

necting medium do not give any better results than electrodes made of short wires.

5. The size of the metal exposed to the solution determines the precision with which electrodes properly prepared may be reproduced. Very small, short wires give erratic results, larger, short wires give consistent results but larger deviations than foils or longer lengths of wire, but two foils with dimensions greater than one square centimeter give differences of potential, when measured against one another, of less than 0.000010 volt.

6. The composition and age of the metal comprising the electrode is of little importance if the electrode is large enough. However, in 0.1 *N* hydrochloric acid when the electrodes were much smaller than one square centimeter, old roughened platinum seemed to give better results than either new platinum, platinum alloyed with iridium or gold, but the platinum and platinum alloys gave better results than the gold.

Two pieces of metal, cleaned and dried by the method suggested give very nearly the same potential differences whenever they are measured against one another, which fact enables an investigator to select, from a group of electrodes, a few electrodes whose potential differences will invariably be reproduced with great precision.

Work on the effect of nitrogen and on the reproducibility and accuracy of the electrode under other conditions is in progress.

NEW YORK, N. Y.

POUGHKEEPSIE, N. Y.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 273]

REDUCTION POTENTIAL OF QUADRIVALENT TO TRIVALENT IRIDIUM IN HYDROCHLORIC ACID SOLUTION

BY SHO-CHOW WOO

RECEIVED NOVEMBER 10, 1930

PUBLISHED FEBRUARY 9, 1931

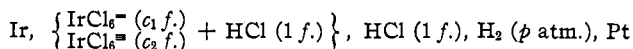
Introduction

It is well known that the most stable compounds of iridium in hydrochloric acid solution are the ions of hexachloriridic and hexachloriridous acids, H_2IrCl_6 and H_3IrCl_6 , in which the iridium is present in the quadrivalent and the trivalent states, respectively. Earlier investigations of these compounds were restricted to the determination of their formulas, and until very recently no studies had been made to determine their physico-chemical properties. Since this research was undertaken, however, Ogawa¹ has published measurements of the electromotive force of cells in which the sodium salts of the chloriridic and chloriridous acids were used. He observed steady changes in the electromotive force, and

¹ E. Ogawa, *J. Chem. Soc. Japan*, 50, 123 (1929).

attributed this to the hydrolysis of the salts in the absence of any added acid. In view of the inconstancy of his results it seems desirable to present the determinations that have been made in this Laboratory of the reduction potential for the combination quadrivalent-trivalent iridium in hydrochloric acid solution.

The value of this potential was derived from measurements of the electromotive force of the cell



The methods of preparation of the iridium solutions and the analytical procedures employed will be described in a later article.

This research was suggested by Professor A. A. Noyes, and to him and to Professor Don M. Yost the author is indebted for many helpful suggestions.

Procedure for the Electromotive Force Measurements.—The type of electrode vessel used was that commonly employed in this Laboratory.² The hydrogen was prepared by electrolyzing a solution of sodium hydroxide between nickel electrodes, and it was freed from oxygen by passing it over a glowing tungsten spiral. Before entering the cell, the gas passed through a hydrochloric acid solution of the same concentration as that in the cell.

In order to reduce the liquid potential to a very low value, the concentration of the hydrochloric acid in the iridium solutions was made the same as that used in the hydrogen half-cell, and the total concentration of iridium was made small.

The concentration of the hydrochloric acid in the iridium stock solutions was determined by titrating them with sodium hydroxide, using phenolphthalein as an indicator, after the quadrivalent compound had been reduced to the trivalent state with pure silver. The desired acid concentration for the cell solutions was attained by diluting the stock solutions with the proper amount of hydrochloric acid of known strength. The two half-cells were separated by an ungreased stopcock which was moistened with the acid but was kept closed.

It was found that gold and platinum (to a much less extent) were attacked by the chloriridic acid, but that iridium was not so attacked as was shown by the constancy of the potentials and concentrations. This fact resulted in the use of an iridium-plated glass tube as the electrode in the iridium half-cell. When nitrogen was bubbled through the iridium solution for the purpose of stirring it, the potential did not attain a constant value but usually decreased steadily. With a mechanical stirrer, however, the final electromotive force was reached in a few hours and then remained constant over long periods. The nitrogen may have

² Schuhmann, THIS JOURNAL, 46, 52 (1924).

contained some oxidizable impurity, for the concentration of the quadri-valent iridium was found to be always less (even 30–40% less) at the end of an experiment than at the beginning. No concentration changes were observed when the mechanical stirrer was used.

