The ease of solubility depends to a large extent upon the method of preparation of the fluorides. When they are freshly precipitated from aqueous solutions, they are much more soluble than the anhydrous material, which is, in turn, more soluble than the fluorides which were heated at several hundred degrees.

Oxyfluorides.—When the rare earth fluorides are heated in a muffle furnace to approximately 800°, they slowly lose weight. If this loss in weight is plotted against heating time, the curve shows two definite breaks. Figure 1 illustrates this in the case of neodymium fluoride.

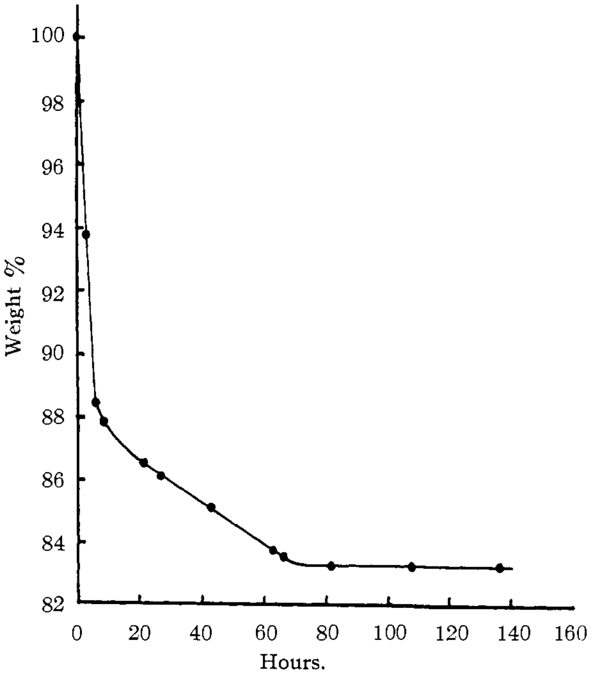

Fig. 1.—Hydrolysis of NdF_3 in air at 800°.

The first break in the curve corresponds to weight loss of 11.4%, which agrees quite well with the theoretical loss of 10.9% calculated for the conversion of neodymium fluoride to the oxyfluoride. The total loss in weight after 80 hours is 16.7% as compared with 16.4% calculated for the conversion of the trifluoride to the sesquioxide. The X-ray powder diffraction pattern of the final product was identical to that of the original oxide. The product also gave a negative test for fluorine with zirconium alizarin solution.

Although the hydrolysis under normal atmospheric conditions and at 800° required some 80 hours for completion, the reaction proceeded much more rapidly when the rare earth fluoride was heated in streams of air or nitrogen, which were saturated with water vapor at room temperature.

The above reaction was subsequently used to prepare the oxyfluorides of lanthanum, neodymium, samarium, europium and gadolinium. When praseodymium and cerium trifluorides were hydrolyzed by moist air, a mixture of the oxyfluoride and the higher oxide (presumably Pr_6O_{11}) was obtained in the first case, and the dioxide, in the second. Hydrolysis in a current of moist nitrogen likewise led to the formation of higher oxides probably due to traces of oxygen present in nitrogen. Good results were, however, obtained by carrying out the reaction in a stream of moist ammonia, or in moist hydrogen. Terbium oxyfluoride also was prepared by hydrolysis in moist hydrogen.

The rare earth oxyfluorides proved to be insoluble in dilute or concentrated acids at room temperature. They dissolved slowly in hot sulfuric or perchloric acids, and consequently the fluoride could be distilled off as fluorosilicic acid, and its amount was determined in the distillate. The distillation residue was then partially neutralized and the rare earth ion was precipitated by cupferron, and ignited to the oxide. Table I summarizes the analytical results.

