## Electrode Potentials and Adsorbed Ionic Films

BY HERSCHEL HUNT, JOSEPH F. CHITTUM, H. V. TARTAR AND H. K. MCCLAIN

Some time ago Tartar and McClain[1] presented data to show that the potential, between two parallel platinum or gold electrodes in certain solutions in contact with oxygen, changes as the electrodes are brought together. They reasoned that the change of potential was due to the rearrangement of an adsorbed ionic film. The variation in potential difference with distance was not found when hydrogen, carbon dioxide or nitrogen was over the solutions. The results indicated that oxygen played a unique role in producing the potential gradient.

Recent experiments at the Chemical Laboratory of Purdue University have shown that the change of potential with distance is not unique for oxygen. Furthermore, a potential change was obtained when electrodes of large area were a centimeter apart. Platinum electrodes fastened to the apparatus with solder did not give the same potential as the electrodes that were held on the supports by frictional contact or cemented on with picein wax. Microscopic examination showed the presence of an alloy of the base metal on the electrode surface. The pure platinum plates without solder gave no potential change regardless of the distance between them. These results lead to the conclusion that the potential change with distance is due to (1) a potential produced by the active metal, (2) localized polarization, (3) an IR drop in the solution due to currents between points of different composition on the same plate, and show (4) that the potential originally observed was not due to an ionic film.

The second paper by McClain and Tartar[2] showed that the zeta potential on gold and platinum particles is unaffected by an electrical field of the strength used in cataphoretic experiments. This finding, too, supports the idea that this potential change cannot be due to an ionic film of the thickness suggested in the first paper.

The above evidence would suffice as an explanation of the results reported by Tartar and McClain in their first paper were it not for the special role played by oxygen. Two platinum electrodes with slightly varying uniformity of surface when immersed in air-saturated electrolytes of the type used by Tartar and McClain give a potential difference of considerable magnitude. It would not seem unreasonable to suppose that local currents in the solution at the surface of a given electrode may also result from such potentials. There is also the possibility that in experimental work of this kind conditions may be obtained which would give local currents in the presence of oxygen that would disappear when this gas is removed.

The authors concur in the opinion that bringing parallel electrodes together would not produce a realignment of the ionic layers which one could measure potentiometrically.

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RECEIVED MARCH 6, 1937

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[1] Tartar and McClain, THIS JOURNAL, **53**, 3201 (1931).

[2] McClain and Tartar, *J. Phys. Chem.*, **38**, 161 (1934).

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## Fluorinated Derivatives of Methane

BY ALBERT L. HENNE

This paper presents information on $CHCl_2F$, $CHClF_2$, $CH_2ClF$ and $CH_2F_2$, which is more precise than that previously reported.[1] Large quantities of well purified material have now been prepared, and the boiling point determinations are believed to be correct to 0.1°.

$CHCl_2F$ and $CHClF_2$ are prepared from chloroform, while $CH_2ClF$ and $CH_2F_2$ are prepared from methylene chloride by the usual interaction with antimony trifluoride in the presence of a catalyst. It is to be noted that in both cases the reaction proceeds spontaneously to the difluoride stage; it is only by efficient dephlegmation of the reaction products that it is possible to obtain good yields of the monofluoride, $CH_2ClF$ or $CHCl_2F$. Moreover, this Laboratory has never obtained any evidence of fluorination to a further extent than $CHClF_2$, by $SbF_3$ and all efforts to cause such a reaction have consistently caused the replacement of the hydrogen by chlorine.

The stability of the difluorides is much greater than that of the monofluorides; they are practically inert to chemical reagents, except at exceedingly elevated temperatures. The physiological effect of the difluorides is slight, as illustrated by the fact that guinea pigs can stand concentrations of more than 20 volumes in air for hours with impunity. Conversely, $CHCl_2F$ and $CH_2ClF$ cannot be tolerated for long periods in concentration greater than a few per cent.; and it is found that their halogen atoms are still capable of the usual reactions of non fluorine bearing halides although in a much more sluggish way, and

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[1] Midgley and Henne, *Ind. Eng. Chem.*, **22**, 542 (1930).

