An Unknown Property of the Calomel Half-Cell and the Estimation of Bromide–Chloride Mixtures

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It is a well-known fact that calomel reference electrodes, although prepared in the same manner and with carefully purified salts, do not always show exactly the same potential and they sometimes change as to their potential some months after their formation. The reasons for this change are not known. The author has found that rather small amounts of bromide contained in the potassium chloride vary the potential of the electrodes to such a degree that no one could anticipate it.

Furthermore, it was found that commercial potassium chloride always contained bromide, up to a degree of 0.1 and 0.01% or occasionally somewhat more even in the purest grades.[1] Potassium chloride free from bromide may be prepared by precipitating a saturated solution several times with alcohol. The calomel used will also contain varying quantities of bromides. In all cases where for this reason the solid phase is not in equilibrium with the solution the electrodes will not be stable.

Experiments

I. Eight tubes like A and B in Fig. 1 were filled with equal quantities of mercury, calomel and 1 *N* potassium chloride. They were connected with each other by a siphon filled with potassium chloride and agar. The e. m. f. of these cells was measured by a compensation apparatus; the measurements could be made with no more error than 0.2 mv. No difference of potential was found between two of these half-cells during a period of five days. Then 1 *N* potassium bromide solution was added to the tubes and the following differences of potential were measured with tube 1 as a reference electrode (Table I).

TABLE I

Tube	1	2	3	4	5	6	7	8
Mole % KBr	0	0.02	0.05	0.1	0.2	0.5	1	0
E. m. f. (mv.)	..	− .7	−0.9	−3.0	−3.7	−6.2	−12.8	0
Two days later	..	− .5	−0.9	−1.8	−2.7	−5.3	− 6.2	0

(1) It was rather difficult to estimate such small contents of bromide before the colorimetric reaction published by the author was known (*Compt. rend.*, **197**, 245 (1933)).

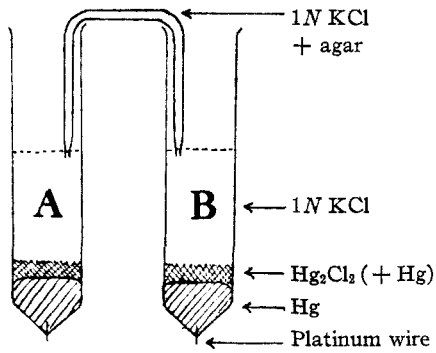

Fig. 1.

II. A calomel half-cell was used as a reference electrode. The siphon of the cell was finely drawn out on the exterior end and stopped by addition of agar. One cc. of mixtures of 1 *N* potassium chloride and bromide was poured into tubes like those in Fig. 1 but smaller, and one drop of a phosphate buffer solution ($p_H \sim 6$) and one drop of 0.01 *N* mercurous perchlorate were added thereto. The e. m. f. of the cell formed in this way was measured by compensation. By standardizing this combination, using mixtures of known percentages of bromide, it was possible to estimate the composition of unknown mixtures within a few minutes.

Summary

1. The potential of a calomel half-cell is strongly influenced by even the smallest contents of bromide in the potassium chloride used.

2. It is possible to use this effect in order to obtain a rapid estimation of bromide in chloride.

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