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)].

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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 dissociation pressure of monohydrate with anhydrous salt is computed as 62 mm. at this temperature [Menzies and Hitchcock, *J. Phys. Chem.*, **35,** 1660 (1931)]. The success of the analytical procedure may be said to rest upon the long duration of the so-called induction period of the monohydrate, during which loss of water fails to begin owing to lack of a starting point, in absence of the new, anhydrous phase.

At 125° a sample of the monohydrate prepared by dehydration of pentahydrate showed, under Fresenius' conditions, an induction period of seventy hours (although monohydrate prepared from the anhydrous salt by rehydration showed no induction period because of its richness in "reaction centers") [Furman and Menzies, unpublished work].

At 75° the apparent stability of monohydrate prepared by dehydration is greater still, and its single water molecule appears to remain undisturbed in the absence of deliberate provocation directed at lessening the effective activation energy for dehydration.

For the three consecutive stages of dehydration of pentahydrate to anhydrous salt, the comparative energies to yield one mole of (unabsorbed) water vapor near 50° are about 13.2, 13.5 and 17.5 large calories [Menzies and Collins, unpublished work; Menzies and Hitchcock, *loc. cit.*].

In these circumstances it appeared to be of interest to prepare $CuSO_4 \cdot H_2O$ by dehydration from pentahydrate, to rehydrate this through the vapor phase by means of vapor of D_2O (heavy water), and then to dehydrate the salt once more in order to find whether the original H_2O had remained *in situ*. Should a solution phase form during the process of hydration, interchange between heavy and light water molecules would appear inevitable, and we endeavored, therefore, to avoid this.

At 35° the pressure of ordinary water vapor in equilibrium with the penta- and trihydrates is 16.2 mm.; with the tri- and mono-hydrates, 10.9 mm.; and with the monohydrate and the anhydrous salt <0.1 and 1.2 mm., respectively at 35 and 75°; and at 35° with the saturated solution of pentahydrate, 40.4 mm. [Collins, Hitchcock, Menzies, *loc. cit.*].

We prepared $CuSO_4 \cdot H_2O$ by dehydrating the pentahydrate at 75° for a few hours in presence of H_2O vapor in equilibrium with H_2O ice at 0° (4.6 mm. pressure) and obtained analytical results little vitiated by adsorbed water. We placed this monohydrate in an evacuated system at 35° and applied vapor of D_2O at a pressure somewhat over 20 mm. The apparent degree of over-all hydration reached a value exceeding four molecules of water overnight. In one experiment, lasting a few hours, we dehydrated this product at 75° in presence of D_2O vapor in equilibrium with D_2O ice at 0°. The weight of the residual monohydrate, constant over many more hours, showed that complete interchange of heavy and light water had taken place, and that the original H_2O had been expelled. In a second experiment, we dehydrated at 35°, which is a much slower process. Here also we found that interchange had taken place.

Further experiments and various interpretations suggest themselves which may find place elsewhere.

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CRYSTALLINE B_2O_3

Sir:

Of all the glass-forming oxides B_2O_3 is probably the most typical [Zachariasen, THIS JOURNAL, **54,** 3841 (1932)]. Numerous attempts have been made to devitrify boric oxide glass, without success. The usual process of heating H_3BO_3 to drive off the water leaves an extremely viscous liquid which does not crystallize.

Recently we have been able to produce crystalline B_2O_3 by vacuum dehydration of H_3BO_3 at temperatures below 225°. Using a water suction pump, with the sample of boric acid at 180°, we first obtained $2B_2O_3 \cdot H_2O$. On connecting a good oil pump to the sample heated at 200°, we removed the last half molecule of water and obtained material giving three or four sharp lines on an x-ray pattern. The product was sintered for 400 hours at 225° in order to permit crystal growth, after which the x-ray pattern showed about a dozen sharp lines and was free of the diffuse band which characterizes the glass phase. The melting point has been determined by two different methods to be $294 \pm 1°$. The index of refraction is 1.458 ± 0.002. The crystals are apparently isotropic. The specific gravity at 25° is 1.805, while that of the B_2O_3 glass is 1.844, making it expand on freezing, like H_2O. The anhydrous crystalline B_2O_3 is highly desiccant.