The writer wishes to acknowledge his indebtedness to Dr. Herbert S. Harned at whose suggestion this investigation was undertaken, for help and many valuable suggestions throughout its execution.

Summary

Values are given for the activity coefficient of barium chloride from 0.01 to 1.65 M, of strontium chloride from 0.01 to 3.015 M, and of calcium chloride from 0.01 to 3.5 M.

Values for the cation transference numbers of these salts over similar concentration ranges are also given.

Values for these two quantities for the alkaline earth chlorides are grouped at round concentrations into a single table.

The values of the electromotive forces of cells without and with liquid junction from which these quantities were calculated are also given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, McGILL UNIVERSITY]

THE VISCOSITIES OF THE LIQUID HALOGENS

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On account of the interesting relationships existing between viscosity and chemical constitution, a great many determinations of the viscosities of organic liquids have been made. Little attention, however, has been paid to inorganic compounds and to the elements themselves.

The viscosity of bromine has been measured over a wide range of temperature by Thorpe and Rodger,[1] and also, at one temperature only, by Kann[2] and by Beck.[3] Beck has also measured the viscosity of liquid iodine at the melting point only. We have been unable to find any previous measurement of the viscosity of liquid chlorine. It was therefore considered of interest to determine the viscosities of liquid chlorine, bromine and iodine.

Chlorine

Preparation.—The chlorine was prepared from hydrochloric acid and potassium permanganate. The gas was washed twice with water and dried by bubbling through concd. sulfuric acid. It was then liquefied with solid carbon dioxide and ether and fractionally distilled four times, the middle portion always being retained. It was finally liquefied in the viscosimeter. At no time during its preparation did the gas come into contact with rubber or grease.

[1] Thorpe and Rodger, *Phil. Trans.*, **185A**, 397 (1894).

[2] Kann, *Wien. Ber.*, **106**, 2a, 431 (1897).

[3] Beck, *Z. physik. Chem.*, **48**, 641 (1904).

Description of Viscosimeter and Procedure.—The viscosimeter devised by Maass and Boomer[4] was employed with slight variations.

The apparatus, a sketch of which is shown in Fig. 1, consisted of an ordinary Ostwald viscosimeter A with two tubes sealed to it, one of which, B, was of about 25-cc. capacity. The reservoir B was connected through a tap C to another and larger bulb D.

The parts of the apparatus were cleaned and dried before being assembled. The apparatus was then evacuated and heated during evacuation, in order to drive off any water vapor held on the surface of the glass. The viscosimeter was then sealed to the chlorine generator and chlorine was liquefied in A. After the pressure had fallen to the vapor pressure of the chlorine, the tap H was opened and air, dried by passage over phosphorus pentoxide, was allowed to enter until the pressure was about atmospheric. The taps F and H were then closed and kept closed during the determination.

A was then immersed, with the bulb of a constant-volume hydrogen thermometer, in an unsilvered Dewar flask containing solid carbon dioxide and ether. The temperature was regulated by dropping in solid carbon dioxide as described by Maass and McIntosh.[5]

When the temperature had become constant, the tap C was closed and I opened, and the bulb D was warmed gently with a smoky flame. This increased the pressure on the right-hand side of A, and caused the chlorine to move up on the left-hand side. As soon as the liquid passed the upper etched mark on the viscosimeter, the flame was removed from D and the tap C opened, thus equalizing the pressure and allowing the liquid to fall, the time of fall being observed.

