

to the assumptions that all the antimony exists as  $\text{SbOH}^{++}$  or as  $\text{Sb}^{+++}$ , respectively (computed by introducing the square or cube of  $c_A \alpha_A$  in place of its first power in the equation just given).

TABLE IV

THE MOLAL ELECTRODE POTENTIAL OF ANTIMONY					
Molality of $\text{HClO}_4$	Act. coef. of $\text{HClO}_4$	Conc. of Sb ( $\Sigma\text{Sb}$ )	Molal electrode potential ( $\text{SbO}^+$ )	Molal electrode potential assuming $\Sigma\text{Sb}$ equals ( $\text{SbOH}^{++}$ )	$\Sigma\text{Sb}$ equals ( $\text{Sb}^{+++}$ )
0.2312	0.778	0.000236	-0.209	-0.197	-0.181
0.4970	.762	.000317	- .213	- .204	- .196
0.8610	.798	.000575	- .213	- .210	- .206
1.1330	.852	.000752	- .213	- .213	- .213

Mean - .212

In view of these results we may evidently adopt  $-0.212$  as the molal electrode potential corresponding to the electrode reaction,  $\text{Sb}(s) + \text{H}_2\text{O} + 3\oplus = \text{SbO}^+ + 2\text{H}^+$ .

### Summary

The electromotive force of the cell  $\text{Sb}(s) + \text{Sb}_2\text{O}_3(s), \text{HClO}_4 (c_A \text{ m.}), \text{H}_2(g, 1 \text{ atm.})$  was measured at  $25^\circ$ , and was found to be  $-0.152$  volt; and the free energy of antimony trioxide ( $1 \text{ Sb}_2\text{O}_3$ ) was computed from this value to be  $-148,600$  cal. with an error which probably does not exceed  $\pm 300$  cal.

Solubility determinations of antimony trioxide in four concentrations of perchloric acid ( $0.2$ – $1.1 M$ ) were made. The results indicated that the dissolved antimony existed mainly in the form  $\text{SbO}^+$  at these concentrations of perchloric acid. From the solubility values and the electromotive force of the cell the molal reduction potential corresponding to the electrode reaction  $\text{Sb}(s) + \text{H}_2\text{O} + 3\oplus = \text{SbO}^+ + 2\text{H}^+$  was found to be  $-0.212$ .

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## THE ACTIVITY OF PERCHLORIC ACID IN AQUEOUS SOLUTION

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### Plan of the Investigation

In the research on the molal reduction potential of antimony described in the preceding paper a knowledge of the activity of perchloric acid was required. Moreover, it is of general interest to ascertain the activity relations of this univalent oxyacid, the first one to be investigated. Its activity coefficient was therefore determined by measuring the electromotive force of cells of the type  $\text{H}_2 (1 \text{ atm.}), \text{HClO}_4, \text{HCl}, \text{H}_2 (1 \text{ atm.}),$

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the two acids being at the same or nearly the same concentration. The measurements were made at 25° at four concentrations of the acids lying between 0.1 and 1.0 *M*. The liquid potential between the two solutions is very small in the case of this cell, owing to the slight difference in the mobilities of perchlorate and chloride ions, and it can be estimated with sufficient accuracy to enable a correction for it to be made.

This research was undertaken at the suggestion of Professor A. A. Noyes, to whom I am indebted for many helpful comments.

### Preparation of the Solutions and the Experimental Procedure

The perchloric acid solutions were prepared as described in the earlier paper. The four hydrochloric acid solutions were prepared by distilling a pure commercial acid and diluting the middle constant-boiling portion by weight. The concentrations of the solutions thus prepared were checked by titration with a standard alkali.

The apparatus was similar to that used in the investigation previously described. Two hydrogen half-cells, each containing two electrodes, were sealed to the two sides of the connecting part of that apparatus. The hydrogen was taken from the same generator and passed through the purifier, and then run through the two half-cells in parallel. The measurements were made with one of the stopcocks in the connecting part closed. Such cells after a few hours reached values constant within 0.03 millivolt.

