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On the Use of a Weight Burette for Measuring Out Bromine Water

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In experiments on the rate of bromination, different amounts of bromine water of known concentration and fixed temperature (18° C) were to be added to solutions in a reaction vessel. Pipettes for bromine water have been devised by Ramberg [1] and by Biilmann [2]. The author of this paper used an ordinary weight burette with a stopcock at the bottom. The burette was closed at the top by a ground-on glass bell having a bore which, when the bell was rotated to a certain position, communicated with a corresponding bore in the top part of the burette. The tip below the stopcock was closed by a ground-on glass cup. The burette was divided in ml, from 0 to 100, the total volume being 130—140 ml. Before use the burette was charged with bromine water to above the zero mark and placed in the water thermostat. When temperature equilibrium was established, the burette was taken from the thermostat, and bromine water was tapped out until the surface was on a level with the zero mark. The burette was closed and shaken vigorously for about 15 seconds. It was again left in the thermostat for some time after which it was opened for a moment at the top bore, closed again and, once more, shaken vigorously. It was weighed, and was now ready for use. After each delivery of bromine water it was shaken, weighed and placed in the thermostat. The first and the last two or three samples taken from the burette were analyzed. They were added to potassium iodide and titrated with thiosulphate. In the following, we shall deduce an interpolation formula which may be used for computing the concentrations of the intermediate portions of bromine water.

Let the total volume of the burette be v ml, the volume above the zero mark a ml. From the burette are taken altogether n portions of bromine water weighing $x_1, x_2 \ldots x_n$ g and containing, respectively, $c_1, c_2 \ldots c_n$ gramme-equivalents of bromine per kg. s is the density of the bromine water, α the Bunsen absorption coefficient of bromine in water. We express that the total amount of bromine in the burette, in the vapour phase and in the liquid phase, when p—1 portions have been taken out, is equal to the total amount in the two phases when p portions have been removed, plus the bromine in portion p. We obtain

$$\left(a + \frac{x_1 + \ldots + x_{p-1}}{s}\right)\frac{c_p s}{\alpha} + \left(v - a - \frac{x_1 + \ldots + x_{p-1}}{s}\right)c_p\, s$$

$$= \left(a + \frac{x_1 + \ldots + x_p}{s}\right)\frac{c_{p+1} s}{\alpha} + \left(v - a - \frac{x_1 + \ldots + x_p}{s}\right)c_{p+1}\, s + x_p\, c_p$$

Rearranging the terms we find

$$c_{p+1} = c_p\left(1 - \frac{1}{\alpha - 1}\,\frac{x_p}{u - (x_1 + \ldots + x_p)}\right) \tag{1}$$

where
$$u \equiv \left(\frac{\alpha}{\alpha - 1}\, v - a\right)s \tag{2}$$

The total decrease of the concentration of bromine from the first to the last portion is only a few per cent. Equation 1 may therefore with sufficient accuracy be written as follows

$$c_{p+1} = c_p - \gamma\,\frac{x_p}{u - (x_1 + \ldots + x_p)} \tag{3}$$

where
$$\gamma \equiv \frac{c_1 + c_n}{2\,(\alpha - 1)} \tag{4}$$

Using equation 3 we find

$$c_p = c_1 - \gamma\, F_{p-1} \tag{5}$$

where
$$F_{p-1} \equiv \frac{x_1}{u - x_1} + \frac{x_2}{u - (x_1 + x_2)} + \ldots + \frac{x_{p-1}}{u - (x_1 + \ldots + x_{p-1})} \tag{6}$$

By means of formula 5 we may calculate c_p when v, a, s, and α are known. According to Winkler[3], α is at 18° C 23.4. We prefer, however, to use this value of α only for the calculation of u by means of formula 2, while γ is determined for each run directly from the analyses of the first and last samples taken. The following example may serve as a test of formula 5 and an illustration of its application.

The total volume of the burette was $v = 136.9$, the volume above the zero mark $a = 19.0$. The bromine water was about 0.08 normal, its density [4] at 18° $s = 1.004$. Hence, $u = 124.5$. 14 samples of bromine water were taken from the burette. They were all titrated with 0.04 normal sodium thiosulphate. The results are given in the table. F_{p-1} was computed from the weighings by means of formula 6. With the aid of a calculating machine, this took only a few minutes. The first three and the last two titrations were used for determining the constants c_1 and γ of equation 5. The best agreement is obtained when the values $c_1 = 0.07736$ and $\gamma = 0.00324$ are chosen. We may now calculate c_p from formula 5. The results are given in the next to the last column of the table. The last column shows Δ, the difference between the amount of bromine found by analysis and that calculated from formula 5, expressed in ml 0.04 N thiosulphate. The agreement is satisfactory, not only for the samples used for fixing c_1 and γ, but also for the other portions (nos. 4—12). When the value of γ found here is used, we calculate from equation 4 the Bunsen absorption coefficient $\alpha = 24.2$ in good agreement with $\alpha = 23.4$ found by Winkler [3]. The average of α from 118 experiments, where the bromine water was used for kinetic measurements, was 22.9. The probable error of the single determination was $\pm$ 0.9.

Table 1.

p	x_p	F_{p-1}	c_p found	c_p form. 5	Δ
1	8.24	0	0.07726	0.07736	— 0.02
2	8.06	0.0709	0.07726	0.07713	+ 0.03
3	7.88	0.1454	0.07687	0.07689	0.00
4	9.71	0.2239	0.07673	0.07663	+ 0.02
5	8.20	0.3311	0.07627	0.07629	0.00
6	6.72	0.4306	0.07588	0.07596	— 0.01
7	4.07	0.5194	0.07586	0.07568	+ 0.02
8	2.38	0.5762	0.07516	0.07549	— 0.02
9	5.38	0.6106	0.07521	0.07538	— 0.02
10	5.17	0.6948	0.07499	0.07511	— 0.02
11	8.02	0.7829	0.07470	0.07482	— 0.02
12	8.26	0.9412	0.07415	0.07431	— 0.03
13	8.74	1.1359	0.07372	0.07368	+ 0.01
14	9.60	1.3955	0.07278	0.07284	— 0.01

Three sources of error in the method may be mentioned. (1) Insufficient saturation of the vapour phase. (2) When the burette is shaken after the removal of bromine water, the pressure in the burette increases slightly owing to evaporation of bromine. When the burette is opened at the top before the next portion is taken out, a small amount of bromine excapes. (3) If the temperature of the air that enters the burette while bromine water is running out is different from that of the thermostat, a change of pressure in the burette will take place when it is left in the thermostat, and this will either diminish or augment the loss of bromine when the next sample is taken. It holds for all three kinds of error that they will affect rather the values found for γ and a than those for c_p when the computation is carried out as described above.

When the loss of bromine owing to error (2) is taken into account, it may be shown that formulae 2, 4, and 5 remain the same, while a correction must be added to the right side of formula 6. This correction is given by the expression

$$\frac{6\,(c_1 + c_n)}{a + 6(c_1 + c_n)} \left(\frac{x_1^*}{u-(x_1 + x_2)} + \ldots + \frac{x_{p-2}}{u-(x_1 + \ldots + x_{p-1})} \right)$$

A recalculation of the example in the table using this correction gave the same values of c_p; only changes of one in the 5th decimal were found. a, however, increased from 24.2 to 24.9.

SUMMARY

An ordinary weight burette may be used for measuring out bromine water of fixed temperature (near room temperature). A formula is given which makes it possible to calculate the concentration of the bromine water delivered by the burette when the concentrations of the first and last portions taken from the burette are determined by titration.

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