

lysis was brought about either by freezing or by the addition of water. When haemolysis by water was completed sufficient NaCl was added to make the salt content up to 0.9 % again.

I. Setschenow [1879, p. 44] reported the following experiment at 37°–37°·5. Emulsion of dog blood corpuscles:

514.6 mm. CO₂, total CO₂ in 50.18 cc. = 50.31 cc. (0°, 1 mtr.).

After freezing:

513.3 mm. CO₂, total CO₂ in 50.18 cc. = 49.98 cc. (0°, 1 mtr.).

From this p_{H} is 6.22 if $\Psi = 15$ and $p\lambda_{(m)} = 6.20$, at which reaction there seems to be the same reaction in dog blood cells and serum.

RÉSUMÉ.

The apparent hydrogen ion activity in horse blood corpuscles has been determined.

CHAPTER VIII

THE DETERMINATION OF THE FIRST DISSOCIATION CONSTANT OF CARBONIC ACID AND THE DEVIATION COEFFICIENTS OF THE BICARBONATE ION.

In the foregoing chapters we have determined the value of $p\Lambda_{(s)}$ and $p\Lambda_{(c)}$, and it will now be interesting to inquire into the factors which control these constants rather more closely.

It will be remembered that in chapter III it was shown that the apparent activity coefficient of the continuous phase of serum and of the blood cell fluid participates in the constants and a rather large number of determinations have therefore been performed of the apparent activity coefficients in salt solutions. I have at several points pursued the investigations further than was absolutely necessary for the problem being dealt with, because it may be of particular interest from a purely physico-chemical standpoint, especially since the appearance of Bjerrum's theory.

The first dissociation constant of carbonic acid has been determined by the conductivity method by J. Walker and W. Cormack [1900] and by J. Kendall [1916] on the basis of experiments carried out by himself, by Pfeiffer¹, by Knox¹ and by Walker and Cormack. The determinations of Walker and Cormack and Kendall are better than the earlier ones (Pfeiffer's and Knox's) and therefore the values calculated from them are the most valuable. The molecular conductivity of the bicarbonate ion at "infinite dilution" comes into the calculation. This value is obtained by extrapolation from conductivity determinations of sodium bicarbonate solutions (and also calcium bicarbonate solutions), but it seems to the author that Walker and Cormack and Kendall have not executed this extrapolation in a satisfactory

¹ Cited from Kendall [1916].

manner. A slight error in the extrapolation is of hardly any consequence in the determination of the first dissociation constant of carbonic acid because the molecular conductivity of the bicarbonate ion has to be added to the much greater molecular conductivity of the hydrogen ion and it is the sum of these quantities which is used as a factor in the calculation (see chapter I). But if it is required to determine the conductivity coefficient an error in μ_{∞} will have a great effect particularly in weak solutions. The question as to how μ_{∞} should be obtained by extrapolation from conductivity determinations of salt solutions has up to the present been the subject of much controversy but I am unacquainted with any well-grounded theoretical method of performing the extrapolation. The best way must therefore be to obtain a relation between a function of the salt concentration and a function of the molecular conductivity which is the equation for a straight line. We can then determine μ_{∞} either graphically or by the method of least squares.

It will as a rule be much the most convenient method to perform the extrapolation graphically but the method of least squares has the advantage of giving an estimation of the accuracy of the determinations.

That I only occasionally estimate the error in this chapter is because the value obtained is only of real significance if a systematic error can be excluded and a determination of the error can only be used in comparing results obtained by the same experimentalist with the same technique in a similar process. In the majority of cases the graphic method carried out in a suitable way, coupled with a good idea of the accuracy of the technique, will give more valuable information than the more arduous determination of the error.

Kohlrausch (cited from Lehfeldt [1908, p. 61]) recommends that the cube roots of the concentrations be plotted as abscissae and the molecular conductivities as ordinates. The curve will then be a straight line for many salt solutions. This kind of extrapolation has proved very suitable in the case of Walker and Cormack's determinations but particularly so for Kendall's measurements of conductivity in sodium bicarbonate solutions.