### The Observed and Corrected Electromotive Forces

Table I contains the final results of the measurements of the electromotive force at 25° in the direction from the perchloric to the hydrochloric acid solution. The concentrations are expressed as molalities, that is, in moles per 1000 g. of water. The headings are for the most part self-explanatory. The electromotive force ( $\delta E$ ) due to the unequal molalities, and that ( $E_L$ ) due to the liquid potential, were calculated by the equations,

$$\delta E = -0.05915 \log \frac{C_{\text{HClO}_4}}{C_{\text{HCl}}}; \text{ and } E_L = -0.05915 \log \frac{\Lambda_{\text{H}} + \Lambda_{\text{ClO}_4}}{\Lambda_{\text{H}} + \Lambda_{\text{Cl}}}$$

The values of the equivalent conductances at 0.05 *M* concentration were used, namely, 391.4 for perchloric acid<sup>2</sup> and 398.5 for hydrochloric acid,<sup>3</sup> since accurate data are not available for perchloric acid at lower concentrations; and the liquid potential was calculated to be +0.00047 volt.

TABLE I  
THE OBSERVED AND CORRECTED ELECTROMOTIVE FORCES

Molality of		Observed e.m.f.	E.m.f. corrected for	
HClO <sub>4</sub>	HCl		unequal molalities	liquid potential also
0.1000	0.1005	0.00060	0.00047	±0.00000
0.2312	0.2334	.00071	.00048	+ .00001
0.5194	0.5194	.00056	.00056	+ .00009
1.1380	1.1382	.00030	.00030	- .00017

<sup>2</sup> Smith, *THIS JOURNAL*, **45**, 360 (1923).

<sup>3</sup> Bray and Hunt, *ibid.*, **33**, 781 (1911).

### The Activity Relations of Perchloric Acid. Summary

The corrected electromotive forces given in Table I are so small as to be negligible in determining the relative activities of the two acids at the same concentration. Thus the largest value (0.00017 volt) would correspond to a difference of only 0.7% in the value of the activity coefficient of the hydrogen ion. The conclusion may therefore be drawn that the activity coefficient of perchloric acid is substantially the same as that of hydrochloric acid up to 1.1 *M*; and the values derived for the latter acid (for example, as summarized by Lewis and Randall<sup>4</sup>) may therefore be employed in mass-action and thermodynamic expressions relating to perchloric acid.

This conclusion is of general interest, inasmuch as it indicates that the behavior of both these acids, including the pronounced minimum in their activity-coefficients in the neighborhood of 0.5 *M*, is primarily determined by the hydrogen ion; the effects of the two anions being apparently relatively small and nearly equal.

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## THE SOLUBILITY OF SILVER BROMATE IN SOLUTIONS OF OTHER SALTS AND THE CORRESPONDING ACTIVITY RELATIONS

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### Introduction

The activity relations of largely ionized salts in the presence of other ions can be conveniently studied by determining their solubilities in the presence of other salts. Thus, for any salt the ratio of the solubility product in pure water to that in the presence of other ions is equal to the reciprocal of the ratio of the corresponding activity-coefficient products; that is, for a uni-univalent salt whose ions may be assumed to have the same activity coefficient  $\alpha$ , we have  $\alpha_0^2/\alpha^2 = s^2/s_0^2$  where the zero subscripts refer to the activity and solubility of the salt in pure water. It was the purpose of this investigation to obtain new data concerning this activity effect in the case of silver bromate, in order to test more fully the conclusion drawn by Lewis and Randall<sup>1</sup> that the activity coefficient  $\alpha$  of any ion is some function of the sum (called by them the "ionic strength") of the products of the molality  $c$  of each ion in the mixture by the square of its valence  $\nu$  (that

<sup>4</sup> Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 362.

<sup>1</sup> Lewis and Randall, THIS JOURNAL, 43, 1112 (1921).