lations obtained by substitution of equation (2) in the proper thermodynamic equations.

TABLE II

THE VALUES OF *pK*, AND OF VARIOUS THERMODYNAMIC FUNCTIONS FOR THE IONIZATION OF GLYCOLIC ACID AT INFINITE DILUTION

Temp., °C.	*pK*, extrap.	*pK*, eq. (2)	$\Delta F°$ cal.	$\Delta H°$ cal.	$\Delta S°$ cal./deg.
0.3	3.875	3.8743	4850	1020	−14.00
12.5	3.844	3.8453	5028	660	−15.29
25.0	3.831	3.8310	5229	210	−16.83
37.5	3.833	3.8323	5450	−320	−18.59
50.0	3.849	3.8492	5695	−920	−20.55

For the ionization constant of glycolic acid at 25°, 1.49×10^{-4} is given in the "International Critical Tables"[7] whereas 1.475×10^{-4} is obtained from the present experiments. Larsson and Adell[8] report a value of *pK* for 18° only 0.002 lower than that given by equation (2), while Pedersen's[9] results are 0.008 lower at 0 and 18°.

The observed differences in the initial slopes of the lines in Fig. 1 are due to the specific effects of the cations present upon the term $-\log \gamma_{\mathrm{Cl}^-}\gamma_{\mathrm{HG}}/\gamma_{\mathrm{G}^-}$ in equation (1). This behavior is not inconsistent with the principle of specific interaction of Brönsted[10] but is in disagreement with the ionic strength principle of Lewis and Randall.[11]

Summary

1. The thermodynamic ionization constant of glycolic acid has been determined over the temperature range of 0 to 50°.

2. The free energy, heat content and entropy change for the ionization of glycolic acid at infinite dilution have been computed.

---

[7] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, p. 262.

[8] Larsson and Adell, *Z. physik. Chem.*, **A157**, 342 (1931).

[9] Pedersen, *J. Phys. Chem.*, **38**, 993 (1934).

[10] Brönsted, THIS JOURNAL, **44**, 877 (1922).

[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 380.

NEW HAVEN, CONN. RECEIVED MARCH 25, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrobromic Acid in Aqueous Solution from Electromotive Force Measurements

BY HERBERT S. HARNED, ALBERT S. KESTON[1] AND JOHN G. DONELSON

The activity coefficient and relative partial molal heat content of hydrochloric acid in aqueous solution recently have been evaluated over considerable temperature and concentration ranges from electromotive force measurements by Harned and Ehlers.[2] A similar study of aqueous hydrobromic acid solutions will now be described. A thorough investigation of the electromotive forces of the cell

$$\mathrm{H_2} \mid \mathrm{HBr}\ (m) \mid \mathrm{AgBr} - \mathrm{Ag}$$

has been made at temperatures varying from 0 to 60° and at concentrations of acid varying from 0.003 to 0.2 *M*. These results are supplemented by a few measurements at concentrations between 0.2 and 1 *M*. From these data, the standard potential of the cell, and the thermodynamic properties of aqueous hydrobromic acid solutions have been computed.

To meet the requirements of certain theoretical computations, the densities of these solutions were determined. From these, equations have been derived so that the normal concentrations may be calculated from the molal concentrations and *vice versa* at any temperature at which the cells were measured.

Experimental Procedure and Examination of Silver–Silver Bromide Electrodes

1. Hydrogen electrodes were the customary platinized platinum type.

2. The cells were of the usual U-shaped type. They were arranged so that they could be completely drained through suitable tubes through the bottom of the thermostat and subsequently filled *in vacuo*.

3. All solutions of hydrobromic acid were boiled *in vacuo* until free of dissolved air, saturated with hydrogen and then introduced into the cell.

4. Each solution was introduced into three cells. The electromotive forces were measured from 0 to 60° at 5° intervals. Three cells prepared in this manner possessed electromotive forces which varied from the mean by not more than ±0.05 mv. Triplicate results at twenty-

---

[1] The major portion of the material in this communication was taken from a Dissertation presented by Albert S. Keston to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1935.

[2] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

H_2 | HBr (m) | AgBr–Ag

m		0.01	0.02	0.05	0.1	0.2	0.5	1
E	Electrolytic[a]	0.3126	0.2791	0.2343	0.2006	0.1664	0.1188	0.0780
	Thermal[b]	.3127	.2786	.2340	.2005	.1663	.1190	.0781

[a] James. [b] This investigation.