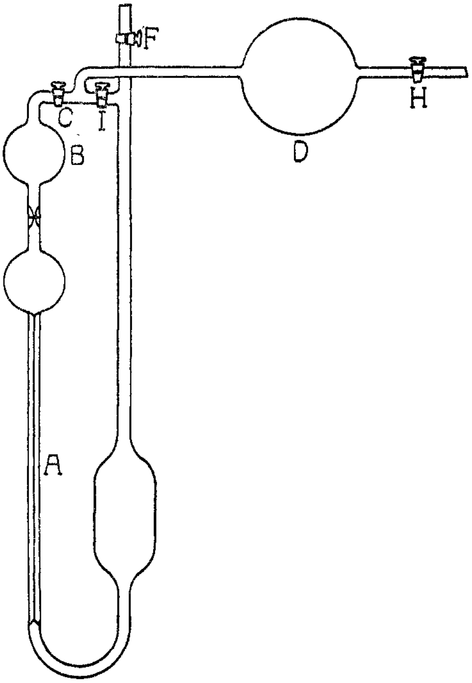

Fig. 1.—Chlorine viscosimeter.

When the required temperature range had been covered, the weight of the chlorine was determined by absorption in potassium hydroxide solution. Air was forced in at H, in order to sweep out the last traces of chlorine.

In order to avoid any possible contamination from tap grease, all the taps were lubricated with a paste made from phosphorus pentoxide and water.

The temperatures were measured by means of a constant-volume hydrogen thermometer.

Two series of measurements were made using different weights of chlorine.

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[4] Maass and Boomer, This Journal, **44,** 1709 (1922).

[5] Maass and McIntosh, *ibid.,* **35,** 536 (1913).

Calibration of Viscosimeter.—Known weights of water were placed in the viscosimeter and their times of fall at 20° determined. These times of fall were plotted against weight of water and from the curve the time of fall of any weight of water at 20° could be found.

Calculation of Results.—The weight of the chlorine and its density being known, the volume at each temperature was calculated. This volume was not corrected for the amount of chlorine present as vapor, because the much larger proportion of air present would render diffusion extremely slow and hence the amount of chlorine in the gaseous state was considered negligible. The time of fall of an equal volume of water was then found from the calibration curve. Then we have $\eta = \frac{\eta_0 dt}{d_0 t_0}$ where η, d and t are the absolute viscosity, density and time of fall, respectively, of chlorine and η_0, d_0 and t_0, the corresponding quantities for water at 20°. The values used for the density of chlorine were those previously determined by one of us.[6]

Results.—The values obtained are given in Table I and are plotted in Fig. 2.

TABLE I

VISCOSITY OF CHLORINE

DETERMINATION 1

Temp., °C.	−76.5	−70.5	−65.4	−60.0	−53.0	−45.1	−33.8
Abs. vis.	0.00729	0.00680	0.00646	0.00610	0.00569	0.00530	0.00489

DETERMINATION 2

Temp., °C.	−74.0	−65.8	−60.2	−52.4	−44.1	−35.4
Abs. vis.	0.00710	0.00649	0.00616	0.00566	0.00524	0.00494

As may be seen from the curve, Fig. 2, the results of the two determinations are in good agreement. The maximum divergence of any individual value from the smoothed curve is about 0.3%.

The equation of the viscosity-temperature curve, $\eta_t = \frac{\eta_0}{1 + At + Bt^2}$ was solved, using values of viscosity obtained from the curve. It was found that $A = 0.005878$, $B = -0.00000392$ and $\eta_0 = 0.00385$. This equation gave results in good agreement with the curve. From the curve the absolute viscosity at the boiling point was 0.00488.

Bromine

Preparation.—The bromine was prepared in two different ways, both given by A. Scott.[7]

The first method consisted of purification of the commercial product by shaking with several portions of dil. sodium hydroxide solution.

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[6] Johnson and McIntosh, THIS JOURNAL, **31**, 1138 (1909).

[7] Scott, *J. Chem. Soc.*, **103**, 847 (1913).

In the second method bromine was prepared from purified potassium bromide that had been freed from iodine as described by Scott.

Procedure.—On account of the high vapor pressure of bromine the apparatus used with chlorine was unsuitable as the volume of bromine present as vapor was not negligible. The apparatus was accordingly made much smaller, the total volume being about 75 cc. The reservoir B (Fig. 1) was omitted. In order to cause the liquid to rise in the viscosimeter, the tap C was closed and I opened. When D was warmed, some liquid was driven up: I was then closed and C opened, and when D was then cooled, more liquid was drawn up. It was usually necessary to repeat this process twice in order to drive the liquid past the upper mark on the viscosimeter.

