XC. A CONDUCTIVITY METHOD FOR THE DETERMINATION OF CARBON DIOXIDE.

By LEONARD ERNEST BAYLISS (*Sharpey Scholar*).

*From the Department of Physiology and Biochemistry,
University College, London.*

BEING faced with the necessity of absorbing some 100 cc. of CO_2 in 10 minutes and of estimating the quantity absorbed as rapidly as possible and with a possible error not greater than 0·5 %, the usual methods for determining CO_2 were all examined and found wanting in some respect.

It was necessary, therefore, to devise a new and rapid method of estimating carbonate in a mixture of carbonate and hydroxide, and use was made of the fact that the migration velocity of the CO_3'' ion is considerably smaller than that of the OH' ion, so that the conductivity of a solution of NaOH falls as it absorbs CO_2.

Calibration.

This is very easily performed, since it is only a matter of plotting a calibration curve showing the conductivities of mixtures, in varying proportions, of solutions of NaOH and Na_2CO_3 of equivalent concentration. Such a curve is shown in the figure, and it will be seen that it is nearly a straight line for carbonate proportions above 0·3. As points lower than this will practically never be required (the volume of solution used to absorb the CO_2 can be adjusted so as to avoid them) only a few points are required to determine the curve.
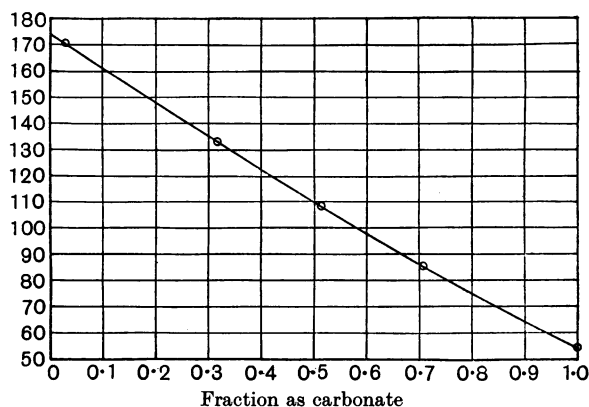
Conductivity of mixtures of 0·997 N NaOH and 0·997 N Na_2CO_3 in varying proportions. Ordinates, equivalent conductivity at 24·5°. Abscissae, proportion of Na_2CO_3 in mixture.

It is not, of course, necessary to use CO_2-free NaOH either for calibrating or for absorbing, since the carbonate content can be determined, and hence the true proportion of carbonate in any mixture of the impure NaOH with pure Na_2CO_3 solution. If c cc. of sodium carbonate solution be mixed with $(1 - c)$ cc. of sodium hydroxide solution containing α equivalents of carbonate per equivalent of total base, then the proportion of carbonate in the mixture is given by

$$\beta = c + \alpha (1 - c).$$

Similarly, if a volume v cc. of CO_2 is absorbed by b cc. of sodium hydroxide solution of total base concentration B, of which a proportion α' is carbonate, then the final proportion of carbonate in the mixture is given by

$$\beta' = \frac{\alpha'Bb + v/11\cdot15}{Bb} .$$

Hence $v = (\beta' - \alpha') 11\cdot15\ Bb$, β' being, of course, determined from the measured conductivity by means of the calibration curve.

As a special case of the above equations, we have the possibility that the solution used for absorbing has the same carbonate content as that used for calibrating, and then it can be seen that

$$v = c (1 - \alpha) 11\cdot15\ Bb.$$

If the method is used for a large number of routine determinations, several samples of caustic soda solution for absorbing will have to be made up; and since it is not easy, or indeed necessary, to ensure that all have exactly the same concentration, a correction will have to be made that will reduce the observed conductivity to that of a $NaOH$–Na_2CO_3 solution of the same proportion of carbonate as that used for absorbing, but of the total base concentration used in plotting the calibration curve.

An empirical equation has been derived experimentally—by measuring the conductivities of $NaOH$–Na_2CO_3 mixtures of various concentrations—which holds for concentrations differing from that of the calibrating solution by less than 20 % and for proportions of carbonate greater than $0\cdot3$. If the concentration of the solution used for absorbing CO_2 is B/γ (B being that of the solution used for calibrating), λ is the conductivity of the absorbing solution as measured after absorption of CO_2 and λ_0 is the conductivity required, $i.e.$ that which the calibrating solution would have if it had the same proportion of carbonate as the absorbing solution, then

$$\lambda_0 = \gamma\lambda \{1 + (1 - \gamma) [0\cdot15 + 0\cdot10 (\beta - 0\cdot03)]\}.$$

In this equation c can be written instead of β if the initial carbonate content of the alkali solutions is small, as it usually is. The values of the constants have been arrived at experimentally, and are subject to an inaccuracy of about 1 %. There will be further errors if very concentrated solutions are used, since the calibration curve will depart too far from the straight line which the analysis assumes.

We can write $\lambda_0 = \gamma\lambda$ with an error of less than 0·5 % when

$$1 - \gamma < 0·07 \text{ irrespective of sign, for } \beta = 1·0,$$
$$1 - \gamma < 0·05 \qquad ,, \qquad ,, \qquad \beta = 0·5.$$

Having thus determined the proportion of carbonate in the absorbing solution from the calculated value of the conductivity, the volume of CO_2 absorbed is calculated from the equation given above, putting, of course, the value of the concentration of the absorbing solution, not that of the calibrating solution, for B.

Technique.

The standard conductivity apparatus is suitable for these measurements, except that, as the equivalent conductivities of the solutions to be used are relatively high, a conductivity cell must be employed which has small electrodes set well apart, so that the actual value of the resistance measured is not less than 10 ohms; trouble may be experienced otherwise, from heating of the solution during measurement, and from the fact that the resistance of the leads to the cell may not be negligible.

The values given on the figure were obtained by means of a metre slide-wire and resistance box as standard resistance, so that only the central portion of the slide-wire need be used. A double commutator and galvanometer were substituted for the usual induction coil and telephones since the measurements had to be made in a noisy laboratory. The position of the contact on the slide-wire could be set to 0·2 mm. so that the error on the resistance measurements was about 0·1 %. It is necessary to keep the temperature of the solution constant to about 0·1°, if readings are to be taken to this accuracy.

SUMMARY.

A method is described of determining the amount of carbonate in a sodium hydroxide-sodium carbonate mixture, by measurement of the conductivity of the solution. This method is chiefly valuable for determining the amount of CO_2 absorbed by a caustic soda solution, and it is believed that it forms the best and quickest method for rapidly absorbing and measuring relatively large quantities of this gas.