$m = 0.01$

t		0	5	10	25	35	45	50
E	Electrolytic[a]	0.3023	0.3046	0.3069	0.3124	0.3154	0.3179	0.3189
	Thermal[b]	.3025	.3049	.3071	.3127	.3156	.3180	.3191
	Thermal[a]	.3028	.3051	.3073	.3129	.3157	.3182	.3192

[a] Donelson. [b] Keston.

five concentrations between 0.003 and 0.2 *M* were obtained, and five results between 0.2 and 2 *M*.

5. Silver–silver bromide electrodes have been studied with varying success by a number of investigators.[3] Like the other silver halide electrodes, silver–silver bromide electrodes are influenced greatly by the presence of oxygen, particularly in dilute solutions of hydrobromic acid. This is probably the principal cause of the discrepancies. On the other hand, there is the possibility that due to difference in preparation discrepancies may arise. The following results, however, will show that if oxygen is eliminated, results in close agreement may be obtained by the use of two types of electrodes. The first kind, those employed in the present study, were made as described by Keston[4] by heating an intimate mixture of 10% silver bromate and 90% silver oxide on a platinum spiral to 650°. The second kind were made by heating silver oxide on a platinum spiral to 450°, and then forming silver bromide upon the porous silver by electrolyzing either hydrobromic acid or a bromide solution. We shall refer to these types as thermal and electrolytic, respectively.

In Table I, electromotive forces of the cells at 25° determined by James[5] with electrolytic silver bromide electrodes are compared with the results with thermal electrodes. James rendered the hydrobromic acid solution air-free by the prolonged passage of nitrogen. The other series of results were made with hydrobromic acid solutions which had been boiled *in vacuo*, and thermal silver–silver bromide electrodes. The agreement is quite good.

That both the thermal and electrolytic types of electrodes give essentially the same result over a wide temperature range is shown by the second part of Table II, where values of the cell containing 0.01 *M* hydrobromic acid from 0 to 50° are shown. The first and third rows were obtained from cells containing the same solution of hydrobromic acid. The second and third rows represent completely separate results obtained with different apparatus and materials. The over-all reproducibility of the thermal type electrodes is within 0.2 mv. The electrolytic type electrodes in the oxygen free hydrobromic acid solution gave results at the lower temperatures 0.2 to 0.5 mv. lower than the thermal type. At higher temperatures, the agreement is better and of the order of 0.1 mv. A similar agreement for silver–silver iodide electrodes has been obtained by Owen.[6] All subsequent results were determined by employment of the thermal type electrodes.

Experimental Results

Since the actual observations were too numerous for convenient tabulation, they have been smoothed to round concentrations, then expressed as a function of temperature by the equation

$$E = a + b(t - 30) + c(t - 30)^2 \qquad (1)$$

The data from the lowest concentration to 0.1 *M* were smoothed by plotting $(E + 2k \log m - k\text{-}um^{1/2})$ against m (Eq. (5)) which was the plot employed for the evaluation of the normal potential of the cell, E_0. At the higher concentrations a different suitable function was plotted for the purpose of smoothing.

The over-all reproducibility of the cells was within ±0.1 mv. At a given concentration, the

---

(3) Lewis and Storch, THIS JOURNAL, **39**, 2544 (1917); Harned and Hamer, *ibid.*, **55**, 4496 (1933); Vance, *ibid.*, **55**, 4519 (1933); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

(4) Keston, THIS JOURNAL, **57**, 1671 (1935).

(5) These electromotive forces were determined by Dr. Geoffrey M. James at the University of Pennsylvania in 1927, and have not been published previously although activity coefficients derived from them are given in Taylor, "Treatise on Physical Chemistry," Chapter XII, 2d ed., D. Van Nostrand Co., New York, 1931, p. 772.

(6) Owen, THIS JOURNAL, **57**, 1526 (1935).

values of E calculated by equation (1) agreed with the smoothed electromotive forces to within ± 0.05 mv. Values of the constants a, b and c at convenient concentrations are given in Table II.

