

surface containing a potential; and the cell is not in equilibrium and hence will not give a constant electromotive force, if the two portions are mixed.

(c) Cells containing a liquid junction between two solutions having a single ion in common are not in equilibrium unless there is a restriction placed on the method of making the liquid junction, so as to remove an irreversibility at this boundary.

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NOTES

An Attempt to Measure the Potential of the Fluorine Electrode.—Elementary fluorine is apparently the strongest oxidizing agent that has yet been prepared, as is seen from its extreme chemical activity and the ease with which it replaces oxygen and chlorine from their compounds. A determination of the potential of the fluorine electrode would therefore be of very great interest, and serve as a basis for the calculation of the free energies of fluorine compounds.

The only attack upon this problem of which we are aware is the rough estimate of the free energy of formation of hydrogen fluoride gas made by Lewis and Randall¹ using an empirical rule suggested by Eastman. The problem, although obviously difficult from an experimental standpoint, was so inviting in view of its importance that we attempted to measure the electromotive force of a cell consisting of a hydrogen electrode and a fluorine electrode with an electrolyte containing both hydrogen and fluoride ions and in which the activity of hydrogen fluoride either is known or may be determined. Two such liquids are fused potassium acid fluoride and liquid anhydrous hydrofluoric acid containing some ionized material such as potassium fluoride. Aqueous or organic solvents may not be used due to the violence of the reaction of fluorine with water and organic materials.

Although we were unsuccessful, a brief account of the experiments may be of value in guiding others who later attempt the same task.

Anhydrous hydrofluoric acid failed to work for two reasons. The first and most important of these is that no electrode material could be found that would withstand the combined action of fluorine and hydrofluoric acid. Platinum, iridium, gold, and nickel all react with fluorine under these conditions. Moissan² was able to obtain only a 20% yield of fluorine from a platinum electrode in hydrofluoric acid at low temperatures, the rest of the fluorine going to form platinum fluoride. After trying these metals there remained only one material, graphite, which

¹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., 1923, p. 463.

² Moissan, *Compt. rend.*, 102, 1543 (1886); 103, 202, 256 (1886).

held out any hope of success. As has been previously noted³ graphite rods placed in liquid hydrogen fluoride quickly disintegrate and fall to pieces, and the disintegrated material seems to react readily with fluorine; in fact in these experiments several explosions resulted. The second difficulty encountered was the choice of suitable insulating material for the electrodes. This, although not insuperable, involves difficult design of the apparatus. The problem as to suitable containing material was not solved. A fluorite vessel could of course be used, but it is open to question whether this menstruum of fluorine and hydrofluoric acid would not react with gold or platinum sufficiently rapidly to cause trouble.

In fused potassium bifluoride a metallic electrode for the fluorine is out of the question for at that elevated temperature the metals react rapidly with fluorine, at least superficially. In contrast to its behavior in the liquid acid, graphite is but little affected in the fused salt bath. Graphite is used as the anode in the preparation of fluorine.³ Graphite electrodes of various shapes and sizes were tried for the fluorine side of the cell; and platinum and iridium electrodes of many varieties were tried for the hydrogen side, but of no avail. Current was supplied to the cell to electrolyze fluorine on the graphite electrode and saturate it and the bath with gas. The back electromotive force of the cell was measured after the electrolyzing current was stopped, but this decayed rapidly to zero giving no indications of the desired potential. Two difficulties in technique were encountered in handling these fused salt cells. The salt had a tendency to creep up the gas entry tube and congeal in the colder portions of it, and only small pressures could be put on the fluorine stream from the generator. Both these difficulties were overcome, but the desired electrode potential was not obtained.

The difference of behavior of graphite in the two liquids is a point of some interest. The fused salt does not wet the graphite while the acid does and is absorbed by it. This may partially account for the action, as the acid would then be able to react with the small amount of silicious material necessary for binding. On the other hand it is hard to explain the reaction of fluorine with the disintegrated material by this means, for fluorine can be electrolyzed on graphite in the fused salt with but little effect. It may be impossible to prepare compact graphite without a small amount of reactive binding material.