Results of the Electromotive Force Measurements.—In Table I is given a summary of the observed values of the electromotive force. The total acid concentration was always 0.998 *f.* (hereafter regarded as 1.0 *f.*). The "corrected" electromotive forces given in the last column are the values of the electromotive force calculated by the usual logarithmic formula for the case that the pressure of hydrogen is one atmosphere and the concentrations of the two forms of iridium are equal. The given electromotive forces, expressed in volts, are those of the cell in the direction in which it was written above.

TABLE I
RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS

Cell	Temp., °C.	Formal concentration		Pressure of hydrogen	Electromotive force	
		IrCl ₆ ³⁻	IrCl ₆ ⁴⁻		Observed	Corrected
1	25	0.004864	0.005163	719.5	-1.02403	-1.0263
2	25	.004838	.005189	720.2	-1.02365	-1.0261
3	25	.002477	.007631	719.7	-0.99689	-1.0265
4	25	.001976	.008148	720.1	-.98910	-1.0262
5	25	.001976	.008148	719.7	-.98953	-1.0267
					Mean	-1.0264
6	25			721.6	-1.02355	-1.0264
	20			719.8	-1.02840	-1.0313
7	25			721.7	-1.02243	-1.0264
	20			720.7	-1.02735	-1.0313

Discussion of the Results

The constancy of the corrected electromotive forces in Cells 1–5 shows that the ratio of the activity coefficients of the chloriridate ion and chloriridite ion does not change appreciably with change in their relative concentrations within the limits here involved. This behavior was to be expected since the difference in the ionic strengths of the solutions is small. Mention should be made, however, of the fact that less satisfactory corrected values were obtained with cells in which a large excess of the chloriridate was present. No explanation of this fact could be found. The difference, however, did not exceed 10 millivolts.

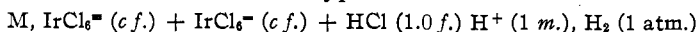
The mean value of the electromotive force at 25° is -1.0264 volts for the cell



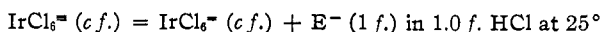
By taking the mean activity coefficient of the ions in 1.0 *f.* HCl to be 0.823 as given by Lewis and Randall³ and assuming that the H⁺ and Cl⁻

³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 336.

ions have in this acid equal activities, this electromotive force may be referred to the molal hydrogen electrode, in which case it becomes -1.021 volts. This is the value for the hypothetical cell



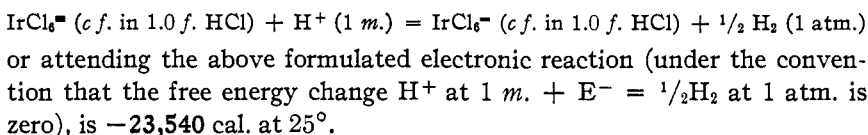
Under the usual conventions⁴ this value is also the molal electrode potential for the electronic reaction



In all these cases c is understood to have a value between 0.002 and 0.008 molal.

This potential corresponds to a greater reducing power than the value (-1.369 volts) for the chlorine electrode. It shows that chloriridous acid is oxidized to chloridic acid by chlorine at atmospheric pressure so completely that the unoxidized portion is entirely inappreciable.

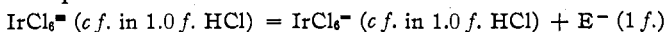
The corresponding value of the free energy decrease attending the reaction



From the measurements of the electromotive force of cells 6 and 7 at 25 and at 20° the value $+0.00098$ volt/degree is obtained for the temperature coefficient dE/dT ; and from this the corresponding value of the heat content increase ΔH attending this last reaction is found to be $+30,400$ cal.

Summary

There have been here presented measurements which show that half-cells consisting of metallic iridium in contact with a 1.0 formal hydrochloric acid solution of equimolal quantities of chloriridic and chloriridous acids (H_2IrCl_6 and H_3IrCl_6) at a concentration (c) between 0.002 and 0.008 formal, when measured against a half-cell consisting of a platinum electrode in contact with hydrogen gas at one atmosphere and with 1.0 formal hydrochloric acid solution, have an electromotive force of -1.0264 volts at 25° , and of -1.0313 volts at 20° . Referred to the molal hydrogen electrode (H^+ with activity 1.0 molal), the value of the reduction potential at 25° is computed to be -1.021 volts for the reaction



The corresponding value of the free energy decrease is $-23,540$ calories. From the temperature coefficient of the electromotive force, the heat content decrease for this electronic reaction is found to be $-30,400$ cal.

PASADENA, CALIFORNIA

⁴ See Noyes and Sherrill, "Chemical Principles," The Macmillan Co., New York, 1922, pp. 255-258.