TABLE II

CONSTANTS OF THE EQUATION $E = a + b(t - 30) + c(t - 30)^2$

E = Electromotive Force of Cell: $H_2 | HBr (m) | AgBr–Ag$

m	($a = E_{30}$)	($b \times 10^6$)	($-c \times 10^6$)
0.001	0.43118	682.0	2.930
.005	.34910	416.0	2.860
.010	.31421	303.2	2.818
.020	.27958	192.3	2.742
.05	.23427	48.2	2.739
.1	.20021	− 57.0	2.571
.2	.16550	−162.5	2.620
.5	.11735	−303.9	2.662
1.0	.07612	−416.7	2.595

The densities of the hydrobromic acid solutions from 0 to 60° were determined by employing dilatometers which consisted of 125-cc. flasks, to which were sealed suitable lengths of uniform carefully calibrated capillary tubing upon which a mark was etched. The volume of the dilatometer at the designated temperature was found by introducing a known weight of pure boiled water, and measuring the height of the water meniscus above the etched mark; 1 mm. on the capillary corresponded to about 0.007% in the density. Known weights of carefully analyzed solutions of hydrobromic acid were introduced in the dilatometers, and their volumes determined by measuring the height of the meniscus at various temperatures between 0 and 60°. From these data, the densities of the acid solutions were computed.

It has been shown[7] that the densities of many aqueous solutions at a given temperature can be calculated by the equation

$$d = d_0 + Ac + Bc^{3/2} \qquad (2)$$

where d_0 is the density of water, and A and B are constants. In the range of concentration under consideration, it was found that for hydrobromic acid solutions, the third term on the right contributed a negligible amount. The simpler formula

$$d = d_0 + Ac \qquad (3)$$

was found to express the observed results to within $\pm 0.01\%$.

In Table III the constants of this equation are given at certain temperatures. To facilitate computations of normalities from molalities an equation used by Harned and Ehlers has proved convenient though less accurate than equation (3). Thus, at a given temperature

$$c/m = A' - B'm \qquad (4)$$

was found to hold to within 0.05%. The constants A' and B' are also given in Table III.

TABLE III

CONSTANTS OF EQUATIONS (3) AND (4)

t, °C.	d_0	A	A'	B'
0.25	0.99985	0.05714	0.9997	0.02278
4.60	1.00000	.05666	.9997	.02318
9.90	0.99971	.05618	.9995	.02360
17.30	.99872	.05556	.9984	.0241
25.00	.99704	.05538	.9969	.0243
32.85	.99475	.05505	.9944	.0245
40.15	.99216	.05495	.9919	.0245
50.00	.98804	.05488	.9878	.0245
59.80	.98310	.05500	.9830	.0244

Standard Potential from 0 to 60°

The standard potential of the cell, E_0, was determined graphically from the original electromotive forces. By combining the equation of the cell with the limiting equation for log γ of the theory of Debye and Hückel to which a term linear in m was added, the equation

$$E + 2k \log m - 2kum^{1/2} = E_0 - 2kbm \qquad (5)$$

is obtained. E is the measured electromotive force, k is 2.3026 RT/NF, u is the universal constant of the Debye and Hückel theory[8] and b is an empirical constant. The left side of this equation was plotted against m, and its value at zero m, or E_0, evaluated. The results are given in

TABLE IV

STANDARD POTENTIALS OF THE CELL

$H_2 | HBr (m) | AgBr–Ag$

t, °C.	E_0	(E_0 calcd. − E_0 obsd. (mv.))
0	0.08127	+0.07
5	.07955	+ .01
10	.07770	− .06
15	.07561	− .04
20	.07340	− .03
25	.07103	− .05
30	.06845	+ .01
35	.06575	+ .05
40	.06292	+ .07
45	.05997	+ .04
50	.05687	+ .03
55	.05363	+ .01
60	.05031	− .09

($E_0 = -\pi^\circ_{(AgBr)}$ where π°_{AgBr} is the standard potential of the AgBr–Ag electrode.)

---

(7) Root, THIS JOURNAL, **55**, 850 (1933).