The apparently insuperable difficulties we encountered indicate that a more promising approach would be the study of chemical equilibria involving the dissociation of some fluoride such as gold fluoride, or the replacement of oxygen or chlorine from their compounds, by fluorine. It

³ Argo, Mathers, Humiston and Anderson, *Trans. Am. Electrochem. Soc.*, **35**, 335 (1919).

should also be possible to calculate such free energies from specific-heat curves. We hope to be able to carry out work along these lines.

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Attempts to Prepare a Fluocarbonate and their Bearing upon the Coördination Number of Carbon.—The maximum number of atoms that can be directly linked to a carbon atom is considered by the organic chemist to be four. However, the existence of such a compound, as H_2SiF_6 , containing the closely related element silicon, and where the silicon atom is probably surrounded by six atoms of fluorine, suggests the possibility that carbon also, under exceptionally favorable circumstances, might show a higher coördination number than four. When we examine the factors that determine whether or not two binary compounds possessing a common negative constituent will unite to form a double compound certain generalizations are at once apparent. We note first that complex halides are more stable, the more positive the ionized metal; hence, cesium which "lets go of its electrons most readily," should be the most favorable positive element to use; second, we note that fluorine gives more stable complexes than chlorine, etc. For example, we have fluosilicates but no chlorosilicates. We may, therefore, conclude that the compound most likely to show a carbon atom surrounded by six negative atoms would be cesium fluocarbonate.

The preparation of this compound was attempted by allowing carbon tetrafluoride to act upon cesium fluoride at various temperatures. Carbon tetrafluoride was prepared according to one of the methods given by Moissan,¹ that is, the action of carbon tetrachloride upon silver fluoride, the latter prepared by the action of fluorine upon silver oxide or silver chloride. Silver fluoride being deliquescent, the preparation of the anhydrous salt from the wet salt is not satisfactory.

Attempts to make the carbon tetrafluoride react with the cesium fluoride were made as follows. The former was condensed to a liquid on a weighed sample of the latter in a platinum boat cooled to -80° . The boat and contents were brought to room temperature and weighed; there was no increase in weight. Carbon tetrafluoride was passed into a suspension of cesium fluoride in alcohol at -80° . Upon evaporation of the alcohol at room temperature there was again no evidence of increase in weight. Upon introduction of an excess of solid cesium fluoride into gaseous carbon

¹ Moissan, *Compt. rend.*, 110, 951 (1890).

tetrafluoride at -10° there was no diminution in pressure. The same negative result was found upon using barium fluoride.

Other attempts to prepare a fluocarbonate by the action of fluorine upon cesium carbonate and upon potassium bicarbonate resulted in the formation only of cesium fluoride and potassium acid fluoride.

It was thought that in spite of the theoretical considerations previously announced it might be worth while to determine whether hydrogen fluoride and carbon tetrafluoride would show any tendency to react. Mixtures of the two liquids were made in enclosed copper apparatus. The liquids were shaken together and then frozen. As the mixture was allowed to warm very slowly a time-temperature curve was taken. In every experiment the curves showed breaks only at the freezing points of the two liquids, indicating not only that there is no reaction between them, but that they are not appreciably soluble in each other.

The negative results of all these attempts to prepare fluocarbonic acid or a fluocarbonate render the possibility very remote of obtaining a carbon compound in which the carbon would show a greater coördination number than four.

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THE DOUBLE BOND

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In his paper, "The Atom and the Molecule," Lewis¹ pointed out that the double bond represents, because of the mutual repulsion of the nuclei, a point of weakness in the molecule; and he showed how dissociation might be supposed to occur at non-polar linkages producing parts more or less polar and reactive.

In the present paper it is proposed to show how this idea together with other specific assumptions of the octet theory may be used to account for the reactions of the double bond.

Discussion will be limited for the sake of brevity to double bonds between any pairs of the following atoms: carbon, nitrogen and oxygen. This can be done without much loss of generality because most important addition reactions occur at such double bonds.

It has been found convenient to represent the more or less cubical structures assumed in the Lewis theory by means of a plane projection. Since

¹ Lewis, THIS JOURNAL, 38, 762 (1916).