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salt by rehydration showed no induction period because of its richness in "reaction centers") [Furman and Menzies, unpublished work].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yield one mole of (unabsorbed) water vapor near 50° are about 13.2, 13.5 and 17.5 large calories [Menzies and Collins, unpublished work; Menzies and Hitchcock, *loc.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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RECEIVED JUNE 19, 1934

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.

Details of measurement and crystal structure data will be given in another publication.

Department of Ceramics
Pennsylvania State College
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Sandford S. Cole

Received June 22, 1934

THE RELEASE OF SUPERCOOLING IN CRYOSCOPIC DETERMINATIONS

Sir:

The freezing point method of determining molecular weights is one of our most useful procedures and the freezing point lowering of solution is of great theoretical importance. The precise determination of a freezing point may be obtained by supercooling the liquid or solution under suitable conditions and releasing the supercooling to allow the system to come to equilibrium. The exact freezing point is determined in this way. The release of the supercooling without too great supercooling has always been a difficult matter but we have found that a little glass bead may be cooled on a cake of dry ice (solid carbon dioxide) and then introduced into the system and so releasing the slightest amount of supercooling.

Ordinary glass beads 3 mm. in diameter with 0.5 mm. bore may be wet with solvent or liquid and placed on the cake of dry ice for a few minutes and then with forceps may be transferred rapidly to the supercooled liquid. At ordinary laboratory temperatures the little core of ice will not melt in thirty seconds or more, so there is ample time. The suitably cooled bead, quite free of ice, will also release supercooling as it may be introduced into the system while at a very low temperature. If the bead is placed in the closed end of a thin-walled tube it may be cooled on dry ice and rapidly rolled into the supercooled system. We have readily released liquids or solutions supercooled only 0.04° and with experience a supercooling of as little as 0.01° is feasible. This should be of importance in determining the true freezing point of dilute solutions.

Frick Chemical Laboratory
Princeton University
Princeton, N. J.
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Received June 23, 1934

THE SEPARATION OF THE OXYGEN ISOTOPES

Sir:

Although Washburn, Smith and Frandsen [*Bur. Standards J. Res.*, **11**, 453 (1933)] state that the electrolysis of sodium sulfate and sulfuric acid solutions produces oxygen with a greater proportion of O^{16} than is present in the water electrolyzed, Lewis and Macdonald [*J. Chem. Physics*, **1**, 341 (1933)] reported that no concentration of O^{18} was found when deuterium was concentrated by the electrolysis of sodium hydroxide solutions with nickel electrodes. Their method of analysis may not have been sensitive enough, however, to have detected small shifts in the isotopic composition of the water. We have electrolyzed 5% sodium hydroxide solutions with nickel electrodes and compared the density of water produced by burning this oxygen in purified tank hydrogen with that of water produced by burning air in the same hydrogen. The water from the electrolytic oxygen proved to be 7.7 p. p. m. lighter than Cambridge tap water and that from the air burned in the same hydrogen 1.1 p. p. m. heavier. Our results thus agree with those of Washburn, Smith and Frandsen in indicating a small but definite separation of the oxygen isotopes.

The Chemical Laboratories of
Radcliffe College and
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Cambridge, Mass.
Charles H. Greene
Roger J. Voskuyl

Received June 25, 1934

THE RELATIVE PROPORTIONS OF DEUTERIUM IN SOME NATURAL HYDROGEN COMPOUNDS

Sir:

The interesting observations of Lewis [This Journal, **55**, 3503 (1933)] upon the antigerminative property of deuterium oxide led us to investigate the isotopic composition of the hydrogen utilized by plants in the synthesis of organic compounds with an expectation of finding a preference for protium in the biological synthesis. We find, however, in common with others who have reported upon parallel investigations [E. W. Washburn and E. R. Smith, *Science*, **79**, 188 (1934); M. Dole, This Journal, **56**, 999 (1934)] since we began our work, that in some natural sources deuterium is more abundant than in ordinary water.

In our experiments "Mazola" corn oil was burned in dried air and the products of combustion passed over hot copper oxide before condensing the water. Natural gas from northern Pennsylvania was burned in air of such low humidity that any admixture of the water formed with ordinary water was negligible. After care-