TABLE I

ANALYSIS OF RARE EARTH OXYFLUORIDES

Oxyfluoride	Color	Fluorine, % Found	Fluorine, % Theor.	Rare earth, % Found	Rare earth, % Theor.
CeOF	Black	9.59	10.85	80.01	79.00
LaOF	Gray-lilac	10.80	10.93	79.68	79.87
PrOF	Brown	10.26	10.80	80.68	80.10
NdOF	Purple	10.54	10.60	80.21	80.43
SmOF	Gray-green	10.00	10.25	81.77	81.13
SmOF	Gray-green	10.08	10.25	81.62	81.13
EuOF	White	...	(10.16)	...	(81.28)
GdOF	Yellow	9.75	9.90	82.03	81.76
TbOF	White	...	(9.78)	...	(81.98)

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Rate of Oxidation of Hydrogen Sulfide by Hydrogen Peroxide

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The rate of reaction of dilute aqueous solutions of hydrogen peroxide with hydrogen sulfide was studied in conjunction with another problem in which it was desired to minimize the disappearance of hydrogen peroxide in its aqueous solutions saturated with hydrogen sulfide. Since no quantitative data have been published on the rate of this reaction, the results may be of some general interest. The reaction proceeds according to equation 1

$$H_2S(aq) + H_2O_2 \longrightarrow 2H_2O + S \qquad (1)$$

Earlier literature describes the reaction qualitatively,[1,2] the possibility of forming other products such as sulfate,[2] and the catalytic effect of iron salts.[3] No sulfate was detected in the products formed in the present studies.

Experimental

The reactor was essentially a thermostated inverted 500-cc. erlenmeyer flask. A fritted glass disc was sealed into the neck, through which hydrogen sulfide, saturated with water vapor, was continuously blown into the flask contents. The exhaust hydrogen sulfide passed through a reflux condenser sealed to the flat base of the flask (now the top of the

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[1] T. Fairley, *J. Chem. Soc.*, **31**, 1, 125 (1877).

[2] A. Classen and E. Bauer, *Ber.*, **16**, 1062 (1883).

[3] A. Wasserman, *ibid.*, **65**, 704 (1932); *Ann.*, **503**, 249 (1933).

reactor). The condenser contained a baffle to aid in separating the entrained liquid. The hydrogen sulfide flow rate was sufficiently rapid that the solution could be assumed to be saturated at all times.

At the start of each experiment, the reactor was filled about two-thirds full of water, the hydrogen sulfide flow was begun, and then a small amount of concentrated hydrogen peroxide solution was injected into the top of the reactor. The agitation caused by the rising hydrogen sulfide bubbles produced rapid mixing. The rate of reaction was followed by removing aliquots from time to time and determining the change of concentration of hydrogen peroxide. Since hydrogen sulfide would interfere with the analytical procedure, each aliquot sample was aerated for two minutes by bubbling a stream of clean air, saturated with water vapor, through the solution. This was found to remove all the dissolved hydrogen sulfide but not to affect significantly the concentration of hydrogen peroxide. A sample was then pipetted from this aerated solution and the hydrogen peroxide concentration determined by titration with standardized potassium permanganate.

Some hydrogen peroxide disappearance in the reactor was caused by decomposition rather than by reaction with hydrogen sulfide. The extent to which this occurred was determined by a series of comparative runs made using the same procedure as above except that nitrogen, instead of hydrogen sulfide, was bubbled through the solution.

Studies were made at temperatures of 24 to 61°, initial hydrogen peroxide concentrations of 0.34 to 1.18 wt. %, and in the presence and absence of sulfuric acid. The concentrations of sulfuric acid used were 0.30 and 0.76 wt. %, corresponding to *p*H values of 1.5 and 1.2, as calculated from the ionization constant of sulfuric acid. The *p*H of the hydrogen sulfide solution alone was similarly calculated to be 4.0. The hydrogen sulfide concentration was assumed to be equal to the saturation value at temperature of study. Studies of the decomposition of hydrogen peroxide alone were made with solutions containing 4 to 12 wt. % hydrogen peroxide. Relative to the rate of reaction with hydrogen sulfide, the peroxide decomposition rate was negligible for all runs except a few at elevated temperatures in the absence of sulfuric acid.

Discussion

The heterogeneous decomposition followed a first order-rate expression

$$-\mathrm{d}C_{\mathrm{H}}/\mathrm{d}\theta = k_{\mathrm{d}}C_{\mathrm{H}} \qquad (2)$$

where C_{H} represents the concentration of hydrogen peroxide in gram moles per liter; θ, reaction time, minutes; and k_{d} the specific reaction rate constant, min.$^{-1}$ The value of k_{d} is dependent upon the specific apparatus used here and has no more general significance.