only at higher temperatures. The monofluorides are inferior anesthetic agents while the difluorides have no such effect. These behaviors are in good agreement with the facts recently demonstrated that the atomic distances between the C and F atoms is 1.41 Å. in the monofluorides, while it is only 1.36 Å. in the difluorides.[2]

| | B. p., °C. | Per cent. F Calcd. | Per cent. F Found | Per cent. Cl Calcd. | Per cent. Cl Found |
|---|---|---|---|---|---|
| $CHCl_2F$ | 8.9 to 9.0 | 18.4 | 18.1 | 68.0 | 68.2 |
| $CHClF_2$ | −40.8 to −40.6 | 43.9 | 43.5 | 40.1 | 40.4 |
| $CH_2ClF$ | − 9.0 to − 9.1 | 27.7 | 27.4 | 51.8 | 51.8 |
| $CH_2F_2$ | −51.6 | 74.1 | 74.1 | ... | ... |

The analyses were carried out as described previously.[3]

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(2) Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(3) Henne and Hubbard, THIS JOURNAL, **58**, 406 (1936), and **56**, 1078 (1934).

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RECEIVED APRIL 3, 1937

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## Standardization of Ceric Sulfate with Potassium Iodide by the Acetone Method

BY DAVID LEWIS

That ceric sulfate can be substituted for potassium permanganate in oxidimetry has been established by many investigators. Among the reactions which take place quantitatively with both reagents is the oxidation of iodides. In a recent paper Kolthoff, Laitinen and Lingane[1] have shown that pure potassium iodide can be used as a primary standard for permanganate.

One of the indicator titration methods studied by them was the acetone method of Berg.[2] They report poor reproducibility and low results by this method. The writer's experience with this titration using ceric sulfate as oxidant is of interest in this connection. As previously demonstrated[3] the titer varies with the acid concentration. Within the range 0.9–2.7 *N* sulfuric acid the results are accurate to 0.1%. Below this range low results, above it high results, are obtained. With potassium iodate Berg recommends that the solution be 2–2.5 *N* in sulfuric acid. The low results of Kolthoff, *et al.*, were obtained in solutions initially 0.9 *N*. Since the reaction between acetone and iodine is acid catalyzed, these low results are attributed to a low rate of reaction. As the end-point of this titration seldom lasts more than three minutes under the best conditions of acidity, it is not the low rate of reaction but probably the concomitant production of new reducing substances which causes too much oxidant to be used. The most suitable acidity seems to vary with the oxidant.

In the routine standardization of ceric sulfate solutions with sodium oxalate, the writer has included a comparison with potassium iodide by the acetone method and potentiometrically. All three agree to ±0.1–0.2%. The potassium iodide was analytical reagent (Mallinckrodt) and was dried at 125–130° for three hours before use. For the accuracy indicated this treatment is sufficient, since titrations of aliquots by the acetone method and potentiometrically check to 0.1%.

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(1) Koltboff, Laitinen and Lingane, THIS JOURNAL, **59**, 429 (1937).

(2) Berg, *Z. anal. Chem.*, **69**, 369 (1926).

(3) D. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **8**, 199 (1936).

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RECEIVED MARCH 23, 1937

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## The Siene Bean. The Composition of Siene Beans. Some Characteristics of Siene Bean Oil

BY TOM S. PERRIN

The sturdy growth and abundance of fruit exhibited by the siene bean plant attracted the writer's attention. This investigation was undertaken with the idea that a knowledge of the composition of the seeds might reveal a use for them, as was the case with soy beans.[1]

The siene bean plant (*Daubentonio longifolia*), sometimes called "coffee bean" or "rattle box," grows abundantly both inland and along the Gulf Coast of Texas and Florida as a wild plant.[2] It is a perennial plant that may grow as large as the average peach tree. The tree produces a seed similar to that of the soy bean, the pod containing from four to eight seeds. Siene beans are very hardy and bear prolifically, producing fruit even the first year. Three pounds of shelled beans were gathered from one tree. The seeds are extremely toxic to sheep[3] and, as found in this Laboratory, to guinea pigs.

Standard procedures[4] were used in all deter-

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(1) Burlison, *Ind. Eng. Chem.*, **28**, 772 (1936).

(2) Schulz, "Texas Wild Flowers," Laidlaw Brothers, New York, 1928, p. 154.

(3) Marsh and Clawson, *J. Agr. Research*, **20**, 507–513 (1922); *Analyst*, **46**, 145.

(4) "Methods of Analysis of A. O. A. C.," Assoc. Agr. Chem. Washington, D. C., 1935, pp. 335–352, pp. 404–429.