In Table XXX Walker and Cormack's and also Kendall's results are given. In the first column the number of litres in which a gram equivalent is present are recorded; in the second column, the concentration in terms of normality; in the third the cube root of this amount; in the fourth, the equivalent conductivity. In Fig. 12 these values are plotted, $\sqrt[3]{c}$ as abscissae and μ_c expressed in reciprocal ohms as ordinates. The ordinates which refer to sodium bicarbonate are on the left, the numbers referring to the calcium bicarbonate series are on the right. It will be seen from the figure that the curve which represents Kendall's measurements of sodium bicarbonate solutions corresponds extremely well to a straight line. Extrapolation can therefore be undertaken with very considerable certainty and it gives $\mu_{\infty} = 99.2$ reciprocal ohms (25°), while Kendall himself made the extrapolation to be 97.5. From this—using the same corrections as Kendall did— μ_{∞} at 18° is 86.3 reciprocal ohms, while Walker and Cormack's determinations on extra-

polation give 88.1 reciprocal ohms. The figure shows that the extrapolation of Walker and Cormack's measurements is rather uncertain, the two estimations in the most dilute solutions being a little high. The want of agreement between Walker and Cormack's and Kendall's results is presumably due to this cause and I shall regard Kendall's as correct.

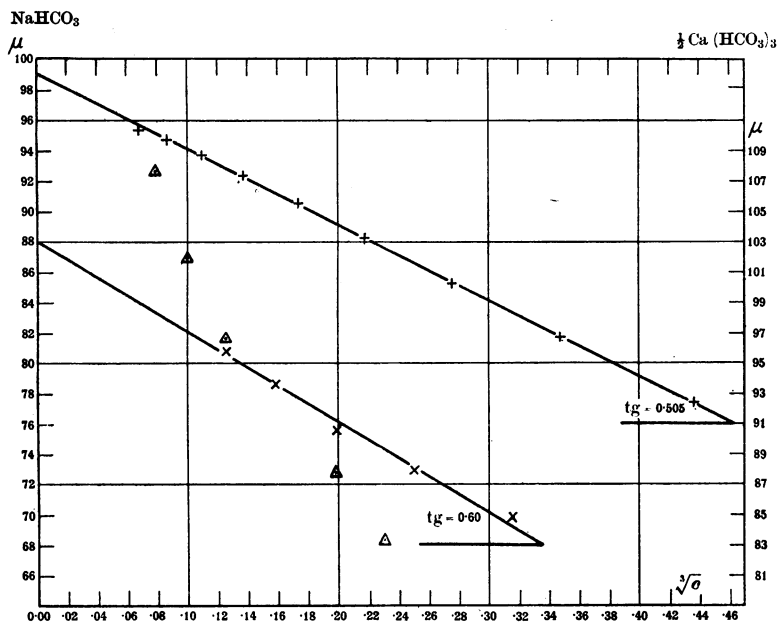


Fig. 12. Conductivity of sodium bicarbonate solutions.
 Upper curve from Kendall's measurements; lower curve from Walker and Cormack's measurements.
 Δ $\frac{1}{2}$ calcium bicarbonate.

The curve of the calcium bicarbonate experiments (triangles) demonstrates that only the three experiments with the strongest solutions lie on a straight line—the experiments with the two weakest solutions lie considerably above. Extrapolation, having regard to these two points, gives quite an unreasonable value for μ_∞ , and I therefore think it cannot be performed with these experiments.

If we calculate the molecular conductivity of carbonic acid from Kendall's experiments with sodium bicarbonate (carbonic acid being regarded as monobasic) we get

at 25°	395.5,
„ 18°	355.8,
„ 0°	265.6.

Using these figures, values for the first dissociation constant of carbonic acid are obtained which diverge in the third decimal place from those calculated by Kendall [1916]. In Table XXXI Walker and Cormack's [1900] and Kendall's results are recalculated. Pfeiffer's and Knox's experiments are not given and the reader is referred to Kendall's paper for these. The small

difference between Kendall's value for μ_∞ for carbonic acid and mine is without real significance in the calculations from these experiments.

The mean of Walker and Cormack's and Kendall's determinations at 18° of the first dissociation constant of carbonic acid is 3.1×10^{-7} , from which $p_{K_1} = 6.509$. At 25° we obtain from Kendall's experiments $K_1 = 3.47 \times 10^{-7}$, $p_{K_1} = 6.460$, and at 0°, $K_1 = 2.21 \times 10^{-7}$, $p_{K_1} = 6.656$; p_{K_1} therefore decreases 0.20 between 0° and 25° which is equivalent to 0.008 per degree.

