as the result of changes in the water content of the surface, rather than in surface area.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Copper(II) and Nickel(II) Complex Ions of Hydroxyethylethylenediamine

BY JEAN L. HARVEY,[1] CHARLES I. TEWKSBURY AND HELMUT M. HAENDLER

Complex ions formed by the action of multidentate amines on metal ions are of considerable interest structurally. In a previous article Haendler[2] reported the formation of copper(II) and nickel(II) complex ions with diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$. Subsequently, Breckenridge[3] isolated specific complexes of this amine and of hydroxyethylethylenediamine (2-(2-aminoethylamine)-ethanol), $H_2N(CH_2)_2NH(CH_2)_2OH$ (abbreviated "hn"). The work on diethylenetriamine led to the conclusion that it probably behaved as a tridentate ligand, a conclusion supported by polarographic studies by Laitinen, *et al.*,[3a] and that the copper and nickel complexes were structurally similar.

Using hydroxyethylethylenediamine, however, Breckenridge was able to isolate copper complexes with a copper:hn ratio of 1:1 and 1:2 from 95% ethanol and a single nickel complex with a nickel:hn ratio of 1:3 from absolute ethanol. Spectrophotometric methods have now been applied to the study of the ions formed in water solution by copper(II) and nickel(II) ions and this amine. It has been found that copper forms the complex ions $[Cu(hn)]^{++}$, $[Cu(hn)_2]^{++}$ and $[Cu(hn)_4]^{++}$, and that nickel forms the ions $[Ni(hn)]^{++}$ and $[Ni(hn)_2]^{++}$.

The results for copper are compatible with the structures suggested by Breckenridge. In $[Cu(hn)]^{++}$ and $[Cu(hn)_2]^{++}$, the amine probably acts as a bidentate ligand, the coördinating power of the hydroxyl group being slight. The shape of the spectral curves for $[Cu(hn)_4]^{++}$ indicates low stability of the ion, consistent with a non-chelated structure involving four primary amine groups. The complex is apparently stable only in solution.

Attempts to identify the ions formed between copper(II) and diethanolamine (2,2′-dihydroxydiethylamine), $HO(CH_2)_2NH(CH_2)_2OH$ (abbreviated "den"), indicate that there are ions with copper:den ratios of both less than 1:3 and greater than 1:3. If the amine were coördinated through both the amine and hydroxyl groups, a ratio of 1:2 would be the maximum expected. No ratio greater than 1:3 could be expected if coördination were through the hydroxyl groups only. It is thus probable that the diethanolamine is coördinated only through the secondary amine group. The ions are stable only in the presence of excess amine, indicating lower coördinating power than with primary amine groups. This supports the proposal that only primary amine groups are involved in the 1:4 ion of hydroxyethylethylenediamine and that both amine groups participate in the formation of 1:1 and 1:2 ions.

The $[Ni(hn)]^{++}$ and $[Ni(hn)_2]^{++}$ are assumed to be similar in structure. No evidence could be found of an ion corresponding to $[Ni(hn)_3]Cl_2$ isolated by Breckenridge. There is evidence, however, that the solvent affects the coördinating power of the amine. Mann[4] reported that only two moles of diaminopropanol would coördinate to nickel in water solution. The compound $[Ni(hn)_2]HgI_4$ has been prepared by reaction in

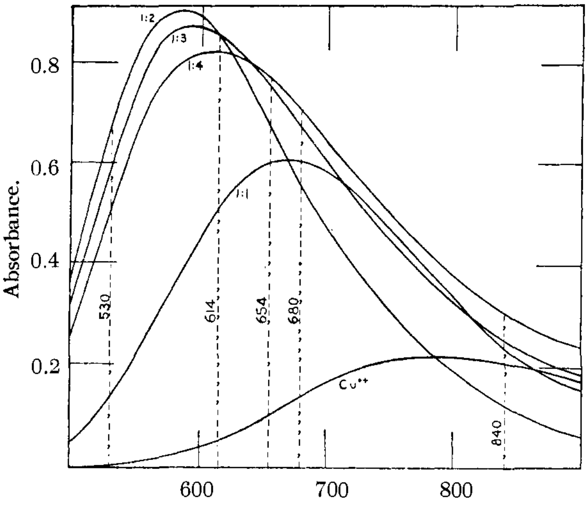

Fig. 1.—The absorption spectra of solutions of Cu^{++} and hn.

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[1] This paper represents in part a thesis presented by J. L. Harvey to the University of New Hampshire in partial fulfillment of the requirements for the degree of Master of Science.

[2] Haendler, THIS JOURNAL, **64**, 686 (1942).

[3] Breckenridge, *Can. J. Research*, **B26**, 11 (1948).

[3a] Laitinen, *et al.*, THIS JOURNAL, **71**, 1550 (1949).

[4] Mann, *J. Chem. Soc.*, 2904 (1927).