

As an explanation of the action of the ether, it is suggested that there is an equilibrium in solution:



and that the function of the ether is to co-ordinate with the aluminium hydride and drive the equilibrium to the right-hand side. It is known independently that aluminium hydride retains ether tenaciously¹.

This explanation implies that the active entity is the H^- ion rather than the AlH_4^- ion; this is being tested both by examining the effect of added aluminium hydride on the reactivity of lithium aluminium hydride solutions, and by transport experiments designed to determine the nature of the ions present.

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¹ Einholt, Bond and Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

² For a review, see A. W. Johnson, *Ann. Rep. Chem. Soc.*, **46**, 140 (1949).

³ Trevo and Brown, *J. Amer. Chem. Soc.*, **71**, 1675 (1949).

⁴ Evans and Lee, *J. Amer. Chem. Soc.*, **55**, 1474 (1933).

Intracrystalline Water in Pollucite

THE natural mineral pollucite is generally formulated as $(\text{Cs}, \text{Na})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. It is isostructural with analcite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, both having cubic unit cells. Values of a reported for analcite range from 13.6₈ Å. to 13.67 Å.¹, and for pollucite from 13.6₆ Å. to 13.6₉ Å.²

The distribution of the water molecules in the pollucite structure raises an interesting point. According to W. H. Taylor³, there are 24 available sites in the analcite unit cell for the 16 sodium ions, each sodium ion lying between four oxygen atoms of the framework and two water molecules. To preserve cubic symmetry, the sodium ions must be randomly distributed. The cations in the identical aluminosilicate framework of pollucite must be similarly distributed. The question then is whether the water molecules in the crystal are associated only with the sodium ions or may also be located in the vacant sites of the framework, of which there are just enough to accommodate the amount of water given in the above formula⁴. In order to decide this point, the following observations have been made.

The water content of some natural pollucites appears to decrease with decreasing sodium content and increasing caesium content⁴. This suggests that the water may be associated only with the sodium ions; but a final proof can be offered only by synthesizing a pure caesium pollucite and demonstrating that it is anhydrous. This synthesis has now been carried out by us, using caesium aluminosilicate gels in hydrothermal systems. (Details of the preparation of synthetic pollucites will be given elsewhere; the mineral has also been grown by the recrystallization of chabazite¹.) The synthetic pollucite of composition $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ has been found to be an anhydrous species. No water is then associated with the 8 vacant sites per unit cell. The correct formula for pollucite will then be $(\text{Na}_x\text{Cs}_{1-x})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2x\text{H}_2\text{O}$.

The identity of the unit cell as between analcites and pollucites requires that, so far as occupation of

the interstitial cavities in the identical aluminosilicate framework of these crystals is concerned, $(\text{Na}^+ + \text{H}_2\text{O})$ is equivalent to Cs^+ . By contrast, the anhydrous crystals in which, through ion exchange, the smaller units K^+ , Rb^+ and Tl^+ replace $(\text{Na}^+ + \text{H}_2\text{O})$ in analcite have slightly distorted anionic frameworks¹. However, unlike sodium, rubidium and thallium ions, the caesium ion is too large to migrate from one interstitial site in the crystals to the next, so that the framework exhibits an ion-sieve effect towards the caesium ions, and this ion when incorporated during crystal growth is locked into the crystal¹. The distribution of the 16 caesium ions among the 24 equivalent sites per unit cell can be random in space but not in time. The mobile cations sodium, rubidium and thallium, on the other hand, may be randomly distributed in time and space. The size and immobility of the caesium ions would then appear to explain the known difficulty in dehydration and rehydration of pollucites containing some sodium, when compared with analcite, since water molecules can escape from or enter the crystals only along the channels occupied by the cations. Dehydration of pollucite requires temperatures as high as 640° C. before completion, and rehydration involves heating the crystals in an autoclave with water at 400–500° C.²

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¹ Barrer, R. M., *J. Chem. Soc.*, No. 481, 2342 (1950).

² Fleischer, M., and Ksanda, C. J., *Amer. Mineral.*, **25**, 666 (1940).

³ Taylor, W. H., *Z. Kristall.*, **74**, 1 (1930).

⁴ Richmond, W. E., and Gonyer, F. A., *Amer. Mineral.*, **23**, 783 (1938).

A Delicate Chromatograph Test for the Presence of Moisture in Alcohol

It has been found in this laboratory that paper-strip ascending chromatography affords a simple means of detecting small quantities of water (of the order of 0.1–5 per cent) present in alcohol.

The principle employed is to allow the alcohol to ascend a test paper strip (approximately 3/16 in. × 4½ in.) passing through two previously prepared zones, the lower being impregnated with iron sulphate and the upper with potassium ferricyanide. Neither of these salts is alcohol-soluble but both are water-soluble; consequently, if the ascending alcohol contains water, iron sulphate will be eluted from the lower zone and carried to the upper, with the production of ferric ferrocyanide, visible as a band of Turnbull's blue. The extent and intensity of coloration depend on the amount of water present. If a pencil mark, say, 2 in. above the beginning of the upper zone, is used as the standard height of alcohol ascent, the method becomes quantitative after calibration runs with alcohol containing known amounts of added water.

At low concentration of water, the blue colour may not be apparent until the test-strip has been air-dried.

Of the various papers tried, 'Devon Mills' white blotting has been the most satisfactory. Solutions: lower zone, 3 per cent in water; upper zone, 1 per cent in water.

Application is made with a glass tube of about ¼-in. bore drawn down in a flame to give a smooth