By thermodynamic methods it is possible to determine the change in p_{K_1} with temperature when the heat of ionisation of carbonic acid is known. Julius Thomsen has estimated it at 2800 calories, from which the change in p_{K_1} can be calculated by van 't Hoff's equation (cf. Henderson [1909], Hasselbalch [1916, 2] and Kendall [1916]), and turns out to be 0.0065 per degree, which is in good agreement with Kendall's direct determination. Kendall has pointed out that the heat of hydration of CO_2 participates in Thomsen's determinations and that the calculation of the change of the dissociation exponent with temperature according to van 't Hoff's equation is only correct if the degree of hydration is independent of the temperature. He thinks however he is justified in concluding, from the good agreement between the calculated and experimental values, that the calculation is permissible—that is to say that the change in the degree of hydration is negligible in this connection.

From Fig. 12 it appears that the relation between the molecular conductivity of sodium bicarbonate and the concentration of the salt is expressed by the following equation:

$$- 50.5 \sqrt[3]{c} + 99.2 = \mu_v, \dots\dots\dots(135)$$

from which we get $f_\mu = \frac{\mu_v}{99.8} = 1 - 0.509 \sqrt[3]{c}. \dots\dots\dots(136)$

No general relation is known between the conductivity coefficient of a salt and its activity coefficient but Hasselbalch, in his frequently cited paper [1916, 2], has carried out determinations which permit of the estimation of the apparent activity coefficient of the bicarbonate ion.

The experiments referred to were electrical estimations of hydrogen ion activity in sodium bicarbonate solutions of known concentration with simultaneous estimation of the CO_2 tension with which the solutions were in equilibrium. From these experiments Hasselbalch determined p_{K_1} (Hasselbalch) with the help of the equations developed in chapter III. In Table XXXII these experiments will be found recalculated to give our p_{K_1} and, as before, the values corrected for depressed hydrogen tension as well as the uncorrected are given. Hasselbalch's experiments were performed by his own method with a plate electrode. For the sake of clearness we will postpone the further examination of these experiments.

Hasselbalch's experiments were carried out, as repeatedly stated, on the principle he evolved himself. I began therefore by repeating these experiments with the earlier described technique on Höber's principle, widening

the scope of the investigation by including sodium bicarbonate solutions which in addition contained NaCl or KCl in the concentrations 0.0718*n*, 0.145*n*, and 0.291*n*. These experiments are given in Tables XXXIII-XXXVIII and belong to series A but were done early in this series. I do not think they are subject to any systematic error but I cannot express myself with absolute certainty on this point.

In the first column of the tables the constitution of the solutions is given. The bicarbonate content of the solutions was estimated with the exhaust pump, at least two samples being used and usually several more. The error of this method is negligible compared with that of the electrical method. NaCl and KCl were added to the solutions in measured quantities, the salts being washed from a watch-glass into a measuring flask containing the bicarbonate solution. In a number of cases NaOH was used instead of NaHCO₃ and the solutions were therefore treated with CO₂ for a quarter of an hour before the actual saturation. It was impossible to demonstrate any difference between solutions prepared with the bicarbonate and the hydroxide.

In calculating the combined CO₂ (*B*), dissociation of the bicarbonate into the monocarbonate is taken into account.

In accordance with what was said in chapter II we have

$$S_1 = \frac{a_{\text{H}^+}}{K'_2 + a_{\text{H}^+}} B,$$

where *S*₁ is the amount of combined CO₂ corresponding to the bicarbonate expressed in vols. %, and *B* is the total amount of combined CO₂ expressed in the same way.