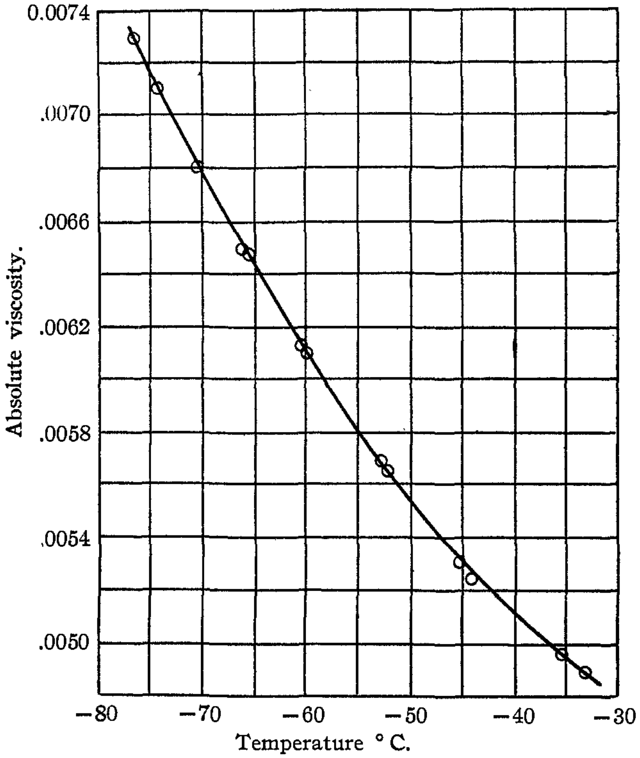

Fig. 2.—Absolute viscosity-temperature curve for liquid chlorine.

Owing to the small dimensions of the viscosimeter it was possible to weigh it on an ordinary balance. Thus the weight of the added bromine could be determined directly.

As in the case of chlorine, the instrument was calibrated with distilled water at 20°.

Temperature Bath.—A large glass water-bath was used, the temperature being regulated by the addition of hot or cold water. The bath was stirred by a motor-driven stirrer and the temperatures were observed by means of a constant-volume hydrogen thermometer. The temperature could be kept constant to within 0.1°.

TABLE II

VISCOSITY OF BROMINE

I. PURIFIED WITH NaOH

Temp., °C.	−2.6	7.0	13.6	19.5	27.0	31.4
Abs. vis.	0.01287	0.01136	0.01058	0.00995	0.00925	0.00901

II. PREPARED FROM PURIFIED KBr

Temp., °C.	−4.3	4.9	12.6	19.1	28.9	32.0
Abs. vis.	0.01311	0.01164	0.01071	0.01003	0.00911	0.00888

