(with the cathode surrounded by a porous cup containing ammonium nitrate solution) gave a manganese dioxide of equal activity and in greater quantities. (Similarly, ozonizing basic lead acetate solution precipitated an oxide which, after washing with nitric acid and drying *in vacuo* at 100°, was active at 80°, whereas Bennett's PbO_2 did not catalyze the reaction except above 180°.)

It is hoped that this communication will be of aid to workers interested in preparing manganese dioxide (or other higher oxides) free of adsorbed alkali salts and capable of catalyzing gas-oxidation reactions. At no time did these oxides or the salts from which they were obtained come in contact with alkali other than that derived from glass, porcelain, etc., or with any foreign material other than nitric acid and volatile ammonium salts. Further work is now in progress.

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RECEIVED JUNE 13, 1934

ASYMMETRIC REARRANGEMENT

Sir:

For some time there has been under way in this Laboratory an investigation of the effect called by Kuhn [*Ber.*, **65**, 49 (1932)] asymmetric rearrangement of the first type (asymmetrische Umlagerung erster Art). Our experiments (as yet unpublished) indicate that Kuhn's hypothesis is not generally valid, and that if it has any field of applicability, that field has not yet been clearly defined. The present communication is prompted by the recent paper of Lesslie and Turner [*J. Chem. Soc.*, 347 (1934); we have searched carefully for the mutarotation described by Lesslie and Turner, but have not been able to find any such phenomenon] in support of Kuhn's idea.

Kuhn bases his hypothesis chiefly on the "anomalous" optical rotation of quinine 4,4'-dinitrodiphenate in chloroform solution; Lesslie and Turner's supporting evidence is derived from the similar behavior of quinine diphenate in the same solvent. The divergences from the normal rotation are explained by what might be called a "dissymmetrizing" effect exerted by the optically active base on the acid. According to this view, the solution of the free acid is an equimolecular mixture of the *d* and *l* forms in labile equilibrium. The dissymmetric base disturbs this equilibrium, and the observed rotation is the resultant of the rotations of the base and the optically activated acid. As soon as the dissymmetrizing base is removed, the equilibrium between the two forms of the acid shifts back very rapidly to form the equimolecular mixture. Physical separation of the stereomeric acids is thus impossible.

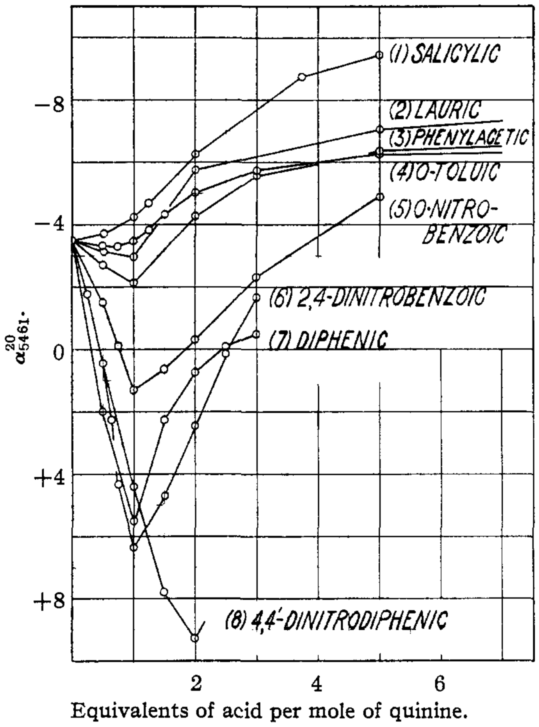

Fig. 1.—Rotations of salts of quinine in chloroform: Curves 1, 2, 3, 4, 5 and 6 were obtained with 0.04 molar solutions, curves 7 and 8 with 0.01 molar solutions of quinine, in a 2-dm. tube. The discrepancy thus introduced is, however, negligible, *e. g.*, for a 0.04 molar solution of quinine containing one equivalent of 4,4'-dinitrodiphenic acid α^{20}_{5461} 4.43°; calculated to the above concentration from a 0.01 molar solution of quinine and one equivalent of acid α^{20}_{5461} 4.40°. Curve 1: Similar curves were obtained with anthranilic, *o*-chlorobenzoic and *o*-iodobenzoic acids. Curves 2 and 3: Similar curves were obtained with acetic, crotonic, chloroacetic, palmitic, phenylpropionic and trichloroacetic acids. Curve 5: Similar curves were obtained with anisic, cinnamic, *m*- and *p*-nitrobenzoic, *p*-toluic and 3,5-dinitrobenzoic acids. Curves 6 and 7: A similar curve was obtained with 2,4,6-trinitrobenzoic acid.

