a few hours for a type of adsorption having all of the characteristics of activated adsorption [Taylor, THIS JOURNAL, **53**, 578 (1931)]. The energy of activation of the adsorption was about 9000 calories. The isobar at 760 mm. showed a gradual decrease from an adsorption of 7 to 8 cc. at −78° to about 5 or 6 cc. at 0°.

Type B Activated Adsorption.—At 100° or higher an additional but much slower adsorption (type B) set in, the total adsorption (type A and type B) reaching at 100° a value of 8 to 9 cc. within two hours. At 212 and 450° the adsorptions were 5.5 and 3.5 cc., respectively, and reached an apparent equilibrium in less than an hour. Isotherms taken at 350 and 410° were reversible and indicated a heat of adsorption of about 8500 calories.

In a previous communication [Harkness and Emmett, THIS JOURNAL, **55**, 3496 (1933)] it was pointed out that the adsorption of hydrogen by the promoted iron catalyst at 100° and at 212° strongly inhibited the low temperature (−190°) catalytic conversion of ortho to para hydrogen. In continuing this study it has now been found that this inhibition produced by the adsorption of a given volume of hydrogen by the catalyst at 100° is about eight times as great as that produced by the same volume of hydrogen adsorbed at −78°.

From the combined adsorption data and measurements of the absolute and relative poisoning effects of types A and B adsorption on the low temperature ortho–para hydrogen conversion it therefore may be concluded (1) that both types A and B are primarily surface adsorptions and not solutions within the metal, and (2) that types A and B represent two distinctly different kinds of activated adsorption, the B type not being merely a slow continuation of type A.

BUREAU OF CHEMISTRY AND SOILS R. W. HARKNESS
WASHINGTON, D. C. P. H. EMMETT

RECEIVED DECEMBER 26, 1933

MOLECULAR REARRANGEMENTS OF OPTICALLY ACTIVE RADICALS

Sir:

Previous investigations in this Laboratory have shown that in certain molecular rearrangements involving optically active radicals, notably of the Hofmann, Curtius and Lossen types, the optically active group maintains an asymmetric configuration during the rearrangement. It has also been shown that such transformations are accompanied with little or no racemization. The optical stability of such radicals during rearrangement can be explained easily on the theory that the shift of the electron pair from the carbon atom to the nitrogen atom includes the group which it holds.

We have continued our studies of molecular rearrangements in order to determine more definitely whether the electronic nature of the migrating group is of great importance in maintaining the asymmetry of the radical during rearrangement. For this purpose a compound was chosen in which the group containing the asymmetric carbon atom is essentially of the nature of a positive group during rearrangement.

Accordingly we prepared *l*-2-methyl-2-phenylbutanol(1), $CH_3CH_2C(CH_3)(C_6H_5)CH_2OH$, $\alpha_D^{19} = -4.90°$ (homogeneous, 1-dm. tube), and studied its behavior when the hydroxyl group was replaced by chlorine. The chloride so produced was found to be a tertiary chloride, and not a primary chloride. This fact is to be expected on the basis of modern conceptions of molecular rearrangements. It was also found to be optically active. The rearrangement however is accompanied by an inversion in sign of the rotatory power. The *l*-alcohol yields a dextrorotatory rearrangement product. In conclusion it is to be pointed out that these facts have an important bearing on all investigations involving configurational relationships of optically active compounds.

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RECEIVED JANUARY 2, 1934

THE INTRODUCTION OF DEUTERIUM ATOMS INTO ACETONE

Sir:

When a solution of acetone in water containing deuterium oxide and a small amount of potassium carbonate is warmed for a short time, an exchange of hydrogen atoms occurs, with the consequent introduction of deuterium into the acetone. We first studied the concomitant decrease in density of the water. For example, six solutions were prepared, each containing 30 cc. of water, 60 cc. of refractionated (0.1° range) "C. P. Analyzed" acetone, and about 0.1 g. of either phosphoric acid or potassium carbonate as indicated in the table. After warming from one to three hours