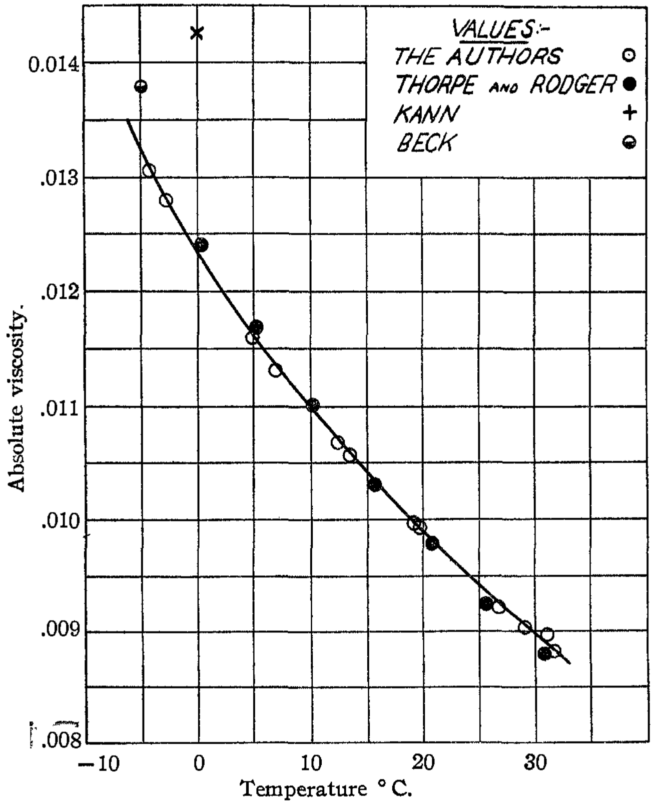

Fig. 3.—Absolute viscosity-temperature curve for bromine.

Results.—The values obtained are given in Table II and are plotted in Fig. 3, together with those of Thorpe and Rodger, Kann and Beck. The values obtained with bromine purified by the two different methods were practically identical. The maximum divergence of any individual result from the smoothed curve was about 0.4%.

The values used for the density of bromine were those of Thorpe[8] and of Andrews.[9]

Discussion.—The values obtained are compared in Fig. 3 with those of Thorpe and Rodger, Kann and Beck. It will be seen that they are in good agreement with those obtained by Thorpe and Rodger and by Beck. Kann's value of 0.014268 at 0° is, however, over 15% higher than that of any of the other observers. How his result should be so widely different is difficult to explain unless his bromine contained several per cent. of impurities.

The equation of the viscosity-temperature curve was solved and these values found $A = 0.012257$, $B = 0.000002721$, $\eta_0 = 0.01241$. From the equation the absolute viscosity at the boiling point was found to be 0.00717.

Iodine

Preparation.—The iodine was prepared by one of the methods of Stas.[10] A solution of 300 g. of commercial "resublimed" iodine in a solution of 200 g. of potassium iodide in 400 cc. of water was diluted with 800 cc. of water, so that about three-quarters of the iodine in solution was precipitated. The separated iodine was washed free from potassium iodide, the crystals were allowed to drain and then dried in a vacuum desiccator over calcium nitrate. The dried iodine was distilled twice from admixture with 5% of powdered barium oxide and was finally distilled alone.

Description of Viscosimeter and Procedure.—Owing to the fact that liquid iodine, flowing in a capillary tube, leaves an opaque film on the surface of the glass, the ordinary type of viscosimeter could not be used. The apparatus shown in Fig. 4 was therefore devised.

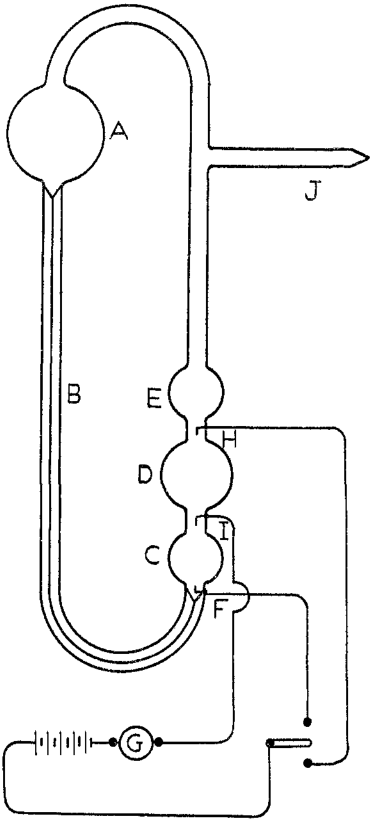

Fig. 4.—Iodine viscosimeter.

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[8] Thorpe, *J. Chem. Soc.*, 37, 141 (1880).

[9] Andrews, This Journal, **29**, 688 (1907).

[10] Abegg, "Handbuch der Anorganischen Chemie," Hirzel, Leipzig, **1913**, vol. 4, pt. 2, p. 347.

