existence of solid solutions between isomorphous crystals. A bromine atom differs considerably from a chlorine atom; however, in the formation of solid solutions of potassium bromide and chloride, replacements of one by the other occur, apparently at random.[12] It is evident that in the case of such a solid solution distortions similar to those presumed to occur in $(NH_4)_3MoO_3F_3$ are present, and that the symmetry of the entire atomic arrangement is retained because of the random distribution of the distortions. For the solid solutions which show simple stoichiometrical relations between the amounts of the constituents present, the formation of larger units of structure may be invoked in explanation, as in (1), but this cannot be done in general.

Summary

Cubic crystals of ammonium fluoferrate, fluo-aluminate and oxyfluomolybdate have been prepared and their structures determined by means of data from spectral, Laue and powder photographs interpreted with the aid of the theory of space groups. The units of structure, based on a face-centered lattice, contain four molecules. The arrangement of atoms within the units is shown in Fig. 4 and the values determined for d_{100} and the parameter u are given in Table VIII.

The structures of these crystals are closely related to those of ammonium chlorostannate and isomorphous salts; the crystals likewise show very good octahedral cleavage.

In interpreting the data for ammonium oxyfluomolybdate, atoms of oxygen and fluorine were considered to be crystallographically equivalent, arguments being given in justification of this supposition.

PASADENA, CALIFORNIA

NOTE

Effect of Pressure on Overvoltage.—A recent article by Bircher and Harkins[1] on the effect of pressure on overvoltage gives results quite divergent from those of Goodwin and Wilson.[2] Some measurements of the author are in concordance with the results of Bircher and Harkins, and it is felt that they are worth publishing in order to give weight to what appear to be the correct data.[3]

Bircher and Harkins concluded that the hydrogen overvoltage on lead, mercury and nickel increases with decrease in pressure from 760 mm. to 11 mm. by the same amount that the reversible hydrogen electrode potential decreases with pressure decrease. Thus the cathode potential,

---

[12] Vegard, *Z. Physik*, **5**, 17 (1921).

[1] Bircher and Harkins, THIS JOURNAL, **45**, 2890 (1923).

[2] Goodwin and Wilson, *Trans. Am. Electrochem. Soc.*, **40**, 172 (1921).

[3] These data were obtained in 1922 but were delayed in publication.

while the electrode is polarized, remains constant, with change in pressure if measured against the Hg,$HgSO_4$ electrode which does not depend appreciably on pressure. Bircher and Harkins used very low current densities (from 2 to 30 micro-amperes per sq. cm.) to prevent stirring, but the same conclusions are obtained by the author, for much larger current densities, where at low pressures, the stirring is violent.

Experimental Data

The experimental details of the present work were all essentially the same as those for previously published measurements on the effect of current density on overvoltage.[4] The electrodes were made of pure, smooth metal (polished with No. 0000 emery paper) 1 cm. square, the electrolyte was 2 *N* sulfuric acid; the reference electrode was the Hg,-Hg_2SO_4 electrode, sealed on to the U-tube containing the cathode and a platinized platinum anode. The cell was immersed in a thermostat at 25°. The system could be evacuated down to the vapor pressure of the electrolyte which is about 2.2 cm. of mercury. The data are given in Table I. In the first column the total pressure over the solution is given in centimeters of mercury. In the other columns the cathode potentials in volts at the stipulated current densities are listed. It is seen that while there is a certain amount of variation in the values, it is hardly more than the usual irregularities of overvoltage measurements. One might conclude that there is a tendency toward lower potentials at the lower pressures, but this could be easily explained as due to the greater stirring at low pressures.

Remembering that the above potentials are measured against an electrode, not changing with pressure and that the reversible hydrogen electrode decreases with decrease in pressure by the easily calculated amount,

$$E_R = \frac{RT}{2F} \ln P_{H_2} \qquad (1)$$

the overvoltage on the above electrodes must be increasing by the same amount. We can therefore express the change of overvoltage, E, with pressure by the equation

$$E = E_0 - \frac{RT}{2F} \ln P_{H_2} \qquad (2)$$

where E_0 is the overvoltage at one atmosphere. As previously mentioned, this is also the conclusion of Bircher and Harkins. They explain the divergence of Goodwin and Wilson's values as due to the non-functioning of the reversible hydrogen electrode. This explanation is probable but in any case the latter determined the so-called "bubble point" overvoltage which lacks the definiteness of an overvoltage for a stipulated current density, particularly at low pressures.

[4] Knobel, Caplan and Eiseman, *Trans. Am. Electrochem. Soc.*, **43**, 55 (1923).

Table I

Change of E.m.f. of Discharging Hydrogen with Pressure at Constant Current Density

	E.m.f. against Hg,Hg_2SO_4 electrode H_2 on platinized Pt				H_2 on smooth lead			
Pressure Cm. of Hg	10 ma. per sq. cm.	50	200	1000	Pressure Cm. of Hg	10	100	1000
76.5	0.7042	0.7197	0.7357	0.78	75.5	1.451	1.753	1.875
36.1	.7051	.7194	....	..	48.3	1.451	1.752	1.868
15.2	.7040	....	.7357	..	27.2	1.451	1.752	1.869
6.3	.7036	.7192	....	.81	12.6	1.450	...	1.875
2.4	.7029	.7183	.7360	..	6.6	1.450	...	...
2.2	.7033	.7186	.7360	.83	2.2	1.451	1.751	1.92

	H_2 on smooth copper			H_2 on smooth nickel		
	10 ma. per sq. cm.	100	1000	10	100	1000
75.5	1.304	1.322	1.800	1.163	1.392	1.605
48.1	1.302	1.320	1.800	1.164	1.392	1.589
27.4	1.301	1.318	1.798	...	...	...
12.6	1.299	1.316	1.802	1.160	1.386	1.605
6.6	...	1.317	1.809	...	1.390	1.63
2.2	1.299	1.314	1.82	1.155	1.392	1.77

The values at the lowest pressure are somewhat uncertain due presumably to the violent stirring.

Contribution from the Electrochemical Laboratory
Massachusetts Institute of Technology
Cambridge A, Massachusetts

Max Knobel

Received June 18, 1924
Published December 13, 1924

[Contribution from the Kent Chemical Laboratory of the University of Chicago and from the Chemical Laboratory of Mount Holyoke College]

THE REACTION OF BROMONITROMETHANE WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE[1]

By Mary L. Sherrill

Received June 17, 1924 Published December 13, 1924

In the field of the nitro aliphatic compounds, a number of investigators, Victor Meyer, Nef, Hantzsch, Holleman and L. W. Jones, have studied the structure and instability of these compounds and have proposed various structural formulas. Jones[2] has given an electronic interpretation of the nitroparaffins and by intramolecular oxidation and reduction has explained the various decomposition products. Very little work has

---

[1] This communication is an abstract of part of a dissertation submitted by Mary L. Sherrill in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago. The experimental work was done in the Chemical Laboratory of Mount Holyoke College.

[2] Jones, *Am. Chem. J.*, 50, 429 (1913).