Since *S*₂ is the amount of combined CO₂ corresponding to the monocarbonate, and *T* is the amount of CO₂ in vols. % which would be combined if the combined CO₂ was in the form of bicarbonate, we have

$$S_1 + 2 S_2 = T, \quad \dots\dots\dots(137)$$

from which with the aid of (102) we get

$$B = \frac{\frac{a_{\text{H}^+}}{K'_2} + 1}{\frac{a_{\text{H}^+}}{K'_2} + 2} T. \quad \dots\dots\dots(138)$$

When *B* and *a*_{H⁺} are known, therefore, *T* can be calculated and inversely *B* can be calculated from *T* and *a*_{H⁺}. In the pumping out experiments for the determination of *C*_{HCO₃'}, *B* was put equal to *T* when *p*_{H⁺} was below 7.70; if it was above, (138) was used in the calculation, *K*'₂ being taken as 10⁻¹⁰. In calculating *p*_{K₁'}, *T* was put equal to *B* when *p*_{H⁺} was less than 7.90; when greater, (138) was used. In these last experiments equation (103) was also used instead of (95) (in logarithmic form) for calculating *p*_{K₁'}.

In Table XXXIX the results of this series of measurements are compared. They show that *p*_{K₁'} undoubtedly decreases with increasing salt concentration and that the effect of the sodium ion on the constant is more pronounced than that of the potassium ion. The measurements in pure sodium bicarbonate

solutions in the case of the two weakest concentrations ($T = 8.88$ and $T = 17.96$) are uncertain because the conductivity of these solutions was so slight that the resistance in the exit tap was very great and the oscillations of the capillary electrometer were too small.

In Table XXXVIII there are a number of determinations of p_{K_1}' at room temperature in sodium bicarbonate solutions with the addition of equivalent amounts of NaCl or KCl. The experiments with the two series of salt solutions were performed on the same day and with the same electrode and they are therefore as comparable as possible, with the technique employed.

In Tables XL and XLIV experiments belonging to series B are given. p_{K_1}' is here determined for sodium bicarbonate solutions partly with the addition of salt, at room temperature and at 38° .

In Table XLI measurements are given, carried out with the Hasselbalch electrodes E III and E VI, employed as Höber electrodes in the manner described in chapter IV, at room temperature. I consider these last measurements to be the best of all from a technical point of view, and I shall examine them a little more in detail. In the first place it will be observed that p_{K_1}' for pure sodium bicarbonate solutions decreases with the concentration.

$n/100$ NaHCO ₃	gives	p_{K_1}'	6.400
$n/40$	"	"	6.393
$n/20$	"	"	6.335
$n/10$	"	"	6.279

In potassium bicarbonate solutions for

$n/100$ KHCO ₃	$p_{K_1}' = 6.413$
$n/10$	" " = 6.317

If we compare the solutions with salt concentrations of $n/10$ we get

$n/10$ NaHCO ₃	$p_{K_1}' = 6.279$
$n/10$ KHCO ₃	$p_{K_1}' = 6.317$
$n/20$ NaCl + $n/20$ NaHCO ₃	$p_{K_1}' = 6.297$
$n/20$ KCl + $n/20$ KHCO ₃	$p_{K_1}' = 6.312$
$n/10$ NaCl + $n/1000$ NaHCO ₃	$p_{K_1}' = 6.313$

It is seen therefore that p_{K_1}' for $n/10$ sodium salt solutions is rather less than the constant for $n/10$ potassium salt solutions. This is still more noticeable in the determinations in $n/5$ salt solutions, and from the latter it also appears that p_{K_1}' for mixtures of Na and K salts lies between those for the pure salts.

$n/10$ NaCl + $n/10$ NaHCO ₃	gives	$p_{K_1}' = 6.246$
$n/10$ KCl + $n/10$ KHCO ₃	" "	= 6.260
$n/10$ KCl + $n/10$ NaHCO ₃	" "	= 6.282

Turning again to the $n/10$ solutions it will be noticed that p_{K_1}' seems to be a little greater for solutions containing NaCl than for those containing equivalent amounts of NaHCO₃. The difference in p_{K_1}' for solutions containing

pure NaHCO_3 and for those containing equal parts of NaCl and NaHCO_3 is however so small that it certainly falls within the experimental error, but the difference between $n/10 \text{ NaHCO}_3$ and $n/10 \text{ NaCl} + n/1000 \text{ NaHCO}_3$ appears to be real. I think that in this case the method of least squares ought to be used.