This theory of Kuhn implies an important departure from classic chemical practice. The principle that isomer numbers can be determined from anomalies in the optical rotations of solutions may well have far reaching consequences. It therefore seemed desirable to us, before accepting so radical an idea, to investigate thoroughly the rotations of salts of various optically active bases in chloroform and other solvents. Such an investigation is now approaching completion. All of our data (which we hope soon to publish) support the views previously stated.

For the sake of brevity, we give here only the data on certain organic salts of quinine in chloroform solution. In so far as solubility conditions permit, a uniform concentration of quinine has been maintained, and (where possible) the amount of acid has been varied from $^1/_{10}$ to 20 moles per mole of base. Some of the curves are reproduced in diagram 1.

Our conclusions from the data there given are as follows: (1) The curves are of such diversified character that we do not feel justified in calling any one of them normal or anomalous. (2) The curves for the diphenate and the 4,4′-dinitrodiphenate so closely resemble those of certain other salts (*e. g.*, the 2,4-dinitrobenzoate) that there are no grounds for assuming that quinine dissymmetrizes one of these acids but not the others. That all these acids exist in pairs of mirror image forms is highly improbable.

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ANOTHER INTERPRETATION OF EXPERIMENTS WHICH ARE SUPPOSED TO INDICATE THE EXISTENCE OF OXYACIDS OF FLUORINE

Sir:

Dennis and Rochow [THIS JOURNAL, **54,** 832 (1932); *ibid.*, **55,** 2431 (1933)] found that the action of fluorine produced, in an alkaline solution, an oxidizing agent, a small part of which could not, under certain circumstances, have been a peroxide or ozonate. They concluded, therefore, that the salt of an oxyacid of fluorine had been formed. However, there is another plausible interpretation of their observations. Of their results, the most indicative was that the passage of fluorine through cold 50% potassium hydroxide left in the solution an oxidizing agent, a part of which was not destroyed either by standing at room temperature for seventy hours or by evaporation of the liquid and subsequent fusion of the alkali in a beaker. Surely a peroxide or ozonate could not have resisted such severe treatment.

Attempts of the author to repeat this experiment have usually met with failure. The substance of considerable oxidizing strength has been decomposed by standing at room temperature for several hours or by boiling the solution for a minute. The destruction has been so complete that an acidified sample of the solution did not give a blue color with starch and potassium iodide for several minutes.

Fusion of potassium hydroxide in a Pyrex beaker has been found to produce a soluble substance capable of liberating iodine from a solution of potassium iodide containing sulfuric acid. This makes it difficult to test for an oxidizing agent which was present in the alkali before fusion.

At times it has been possible to reproduce the observations of Dennis and Rochow, but in each case of this sort the solution was found to contain a small amount of chloride ion. It therefore seems quite possible that the stable oxidizing agent was an oxy salt of chlorine which could result from a trace of chloride in either the potassium hydroxide, the potassium acid fluoride used for the preparation of fluorine or the sodium fluoride employed to remove hydrogen fluoride from the fluorine. Since this type of experiment should be a rather sensitive test for chlorine, it is surprising that any negative results have been obtained.

By means of the customary tests with titanium sulfate and with chromic acid, it has been shown that the oxidizing agent, which is so unstable in a strongly alkaline solution, is actually a peroxide. This confirms the work of Moissan, Fichter and Bladergroen [H. Moissan, "Le Fluor," 1900, p. 228; Fichter and Bladergroen, *Helv. Chim. Acta*, **10,** 549 (1927)].

CONTRIBUTION NO. 40
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RECEIVED JUNE 18, 1934

BINDING AND INTERCHANGE OF WATER MOLECULES IN A SALT HYDRATE

Sir:

The statement of Fresenius ["Quant. Anal.," 1897, p. 799] that cupric sulfate pentahydrate, when heated near 140° in a current of dry air, yields a residue of monohydrate of constant weight is substantially correct for analytical practice, in spite of the fact that the equilibrium