

of the systems yet investigated does the reverse reaction occur at a measurable velocity. A special search is being made for a measurable equilibrium and a homogeneous bimolecular gas reaction between an aldehyde and an anhydride.

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THE SEPARATION OF THE RARE EARTHS BY FRACTIONAL CRYSTALLIZATION

Sir:

No one working on the fractional crystallization of the rare earths seems to have paid much attention to the differences in the ionic radii. The relative ionic radii in the oxides have been determined by Goldschmidt [Hevesy, "Die Seltenen Erden," Verlag von Julius Springer, Berlin, Germany, p. 111, 1927], and they have been found to differ by several per cent. The usual separations, however, are effected from solution and the ions, both in solution and in the hydrated crystals, are surrounded by water molecules, in most cases, probably, as $\text{La}(\text{H}_2\text{O})_6^{+++}$, $\text{Ce}(\text{H}_2\text{O})_6^{+++}$, etc. The *fractional* differences between these augmented ionic radii are certainly much less than those of the unhydrated ions.

It would be natural to attempt separation from molten salts so as to benefit by the maximum differences in the radii since relative solubilities, etc., are determined here by the radii of the bare ions. However, high temperatures may deprive one of most of the expected advantages, for they tend to smooth over factors associated with small energy differences. (This vague statement might be helped by a more precise example, the elementary law that the smaller the difference in energy between two states of a system in equilibrium the lower must be the temperature to bring about an appreciable concentration of the lower energy state.) Nevertheless, a study of molten salts may prove of value because the unknown thermodynamic magnitudes for the crystals and their molten solutions may not be altogether unfavorable.

On the other hand, one can turn one's attention to those salts crystallizing with so little of the solvent that the positive ion is not screened from the negative ions. The acetates, for example, crystallize ordinarily with only one and one-half molecules of water and hence the acetate ions are directly in contact with the positive ions. Fractional crystallization of the acetates has not appeared very promising in the past, perhaps on account of their high solubilities. Very concentrated solutions do not differ much from crystals, the positive ions are completely "acetated" and their distribution between the liquid solution and the solid solution is almost the

same. A greater difference in the solubilities between the two phases would probably occur if dilute solutions were employed. Crystallization from dilute solution can be brought about by the addition of foreign substances and by the use of low temperatures.

The considerations I have brought forward urge the study of the fractional crystallization of the rare earths, especially their unsolvated ions, at as low a temperature as possible. Perhaps fractionation from alcohol near the freezing point should be attempted first. It may happen at this temperature, if the complete difference in the ionic radii is utilized, that two phases (if the mixture consists of two rare earths) will crystallize out of solution each of which contains one of the rare earths predominantly. Possibly this temperature is not yet low enough. Data alone can give the answer.

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SYNTHETIC CELLULOSE AND TEXTILE FIBERS FROM GLUCOSE

Sir:

A chemical investigation of the structure of the membrane obtained by the action of *Acetobacter xylinum* on glucose has now established the identity of the product as a true cellulose. Hydrolysis with hydrochloric acid and zinc chloride yields glucose quantitatively. Treatment of the triacetate with hydrochloric acid in methyl alcohol solution gives a yield of 94.3% methyl glucoside. The triacetate, after purification, has a rotation of $[\alpha]_D -21.3^\circ$, and is identical in all respects with cotton cellulose triacetate. Methylation of the acetate and hydrolysis of the trimethyl ether yields 2,3,6-trimethylmethylglucoside, the latter on hydrolysis giving the characteristic crystalline 2,3,6-trimethylglucose. A chloroform solution of the triacetate yields a cellulose acetate fiber on dry-spinning identical with cotton cellulose acetate fibers. On hydrolysis of the acetate fibers with alcoholic sodium hydroxide, the regenerated cellulose gives an x-ray diagram which, as found by Dr. George L. Clark, has the typical diffraction pattern of natural cellulose.

Preliminary investigations on similar membranes formed by the action of *Acetobacter xylinum* on fructose, sucrose, mannitol, glycerol and glyceric aldehyde would seem to point to the identity of all of these products with natural cellulose.

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