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A METHOD FOR THE PREPARATION OF LARGE QUANTITIES OF VOLUMETRIC SOLUTIONS.

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For a number of years I have had to solve the problem of preparing large quantities of normal volumetric solutions of acids and alkali for students' use. The quantities range from five to ten gallons at a time, twenty to forty litres, and the question of how to prepare them in this large quantity and dilute them to exactly normal concentration was puzzling to say the least. Lately the scheme detailed below has been worked out and it seems to answer the purpose admirably.

The scheme consists of first preparing any quantity of a solution (exact volume unknown) of such a concentration that it is from one-tenth to one-fifth above normal, and then determining its factor by titration; second, diluting this solution with an accurately measured volume of water; third, withdrawing from this solution an accurately measured quantity and once more determining a factor; fourth, from the amount of water added at the second step, and from the factors determined at the first and the third steps, calculating the volume of water that is necessary to be added to make the entire lot exactly normal.

The reasoning, together with the necessary mathematics, is given below.

Let V_1 = the original volume.
V_2 = volume of water added at the second step.
V_3 = volume of solution removed to determine the second factor.
V_4 = volume after dilution and second standardization.
V_5 = volume of finished solution when exactly normal.
V_6 = volume of water necessary to be added to V_4 to make the finished solution exactly normal.

The various volumes may be in any unit, but litres or one hundred cubic centimetres will be found the most convenient.

Let W_1 = original weight of active substance per unit volume.
W_2 = weight per unit volume after the first dilution.
W_3 = weight per unit volume of active substance necessary to make an exactly normal solution.
Let F_1 = factor of the original undiluted solution.
F_2 = factor of the solution after the first dilution.
F_3 = factor of an exactly normal solution.

The value which we wish to know above all others is that of V_6, but first of all we must know the value of V_1. Obviously the product of the weight per unit volume into the original volume should be equal to the product of the weight per unit volume after the first dilution into the volume at that time, plus the same weight per unit volume into the volume withdrawn to make the second standardization. That is:

$$W_1 V_1 = W_2 V_4 + W_2 V_3.$$
$$W_1 V_1 = W_2 (V_4 + V_3).$$

But $V_4 = N_2 + V_1 - V_3.$

$$W_1 V_1 = W_2 (V_1 + V_2 - V_3 + V_3).$$
$$W_1 V_1 = W_2 (V_1 + V_2).$$

Now V_2 may easily be made unity.

Then $W_1 V_1 = W_2 (V_1 + 1).$

Solving this equation for V_1 we have:

FORMULA I.

$$V_1 = \frac{W_2}{W_1 - W_2}$$

The same formula might also be obtained in other ways.

Now, the weight per unit volume of any solution, times the total volume, divided by the weight per unit volume of the active substance contained in a normal solution, will give the volume of the finished solution if diluted to exactly normal. That is:

$$V_5 = \frac{(V_1 + V_2 - V_3) W_2}{W_3}$$

$$\text{But } V_6 = V_5 - V_4$$
$$\text{And } V_4 = V_1 + V_2 - V_3$$
$$\text{Then } V_6 = \frac{(V_1 + V_2 - V_3) W_2}{W_3} - (V_1 + V_2 - V_3).$$
$$V_6 = \frac{(V_1 + V_2 - V_3) W_2 - (V_1 + V_2 - V_3) W_3.}{W_3}$$

Substituting the value of V_1 from Formula I and simplifying:

FORMULA II.

$$V_6 = \frac{\left(\frac{W_2}{W_1 - W_2} + V_2 - V_3\right)(W_2 - W_3)}{W_3}$$

We thus have under control all the values necessary for determining V_6, since W_1 and W_2 may be determined by experiment and W_3 will be known from theory, and V_2 and V_3 may be made anything we please.

Since the weight per unit volume of any solution is directly proportional to the factor of the solution we may substitute for the various weights the various factors determined by experiment. Thus we do away with the necessity of calculating the various weights. Our formula II then becomes:

FORMULA III.

$$V_6 = \frac{\left(\frac{F_2}{F_1 - F_2} + V_2 - V_3\right)(F_2 - F_3)}{F_3}$$

Since the factor of an exactly normal solution is unity, F_3 is unity, and our formula III becomes:

FORMULA IV.

$$V_6 = \left(\frac{F_2}{F_1 - F_2} + V_2 - V_3\right)(F_2 - 1).$$

V_2 may be made unity, say one litre, and V_3 may be made one hundred cubic centimetres, or one-tenth unity, and the calculation is quite simple. For large volumes, twenty litres or more, these values for V_2 and V_3 are convenient. If the quantity of solution is less, say four to five litres, the formula may still further be simplified by making both V_2 and V_3 unity, and the unit volume one hundred cubic centimetres. In this way both V_2 and V_3 will cancel out of the formula and we have:

FORMULA V.

$$V_6 = \left(\frac{F_2}{F_1 - F_2}\right)(F_2 - 1).$$

The following examples are given to show what can be done by using these formulas. These figures are the final factors of various lots of normal sulphuric acid made as described and using formula IV to calculate V_6.

(1) 1.006. (2) 0.9967. (3) 0.9968. (4) 0.9983.

In these experiments ordinary 25 Cc. volume pipettes were used to measure the acid solutions, and a cylinder graduated to 1000 Cc. in 10 Cc. divisions for the water used in the dilutions. The results were obtained on lots of about twenty litres.

By using more refined methods of measurements one lot of about twenty litres finished with a factor of 1.0018.

On lots of about four litres and using Formula V to calculate V_6 results were obtained as follows, using volume pipettes for the measurements:

(1) 1.001. (2) 0.9985. (3) 0.9989.

If we consider the fact that a variation of 0.004 in the factor of a solution means a variation of only 0.1 Cc. on a volume of 25 Cc. used in standardization, these results are accurate enough for the control of all ordinary work of students. Indeed, I believe the method could be made sufficiently accurate for most purposes aside from very exacting scientific work.

The advantages of the scheme as compared with the usual method lie in the fact that:

First, any volume of a solution may be prepared in a vessel of any shape or size regardless of whether the vessel is filled or not, by means of two separate titrations, and the measurement of three relatively small volumes. Because of this, standard graduated flasks need not be employed, nor any device for holding the volume of water necessary to dilute to normal the original solution.

Second, the calculations are not cumbersome, even with arithmetic, and are very simple by means of logarithms, and in any event are more conveniently carried out than the dilution to exact volume which is necessary when proceeding in the usual way.

Third, the original concentration may be considerably above normal and may vary widely. It must, however, be far enough above normal so that the first dilution still leaves it above normal. These conditions may be easily attained by rough calculations. In these respects much less latitude is allowed when proceeding in the usual way.

Fourth, the time necessary to complete the whole operation is short. After a little experience from fifteen to thirty minutes is ample.

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