From equation (89) in logarithmic form we get

$$p_{\text{K}'_1} = p_{\text{K}_1} + \log F_a (\text{HCO}'_3).$$

According to Bjerrum (cf. equation (58))

$$\log f_a (\text{HCO}'_3) = -k \sqrt[3]{c}.$$

If we put

$$F_a (\text{HCO}'_3) = f_a (\text{HCO}'_3),$$

which is permissible at $n/10$ concentration, we get

$$p_{\text{K}'_1} = p_{\text{K}_1} - k \sqrt[3]{c}, \dots\dots\dots(139)$$

where c is the molar concentration of the cations and k is the constant in Bjerrum's above cited equation, while p_{K_1} is the negative logarithm of the first dissociation constant of carbonic acid.

If we have a series of equations of the form

$$ax + y = l, \dots\dots\dots(140)$$

we can calculate the constants which fulfil the conditions best with the following equations:

$$x = \frac{n \sum al - \sum a \sum l}{n \sum a^2 - (\sum a)^2}, \dots\dots\dots(141)$$

$$y = \frac{\sum l \sum a^2 - \sum al \sum a}{n \sum a^2 - (\sum a)^2}. \dots\dots\dots(142)$$

If we employ the above equations in connection with all the 26 experiments which only contain NaHCO_3 in the series recorded we obtain

$$p_{\text{K}_1} = 6.512,$$

$$k = 0.475.$$

An estimate of the mean error of $p_{\text{K}'_1}$ can be obtained by putting the values found for it and k in (139), and determining the deviations from the above value, thus

$$M = \sqrt{\frac{7519}{25}} \times \frac{1}{100} = 0.0173.$$

For a series of nine experiments we may therefore expect a mean error of 0.0058. Thus for such a series of measurements with $n/10 \text{ NaHCO}_3$

$$p_{\text{K}'_1} = 6.291 \pm 0.0058.$$

In the experiments with the solution of $n/10 \text{ NaCl} + n/1000 \text{ NaHCO}_3$

$$p_{\text{K}'_1} = 6.313 \pm 0.0045.$$

The difference is therefore 0.022 ± 0.0073 and in all probability it is a real one.

It is an obvious consequence of Bjerrum's activity theory, as it has been expounded in chapter I and the present chapter, that the activity coefficient in a solution of a binary salt consisting of two monovalent radicles shall not vary¹ if the solution is diluted with another which contains an equivalent amount of a similar salt having no ions in common with the first.

¹ Apart from secondary effects represented by the difference in k in equation (46).

According to a view widely held by physiologists, which for example is put forward by Hamburger [1902], Hedin [1915] and Ege [1920], the dissociation of a monovalent salt will increase if the salt solution is diluted with another monovalent salt having no ions in common with the first, even if the two solutions are equivalent. This view depends however on an incorrect application of Arrhenius' [1888] theory of "isohydric" solutions, but I was myself involved in it until Prof. Bjerrum kindly pointed out the fallacy to me. In view of the general acceptance it has received I will enter a little more deeply into the question regarding for the time being Arrhenius' classical theory of the incomplete dissociation of salts as correct.

Let us consider a $n/1$ solution of NaCl and a $n/1$ solution of KI.

Then according to Arrhenius' theory extended to isohydric dissociation

$$\frac{C_{\text{Na}^{\cdot}} + C_{\text{Cl}^{\cdot}}}{C_{\text{NaCl}}} = k,$$

and

$$\frac{C_{\text{K}^{\cdot}} + C_{\text{I}^{\cdot}}}{C_{\text{KI}}} = k.$$

The equilibria in a $n/1$ KCl solution and a $n/1$ NaI solution will be given by

$$\frac{n/1 \gamma_{\text{K}^{\cdot}} \cdot n/1 \gamma_{\text{Cl}^{\cdot}}}{n/1 \text{KCl} (1 - \gamma)} = k,$$

and

$$\frac{n/1 \gamma_{\text{Na}^{\cdot}} \cdot n/1 \gamma_{\text{I}^{\cdot}}}{n/1 \text{NaI} (1 - \gamma)} = k,$$

γ being the (common) degree of dissociation of the salts.

If we mix some NaCl solution with some KI solution, *e.g.* equal parts, an equilibrium will be established which will satisfy all the four equations. This is only possible at a quite definite degree of dissociation of the different salts as the determining equations can only have one solution.

