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

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

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).