(8) The values of u employed were taken from Table VII of the contribution of Harned and Ehlers.[2]

TABLE V

ACTIVITY COEFFICIENT OF HYDROBROMIC ACID

m	0°	15°	25°	35°	45°	60°
0.001	0.967 (0)	0.966	0.966 (0)	0.965	0.964	0.963 (0)
.005	.932 (0)	.930	.9295 (0)	.928	.927	.924 (−1)
.01	.910 (0)	.908	.906 (−1)	.905	.904	.898 (−2)
.02	.883 (0)	.8815	.879 (1)	.878	.875	.869 (−1)
.05	.843 (1)	.8415	.838 (2)	.834	.831	.826 (2)
.1	.812 (0)	.808	.805 (1)	.902	.797	.788 (0)
.2	.793 (2)	.787	.782 (0)	.777	.772	.758 (−3)
.5	.806 (0)	.797	.790 (1)	.781	.772	.760 (1)
1.0	.900 (3)	.888	.871 (2)	.856	.844	.823 (−2)
E_0	.08127	.07561	.07103	.06575	.05997	.05031

a = 4.4 Å.; $A\sqrt{2}$ = 1.428 at 0°; 1.446 at 25°; 1.484 at 60°.
B = 0.1715 at 0°; 0.1648 at 25°; 0.1555 at 60°.

The number in ( ) is the difference in the third decimal place of γ between observed result and that computed by equations (8) and (9). When positive observed γ is greater than that calculated.

Table IV. It was found that these values may be computed by the quadratic equation

$$E_0 = 0.06846 - 0.0005185\,(t - 30) \\ -2.973 \times 10^{-6}\,(t - 30)^2 \qquad (6)$$

after evaluating the constants by the method of least squares. The third column of this table contains the differences between the observed values and those computed by this equation.

The Activity Coefficient of Hydrobromic Acid in Aqueous Solution.—The equation relating the electromotive forces of the cell to the activity coefficient, namely

$$\log \gamma = -\log m - [(E - E_0)/2k] \qquad (7)$$

was employing in computing γ. Values of γ from 0.001 to 1 M are given at convenient temperatures in Table V.

These activity coefficients were then used to determine the constants of the isothermal equation

$$\log \gamma = -\frac{u\sqrt{c}}{1 + A\sqrt{2c}} + Bc - \log\,(1 + 0.036\,m) \qquad (8)$$

A equals $K'a$, where a is the mean distance of approach of the ions in Ångström units, and B is an empirical constant. The values of u and K' employed are to be found in Table VII of the article of Harned and Ehlers.[2] By substituting values of γ at 0.1 and 1 M and values of c computed by equation (4), two equations were formed from which A and B were computed at 5° intervals from 0 to 60°. From A, "a" was calculated. The thirteen determinations of "a" were between the limits of 4.21 and 4.52 Å. and the mean value was 4.40 Å. Harned and Ehlers obtained 4.2 Å. for hydrochloric acid by the same method. Neither of these cases indicate any definite variation of "a" with temperature. The B values may be expressed as a function of the temperature by the equation

$$B = 0.1715 - 0.000266t \qquad (9)$$

Values of γ were computed by these equations. The differences in the third decimal place of γ between the observed and calculated values are given by the parenthesized numbers in the table. The maximum deviation up to 0.2 M is 0.002, which is good agreement considering the range of temperature over which the equation has been applied. We have not employed the extended terms of the theory in the calculation since for uniunivalent electrolytes with an "a" value of 4.4 Å., their contribution is very small. If these terms had been used, "a" would have had the somewhat larger value of 4.5 Å.

Relative Partial Molal Heat Content and Heat Capacity of Hydrobromic Acid.—The relative partial molal heat content, $\bar{L}_2$, is related to the activity coefficient according to the equation

$$\nu\,\partial \ln \gamma/\partial T = -\bar{L}_2/RT^2 \qquad (10)$$

Upon substituting the value of ln γ given by equation (8), and performing the differentiation, we obtain the isothermal equation

$$\bar{L}_2 = \frac{U'c^{1/2}}{1 + A\sqrt{2c}} - V'\frac{1}{(1 + A\sqrt{2c})^2}\left[c\frac{\mathrm{d}A}{\mathrm{d}T} + \frac{A}{2}\frac{\mathrm{d}c}{\mathrm{d}T}\right] - \\ W'\left[B\frac{\mathrm{d}c}{\mathrm{d}T} + c\frac{\mathrm{d}B}{\mathrm{d}T}\right] \qquad (11)$$

In this derivation, D, c, T and B are variables and a is constant. The above equation is the equivalent of equation (19) of Harned and Ehlers[2] (p. 2170) or equation (10) of Harned and Hecker.[9] The isothermal constants U', V' and W' at 0, 25 and 60° are given in Table VI.

