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CONCERNING THE FORMAL POTENTIAL OF THE Ce(III) - Ce(IV) COUPLE IN PERCHLORIC
ACID SOLUTIONS

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Berkeley, California

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By

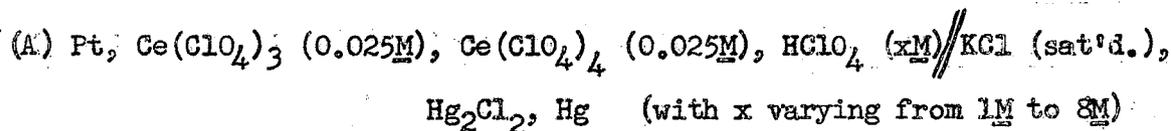
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A recent report by Duke and Bremer (1) has attributed the observations of Smith and Goetz (2) on the potential of Ce(III) - Ce(IV) couple in perchloric acid solutions to a decrease in the degree of hydration of Ce(IV) with increasing perchloric acid concentration.

This conclusion is thought to be unnecessary and an alternative explanation is offered.

The cell investigated by Smith and Goetz may be represented as follows:



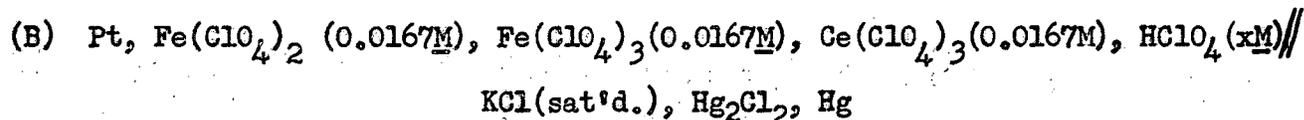
By assigning a single electrode potential to the saturated calomel electrode, Smith and Goetz then calculated the "single electrode potential" of the Ce(III) - Ce(IV) electrode. It is highly probable that a liquid junction potential exists between the perchloric acid solution and the saturated potassium chloride solution. Further, such a liquid junction potential will vary with the concentration of each of the species present in the solutions forming the junction. In particular, when the perchloric acid concentration is varied from 1M to 8M, one might reasonably expect to find large variations in the liquid junction potential. Consequently, an interpretation of the Ce(III) - Ce(IV)

potentials given by Smith and Goetz must await an evaluation of the liquid junction potentials in their cells. However, additional data given by Smith and Goetz permit the evaluation of the potential of a cell without transference provided we assume that the presence of relatively small (that is, 0.05M total) concentrations of Fe(II), Fe(III), Ce(III) and Ce(IV) will not appreciably affect the value of the perchloric acid-potassium chloride liquid junction.

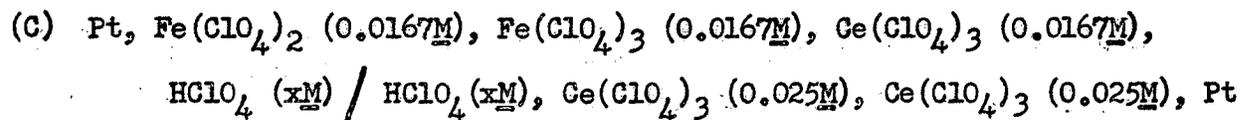
From the "half-equivalence" and "twice-equivalence" points of the titration curves of ferrous perchlorate with ceric perchlorate in various concentrations of perchloric acid given by Smith and Goetz, one may obtain the values (given in Table I) for "single electrode potentials".

It should be mentioned that the values of E_2 agree with those tabulated by Smith and Goetz from measurements on cell (A). This fact shows that the presence of $\sim 0.02M$ Fe(III) in the left hand cell compartment of cell (A) has but a small effect on the liquid junction potential in agreement with the assumption made above.

E_1 is the "single electrode potential" of the left electrode in the cell



By combining cells (A) and (B) we obtain the cell



The potential of this cell is given by the expression

$$(I) \quad E_{(c)} = E^\circ - 0.05914 \log \frac{a_{\text{Ce}^{IV}} \cdot a_{\text{Fe}^{II}}}{a_{\text{Ce}^{III}} \cdot a_{\text{Fe}^{III}}}$$

$$(II) = E^\circ - 0.05914 \log \frac{M_{Ce^{IV}} \cdot M_{Fe^{II}}}{M_{Ce^{III}} \cdot M_{Fe^{III}}} \cdot \frac{\gamma_{\pm Ce(ClO_4)_4}^5 \cdot \gamma_{\pm Fe(ClO_4)_2}^3}{\gamma_{\pm Ce(ClO_4)_3}^4 \cdot \gamma_{\pm Fe(ClO_4)_3}^4}$$

or since in the left cell compartment $(Fe^{II}) = (Fe^{III})$ and in the right cell compartment $(Ce^{III}) = (Ce^{IV})$ or $M_{Fe^{II}} = M_{Fe^{III}}$ and $M_{Ce^{III}} = M_{Ce^{IV}}$

$$(III) E_{(c)} = E^\circ - 0.05914 \log \frac{\gamma_{\pm Ce(ClO_4)_4}^5 \cdot \gamma_{\pm Fe(ClO_4)_2}^3}{\gamma_{\pm Ce(ClO_4)_3}^4 \cdot \gamma_{\pm Fe(ClO_4)_3}^4}$$

But

$$(IV) E_{(c)} = -E_1 + E_2$$

Hence, except in the lowest concentration of perchloric acid

$E_{(c)}$, given in Table I, is constant to within the accuracy claimed by Smith and Goetz (± 0.01 volts), and we may conclude that the rather complicated activity product in (III) is constant over a wide range of perchloric acid concentrations.

TABLE I

$M HClO_4$	$E_1, (Fe^{II}) = (Fe^{III})$	$E_2, (Ce^{III}) = (Ce^{IV})$ or $E_{(A)}$	$E_{(c)}$
1	-0.75 volts	-1.70 volts	-0.95 volts
2	-0.72	-1.71	-0.99
4	-0.76	-1.75	-0.99
6	-0.84	-1.82	-0.98
8	-0.89	-1.87	-0.98

It thus appears that no special explanation of the variation of the formal potential of the Ce(III) - Ce(IV) couple with perchloric acid concentration is necessary, since the formal potential of the Fe(II) - Fe(III) couple must undergo an approximately equal variation according to the above data, and there is no apparent reason for believing the

latter couple to be anomalous. It thus appears that the change in the formal potential of the Ce(III) - Ce(IV) couple as observed by Smith and Goetz is primarily due to a change in the liquid junction potential of the cells used by them.

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Bibliography

1. F. R. Duke and R. F. Bremer, AECU-1193.
2. G. F. Smith and C. A. Goetz, Ind. Eng. Chem., Anal. Ed., 10, 191(1938).