The reaction between hydrogen sulfide and hydrogen peroxide was also found to be first order with respect to hydrogen peroxide. The observed rate of disappearance of hydrogen peroxide due both to reaction with hydrogen sulfide and to heterogeneous decomposition can thus be expressed as

$$\frac{-\mathrm{d}C_{\mathrm{H}}}{\mathrm{d}\theta} = (k_{\mathrm{s}} + k_{\mathrm{d}})C_{\mathrm{H}} = k_0 C_{\mathrm{H}} \qquad (3)$$

It is important to note that k_{s} is a function of the concentration of hydrogen sulfide. The character of this function could not be determined in the present studies since the concentration of hydrogen sulfide was held constant at each temperature at a value corresponding to the equilibrium saturation value. Additional experiments showed that the concentration of hydrogen sulfide at saturation was not significantly affected by the presence of either sulfuric acid or hydrogen peroxide in the concentration ranges studied.

Values of the logarithms of k_{d} and k_0 are plotted against the reciprocal of the absolute temperature in Fig. 1. The values of k_{s} are essentially equal to k_0 at *p*H values of 1.2 and 1.5. Even at a *p*H of 4.0, k_{d} is practically a negligible correction factor.

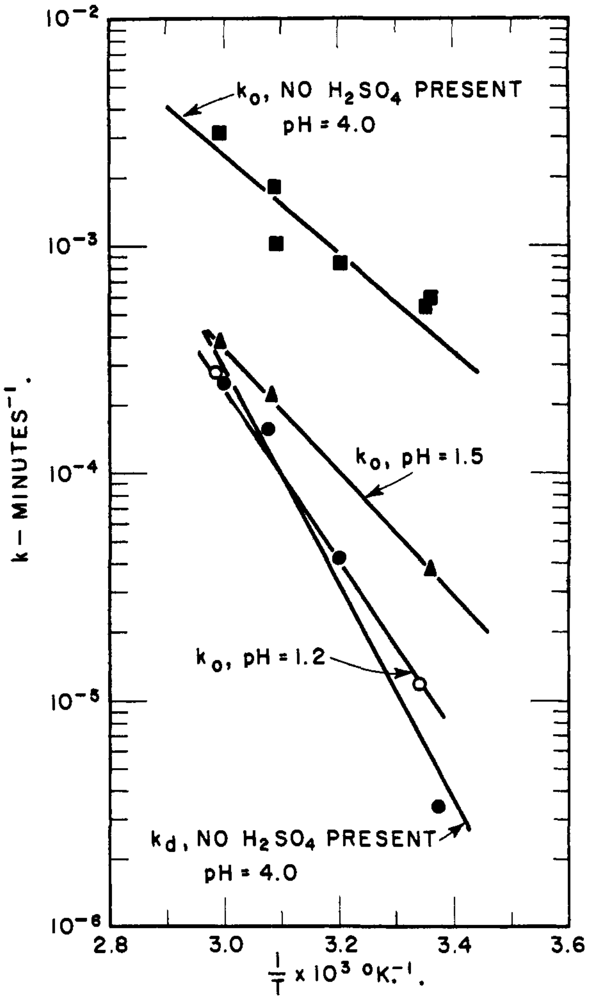

Fig. 1.—Effect of temperature on reaction rate.

It is seen that the reaction rate is a strong function of the acidity, the value of k_{s} being inversely proportional to about the 0.4 to 0.5 power of the hydrogen ion concentration. The values of k_{s} at the highest temperature and highest *p*H values are probably the most accurate because the rate is most rapid under these conditions.

The marked decrease in reaction rate with increased acidity cannot be attributed to a decreased solubility of hydrogen sulfide, since this is negligibly changed over the *p*H range here. Instead some reaction of hydrogen peroxide molecules with HS^- ions or hydrogen sulfide with HO_2^- ions is suggested, although the fact that the rate is inversely proportional to a fractional order of the hydrogen ion concentration indicates a more complicated mechanism.

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