---

(9) Harned and Hecker, THIS JOURNAL, **55**, 4838 (1933).

TABLE VI

QUANTITIES USED FOR THE COMPUTATION OF $\overline{L}_2$ BY EQUATION (11)

	U'	$V' \times 10^{-5}$	$W' \times 10^{-5}$	dA/dT	$-dB/dT$	$-dA'/dT$	dB'/dT
0°	433	4.70	6.83	0.00044	0.000266	0	0.00008
25°	717	5.82	8.14	.00066	.000266	0.000255	.00002
60°	1261	7.85	10.16	.00105	.000266	.00086	0

TABLE VII

$\overline{L}_2$ OF HYDROCHLORIC AND HYDROBROMIC ACIDS AT 0, 25 AND 60°

	$\overline{L}_2$								
	0°		25°		60°				
m	HBr	HCl	HBr	HCl	HBr	HCl	$\alpha = (\overline{C}_p - \overline{C}_{p0})_0$	β	$(\overline{C}_p - \overline{C}_{p0})_{25}$
0.001	13	13	22	22	40	40	0.32	0.002	0.4
.005	29	28	47	45	80	81	.62	.004	.8
.01	39	39	64	63	109	108	.87	.005	1.0
.02	52	52	85	85	148	145	1.12	.008	1.5
.05	76	82	124	130	217	219	1.60	.012	2.2
.1	102	113	163	175	289	295	2.08	.017	2.9
.2	137	159	222	242	384	395	2.89	.020	3.9
.5	220	272	338	391	577	608	4.30	.027	5.6
1.0	(336)	427	(488)	611	(835)	896	(6.00)	(.035)	7.7

The temperature coefficients of B, c and A may readily be determined. $dB/dT = -0.000266$ according to equation (9). The values of $dA/dT = (dK'/dT)\, a$, given in Table VI, were obtained from the values of K' in Table VII of the article of Harned and Ehlers. Differentiation of equation (4) gives at constant temperature the equation

$$\frac{dc}{dT} = m\frac{dA'}{dT} + m^2\frac{dB'}{dT} \qquad (12)$$

from which dc/dT may be evaluated. Values of the temperature coefficients of A' and B' at 0, 25 and 60° are given in Table VI.

The values of $\overline{L}_2$ at 0, 25 and 60°, computed by equation (11) by use of the data in Table VI are given in Table VII. Values of $\overline{L}_2$ for hydrochloric acid calculated in a similar manner by Harned and Ehlers are given also in this table. Similar computations were made at other temperatures, and it was found that at a given concentration the results could be computed to within a few calories by the equation

$$\overline{L}_2 = \overline{L}_0 + \alpha t + \beta t^2 \qquad (13)$$

where α and β are constants, $\overline{L}_0$ the value of $\overline{L}_2$ at 0°, and t is the centigrade temperature. α is equal to the relative partial molal specific heat, $\overline{C}_p - \overline{C}_{p_0}$, at 0°. This quantity at other temperatures may be computed by the equation

$$\overline{C}_p - \overline{C}_{p0} = \alpha + 2\beta t \qquad (14)$$

derived by differentiation of equation (13) with respect to t. Values of $\overline{C}_p - \overline{C}_{p_0}$ at 25° are given in the last column of the table.

Because of the methods of smoothing the results, values of the derived calorimetric data should be more accurate in the intermediate temperature range (*e. g.*, 10–50°), and the maximum discrepancies should occur at 0 and 60°. The results indicate that $\overline{L}_2$ for hydrobromic acid is somewhat lower than the corresponding values of hydrochloric acid at concentrations above 0.05 *M*. Below this concentration, the results for the two acids are practically identical. No accurate values of $\overline{L}_2$ for hydrobromic determined calorimetrically are available for comparison.

As regards the relative partial molal heat capacity, the indications are that it is somewhat lower than that of hydrochloric acid at the lower temperatures and somewhat higher at the higher temperatures. At 25°, this quantity is very nearly the same for both acids. This is in agreement with Rossini's computations of the data of Randall and Rossini.[10] They found that the values of $(\overline{C}_p - \overline{C}_{p_0})$ of sodium and potassium bromides at 25° are nearly the same as the corresponding chlorides. The value of $(\overline{C}_p - \overline{C}_{p_0})$ for hydrobromic acid has not been accurately evaluated by a calorimetric method.