The bulb A of about 15cc. capacity was connected to the capillary B. Three small bulbs, C, D, E, of about 0.5, 2 and 0.5cc. capacity, respectively, were sealed on the other end of the capillary. The tube above E was joined to the top of A. A side tube J was sealed on for the introduction of the iodine. Three platinum electrodes, F, I, H, were sealed in between the small bulbs as shown. The center electrode was connected to one terminal of a galvanometer. The other two electrodes were connected to the outside contacts of a double-throw switch. The center contact of the switch and the other terminal of the galvanometer were connected to a source of 110 volts direct current.

The viscosimeter was weighed, iodine was introduced through J, and the weight again determined. The tube J was then bent at right angles to the plane of the apparatus and sealed off. A larger piece of tubing, into which J just fitted, was clamped in position in an oil-bath and J was inserted in the open end of the larger tube. A pulley was attached to the apparatus beside J, and attached to another pulley outside the bath by means of a belt. Thus by turning the other pulley the viscosimeter could be revolved about J.

The oil-bath was then heated and, when the iodine had liquefied, the apparatus was turned so that JC was nearly horizontal and the liquid was allowed to flow through the capillary into A. When almost all of the liquid was in A, the apparatus was turned so that JC was vertical and the liquid allowed to fall in the viscosimeter. The switch was connected to F and when the meniscus reached I the current flowed through the liquid between F and I and the galvanometer needle was deflected. The switch was then thrown over and when the liquid reached H the needle was again deflected. Thus by noting the time between two deflections of the galvanometer the time of fall was obtained.

Temperature Bath.—The bath used was a large Pyrex glass vessel of about 5liters' capacity, filled with paraffin oil ("liquid paraffin"). The bath was heated by gas burners and the temperature was regulated by regulating the flow of gas to the burners by means of the ordinary type of thermal regulator. The bath was stirred by an electrically-driven stirrer.

The temperature was measured by means of a mercury thermometer, graduated in 0.1°, which had been calibrated by comparison with a constant-volume hydrogen thermometer. The temperature of the bath could be kept constant to within 0.2°.

Calibration of Viscosimeter.—The viscosimeter was calibrated with various weights of distilled water at 20°. It was found that with ordinary distilled water sufficient current flowed to produce a noticeable deflection of the galvanometer.

Results.—The results are given in Table III and are plotted in Fig. 5. The maximum divergence of any value from the smoothed curve was about 1.0%.

TABLE III

VISCOSITY OF IODINE

DETERMINATION 1

Temp., °C...	116.0	121.9	128.7	136.1	142.7	149.0	157.7	169.8
Abs. vis.....	0.02268	0.02157	0.02080	0.01970	0.01870	0.01813	0.01716	0.01572

DETERMINATION 2

Temp., °C...	116.6	122.8	136.1	147.8	152.5	158.9	171.4	178.7
Abs. vis.....	0.02246	0.02180	0.01988	0.01822	0.01770	0.01688	0.01545	0.01462

The values used for the density of liquid iodine were those of Drugman and Ramsay[11] and Billet.[12]

Discussion.—The value obtained by Beck at the melting point is within about 0.4% of the value obtained by us, as may be seen from the curve. The equation of the viscosity-temperature curve was solved and the values found were A = 0.021833, B = 0.00005201, η_0 = 0.0968. The absolute viscosity at the boiling point was found to be 0.01414, from the equation.

