lowered until the mercury passes completely out of D′ and again raised, the air in contact with the walls may be passed out of L. By repeating the above-described operations several times the collecting tube is obtained practically free from gas. The gases to be collected are pumped directly into D′. At the conclusion of the pumping the gases may be passed over into the gas burette M by raising the reservoir and manipulating the stopcocks. Any minute bubbles which may have lodged between the mercury and the glass walls may, of course, be recovered completely, and thus another source of error avoided. The capillary tube G may be fastened to L′, if it is desired to transfer the gases to closed tubes in case the gases are to be preserved for a length of time.

We have found the following stopcock lubricant more satisfactory than the one described by Travers. 18 grams of pure gutta-percha are added in small quantities to 26 grams of melted paraffin (m. 70°) kept at a temperature of about 150° until the gutta percha is dissolved. 20 grams of heavy mineral oil (that supplied with the Fleuss patent pumps answers admirably) are added and the whole maintained in an oven at a temperature of 125–130° for four or five hours.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

ANALYSIS OF MIXTURES OF HALOGEN ACIDS. II.[1]

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Received September 15, 1909.

Most methods of analysis of mixtures of two halide ions require two gravimetric analyses. In addition, usually one distillation is required. The following described method involves one volumetric and one gravimetric determination for the estimation of the two ions.

An excess of silver nitrate is added and the precipitated silver salts are determined gravimetrically, best, of course, filtered and weighed in a Gooch funnel. The filtered solution, containing the excess of silver nitrate, is titrated with thiocyanate and ferric nitrate by the Volhard method.

Let (*a*) equal the weight of silver nitrate required to precipitate both of the halogens present and let (*b*) equal the weight of the silver halides precipitated. Also let (Cl), (Br), and (I) equal the respective weights of the halogen ions contained in the sample analyzed. Then if the estimations are made with the same sample or if the estimations are calculated on the basis of the same sample, we have, in the case of chlorine and bromine, the equations

[1] THIS JOURNAL, **31**, 525; *vide* also **31**, 1220.

$$(1)\quad \frac{169.89\,Cl}{35.46} + \frac{169.89\,Br}{79.92} = a,$$

$$(2)\quad \frac{143.34\,Cl}{35.46} + \frac{187.80\,Br}{79.92} = b,$$

from which, by elimination of Br, we obtain

$$a - \frac{169.89\,Cl}{35.46} \div \frac{169.89}{79.92} = b - \frac{143.34\,Cl}{35.46} \div \frac{187.80}{79.92},$$

and, by solving for Cl, we obtain

$$Cl = \frac{(35.46)(187.80)a - (35.46)(169.89)b}{(187.80)(169.89) - (143.34)(169.89)},$$

or, by further condensation, we obtain the simple equation

(I) $$Cl = 0.8817a - 0.7976b.$$

In a similar manner it can be shown that

(II) $$Br = 1.7976b - 1.5166a,$$

and when chlorine and iodine are involved in the analysis, that

(III) $$Cl = 0.5358a - 0.3877b,$$

(IV) $$I = 1.3877b - 1.1706a,$$

and when bromine and iodine are involved, that

(V) $$Br = 2.3501a - 1.7004b,$$

(VI) $$I = 2.7007b - 2.9851a.$$

Since application is made in these equations of data obtained by standard methods of analysis, the accuracy, as well as the simplicity of this method of indirect analysis, is manifest.

Solutions containing 23.46 g. Cl, 22.41 g. Br, and 22.30 g. I were prepared and 10 cc. of solutions were used for each analysis:

Weight used.	0.1 *N* $AgNO_3$.	Wt. $AgNO_3$.	(*a*) Wt. Ag salts.	Wt. found.
0.2346 g. Cl				0.2372 g. Cl
0.2241 g. Br	94.06	1.5985	1.4801	0.2281 g. Br
0.2346 g. Cl				0.2341 g. Cl
0.2230 g. I	83.74	1.4230	1.3648	0.2283 g. I
0.2241 g. Br				0.2191 g. Br
0.2230 g. I	45.43	0.7720	0.9380	0.2290 g. I

Mixture of the three halide ions can be estimated by this method, provided one of the halogens is separately determined. For instance, having found iodine by the palladious iodide,[1] the thallous iodide,[2] the nitrous acid,[3] the arsenic acid,[4] the chromic acid,[5] the permanganate,[6] the hy-

[1] Lassaigne. See text-books.

[2] Hübner and Spezia, *Z. anal. Chem.*, 11, 397; Hübner and Frerichs, *Ibid.*, 11, 400.

[3] Gooch. Jannasch, *Z. anorg. Chem.*, 1, 144.

[4] Gooch and Browning, *Am. J. Sci.*, 1890, 39; *Chem. News*, 61, 279.

[5] Donath, *Z. anal. Chem.*, 19, 19.

[6] Reinige.

drogen peroxide,[1] the electrolytic,[2] or by other methods, we can form the equations

$$(3)\quad \frac{169.89\,I}{126.92} + \frac{169.89\ Br}{79.92} + \frac{169.89\ Cl}{35.46} = a,$$

$$(4)\quad \frac{234.80\,I}{126.92} + \frac{187.80\ Br}{79.92} + \frac{143.34\ Cl}{35.46} = b.$$

Solving for Cl and Br in the same manner as above we obtain

(VII) $\quad Cl = 0.8817a - 0.7976b + 0.2954\,I,$

(VIII) $\quad Br = 1.7976b - 1.5166a - 1.2951\,I.$

If the chlorine is estimated separately by the acetic acid and manganese or lead peroxide,[3] or other methods, we have equations

(IX) $\quad Br = 2.3501a - 1.7004b - 0.4386Cl,$

(X) $\quad I = 2.7007b - 2.9851a + 3.3857Cl.$

And if the bromine[4] is estimated separately, we have the equations

(XI) $\quad Cl = 0.5358a + 0.3877b - 0.2280\ Br,$

(XII) $\quad I = 1.3877b - 1.1706a - 0.7720\ Br.$

Equations (I) to (XII) may be written in the following, most concise form:

$$Cl - Br\ (I)\begin{cases} Cl = 0.8817a - 0.7976b(+\ 0.2954\ I) \\ Br = 1.7976b - 1.5166a(-\ 1.2951\ I) \end{cases}$$

$$Cl - I(Br)\begin{cases} Cl = 0.5358a - 0.3877b(-\ 0.2280\ Br) \\ I = 1.3877b - 1.1706a(-\ 0.7720\ Br) \end{cases}$$

$$Br - I(Cl)\begin{cases} Br = 2.3501a - 1.7004b(-\ 0.4386\ Cl) \\ I = 2.7007b - 2.9851a(+\ 3.3857\ Cl) \end{cases}$$

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RECENT INVESTIGATIONS IN THERMOCHEMISTRY.[5]

BY THEODORE W. RICHARDS.

Received September 17, 1909.

Within a brief space of time, the world has lost two masters of thermochemistry, Marcellin Berthelot and Julius Thomsen. To these great men chemical science owes much; their places in its history are forever secure. Each, by his indefatigable labors, added both new methods and new data to the sum of human knowledge; and upon the broad foundation which they laid, all the subsequent development of thermochemistry must be built. All honor to their memories! It is no discredit to their faithful work that as science progresses many of their methods must be

[1] Cook, *J. Chem. Soc.*, 1885, 471.

[2] Specketer, *Z. Elektrochem.*, 4, 539.

[3] Vortmann.

[4] McCulloch, *Chem. News*, 60, 259.

[5] Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., on Sept. 16, 1909.