Summary

1. An investigation of the cell $H_2 \mid HBr\ (m) \mid AgBr - Ag$ at temperatures from 0 to 60° and from 0.001 to 1 *M* has been made.

2. The measurements were obtained with silver–silver bromide electrodes prepared by heating an intimate mixture of 10% silver bromate and 90% silver oxide. Comparison with like electrodes prepared by electrolysis was made.

---

[10] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931); **7**, 47 (1931); Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

Both types of electrodes give the same electromotive force within narrow limits.

3. Densities of aqueous solutions of hydrobromic acid over the above temperature and concentration ranges were determined.

4. The standard potential of the cell was evaluated from 0 to 60° at 5° intervals. Its value at any temperature within the above limit is given by equation (6).

5. The activity coefficient was computed by the extended Debye and Hückel theory (Eqs. (8) and (9)). As in the case of hydrochloric acid, the mean distance of approach of the ions was found to be constant from 0 to 60°.

6. The relative partial molar heat content and specific heat of hydrobromic acid was computed from these data. Comparison was made with like quantities for hydrochloric acid solutions, also computed from electromotive force measurements.

NEW HAVEN, CONN. RECEIVED MARCH 24, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 53]

Fluorobromides of Silicon

BY WALTER C. SCHUMB AND HERBERT H. ANDERSON

By the application of two methods previously used successfully in the preparation of the fluorochlorides of silicon[1] we have prepared the three analogous fluorobromides, $SiFBr_3$, SiF_2Br_2 and SiF_3Br. The first method consisted of the cleavage of hexafluorodisilane, Si_2F_6, by an excess of bromine. The two substances were allowed to mix in the gaseous condition in a cylindrical glass bulb and by heating at one point combustion occurred, the flame passing quietly through the whole bulb and the red color of the gaseous mixture becoming very much lighter. The excess of bromine was removed quantitatively by prolonged shaking with mercury in a flask. When the product was subjected to fractionation, in addition to the inevitable silicon tetrafluoride, a mixture in approximately equal amounts of difluoro- and trifluorobromide was obtained.

The second method consisted of the action of metal fluorides upon silicon tetrabromide, including the fluorides of zinc, titanium, silver and antimony. Of these, silver fluoride reacts too violently and titanic fluoride too slowly for satisfactory results. Because of the recent extension of the Swarts reaction[2] by Booth[1b] and co-workers to a variety of inorganic halides, resublimed antimony trifluoride was employed in most of the subsequent experiments. The usual catalyst, antimony pentachloride, could not be employed in this reaction, as at 100° interaction with silicon tetrabromide destroys the pentachloride with copious liberation of bromine. For a similar reason, antimony pentafluoride was not tried. Antimony pentabromide has not been isolated and free bromine itself does not noticeably aid the reaction.

After testing the effect upon the yields of mixed halides of variation in experimental conditions, the best results were obtained as follows. The antimony fluoride was added in 0.5 to 1.0-g. portions, at a rate of about 100 g. per hour, to 1000 g. (an excess) of bromine-free silicon tetrabromide maintained at the boiling point of the solution, which was contained in a three-necked flask, provided with a mercury-sealed stirrer and connected with three condensing traps provided with circular coils. The first trap, held at 20°, retained nearly all the $SiBr_4$ and $SiFBr_3$, with some dissolved material, chiefly SiF_2Br_2. The second and third traps were at -60 and $-65°$ (lower temperatures would cause solidification of the condensate). Uncondensed silicon tetrafluoride passed on through drying tubes and on escaping from the apparatus through an inverted funnel was hydrolyzed by a dilute solution of ammonia.

In each run a total of 300 g. of antimony fluoride was used; more silicon tetrabromide was added at intervals as needed, since some silicon tetrabromide was continuously distilled into the first trap. The yields obtained per 100 g. of antimony fluoride were the following: 30–40 g. of $SiFBr_3$, 8–18 g. of SiF_2Br_2 and 5–12 g. of SiF_3Br. The rate of addition of antimony trifluoride, the temperature, and the effectiveness of stirring, all

---

[1] (a) Schumb and Gamble, THIS JOURNAL, **54**, 3943 (1932); (b) Booth and Swinehart, *ibid.*, **57**, 1333 (1935).

[2] Swarts, *Bull. Acad. Roy. Belg.*, **24**, 309, 474 (1892).