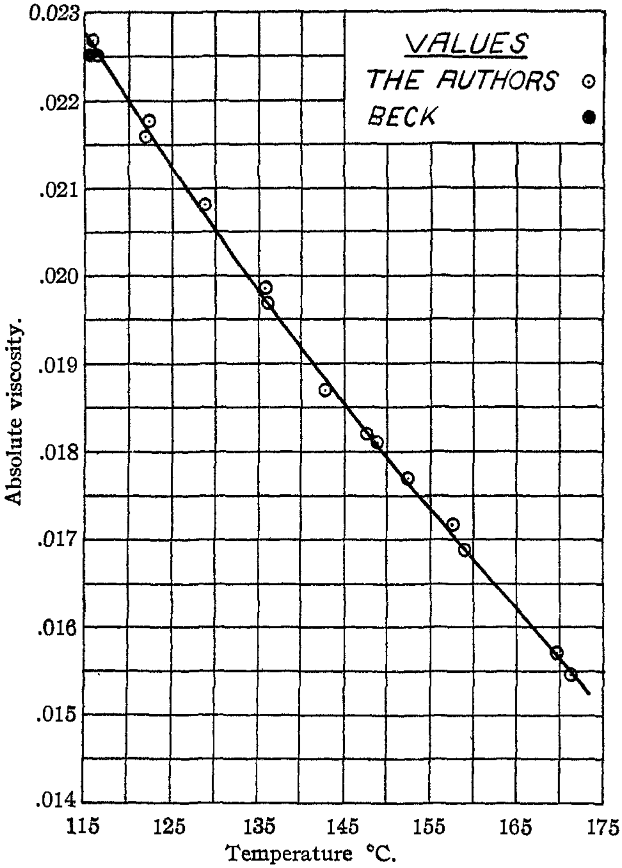

Fig. 5.—Absolute viscosity-temperature curve for iodine.

General Discussion of Results.—A comparison of the results obtained with the different halogens is given in Table IV.

It will be seen that all the values show an increase with increasing atomic weight of the halogen. The general form of the viscosity-temperature

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[11] Drugman and Ramsay, *J. Chem. Soc.*, **77**, 1228 (1900).

[12] Billet, *Mem. l'Institut*, **1885**, 292.

TABLE IV

VISCOSITIES OF THE HALOGENS

	Chlorine	Bromine	Iodine
Absolute viscosity at boiling point	0.00488	0.00717	0.01414
Abs. vis. divided by sq. rt. of density at b. p.	.00390	.00414	.00730
Constant "A" in the viscosity-temperature equation	.00588	.01226	.02183

curve also changes. Thus the constant A increases from 0.00588 for chlorine to 0.02183 for iodine.

The first two values given above increase much more rapidly from bromine to iodine than from chlorine to bromine. This is probably due to the fact that while both chlorine and bromine have association factors around 2 in the liquid state, iodine probably possesses a higher degree of molecular complexity.

Summary

The viscosities of liquid chlorine, bromine and iodine have been determined and the experimental methods described. The viscosity at the boiling point shows an increase with increasing atomic weight of the halogen, as would be expected from the Periodic Law.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION AND DETERMINATION OF THE ALKALI METALS, USING PERCHLORIC ACID. I. THE SOLUBILITIES OF THE PERCHLORATES OF THE ALKALI METALS IN MIXED ORGANIC SOLVENTS

BY G. FREDERICK SMITH

RECEIVED DECEMBER 15, 1924 PUBLISHED MARCH 5, 1925

The quantitative separation and determination of the alkali metals is in general dependent upon the use of organic solvents. The most important separation in this group is that of potassium from sodium. The most common method involves the use of chloroplatinic acid and 80% ethyl alcohol but methods based on the use of perchloric acid have proved satisfactory in this as well as other separations of the alkali metals.[1] Improved methods of procedure in this group depend in part upon a thorough study of new organic solvents.[2] The present work is the first of a series of such studies.

[1] (a) Smith, THIS JOURNAL, **45**, 2072 (1923). (b) Baxter and Rupert, *ibid.*, **42**, 2046 (1920). (c) Gooch and Blake, *Am. J. Sci.*, **44**, 381 (1917). (d) Morris, *Analyst*, **45**, 349 (1920); extensive bibliography.

[2] A list of organic solvents already studied in this connection includes *n*-butyl alcohol [Ref. 1 a; also Willard and Smith, THIS JOURNAL, **44**, 2816 (1922)]; *iso*butyl alcohol [Winkler, *Z. anal. Chem.*, **52**, 628 (1913)]; ethyl alcohol containing methyl