Assuming that the dissociation does not change on mixing the solutions, we have

$$C_{\text{Na}^{\cdot}} = C_{\text{Cl}^{\cdot}} = C_{\text{K}^{\cdot}} = C_{\text{I}^{\cdot}} = n/2\gamma,$$

and

$$C_{\text{NaCl}} = C_{\text{KI}} = n/2 (1 - \gamma).$$

Now NaCl and KI will react with each other and equal quantities of NaI and KCl will be formed if the same laws hold for all the undissociated salts in question. Thus we have the following equilibria:

$$C_{\text{NaCl}} = C_{\text{KI}} = C_{\text{NaI}} = C_{\text{KCl}} = n/4 (1 - \gamma),$$

$$\frac{n/2 \gamma_{\text{Na}^{\cdot}} \cdot n/2 \gamma_{\text{Cl}^{\cdot}}}{n/4 \text{NaI} (1 - \gamma)} = k,$$

$$\frac{n/2 \gamma_{\text{K}^{\cdot}} \cdot n/2 \gamma_{\text{I}^{\cdot}}}{n/4 \text{KI} (1 - \gamma)} = k,$$

$$\frac{n/2 \gamma_{\text{Na}^{\cdot}} \cdot n/2 \gamma_{\text{I}^{\cdot}}}{n/4 \text{NaI} (1 - \gamma)} = k,$$

$$\frac{n/2 \gamma_{\text{K}^{\cdot}} \cdot n/2 \gamma_{\text{Cl}^{\cdot}}}{n/4 \text{KCl} (1 - \gamma)} = k,$$

which are correct in accordance with the four original equations. As only one state of equilibrium is possible the above mathematical reasoning is proof that no change in the dissociation of the salts takes place on mixing.

Finally it may be stated that as far as the proof is concerned it is immaterial whether the dissociation equations are really equal to a constant or only to a function of the total salt concentration, provided that all the equations are equal to the same quantity.

Equation (139) is a straight line and corresponds to one in a rectangular coordinate system in which the abscissae are $\sqrt[3]{c}$ and the ordinates p_{K_1} , the straight line cutting the ordinate axis at p_{K_1} , while the tangent of the angle made by the straight line with the abscissa axis measured in the second or fourth quadrant is equal to x . In Fig. 13 $\sqrt[3]{c}$ is plotted as abscissae and p_{K_1} as ordinates, the total cation concentration in the solutions which contain either sodium salts or potassium salts alone being calculated. Only the experiments for which $\sqrt[3]{c}$ is given in the tables are plotted in the figure.

Hasselbalch's experiments (the two lowest dotted curves) are seen to be about 0.09 lower in the coordinate system than mine, so that Hasselbalch's p_{K_1} (18°) is 6.412, p_{K_1} (38°) is 6.302, p_{K_1} (18°) - p_{K_1} (38°) = 0.11, while k is 0.52.

The continuous line refers to the series of pure sodium bicarbonate solutions fully discussed above, while the uppermost dotted line is the one that best represents, as far as one can judge, all the experiments with sodium salts (the experiments with $n/1000$ NaHCO₃ are however omitted). This line gives

$$p_{K_1} = 6.514,$$

$$k = 0.46.$$

There is only slight uncertainty in drawing the line and without doubt only a small real error. It is worth noting that the equation

$$-\log F_a(\text{HCO}'_3) = 0.46 \sqrt[3]{c} \dots\dots\dots(143)$$

appears to hold up to $0.4n$ with good approximation.

The lowest dotted curve is parallel with the uppermost but 0.11 lower. It represents the determinations at 38° tolerably well. It will be observed that the change in the constant per degree is 0.0055 in Hasselbalch's experiments and also in mine, therefore considerably less than the change found by Kendall [1916], namely 0.008, and rather less than that obtained by thermodynamic methods with Thomsen's value for the heat of reaction, namely 0.0065. The uppermost dotted curve represents the determinations of p_{K_1} for pure potassium salt solutions. It gives $p_{K_1} = 6.497$ and $k = 0.38$. The value found for p_{K_1} is presumably a little too low because it is hardly possible there can be any real difference between p_{K_1} in sodium and potassium solutions, but there are too few determinations in low concentrations in the series to enable us to attribute the same importance to the constants for potassium as to those for sodium salts.

From their experiments on the reaction of CaCl₂ solutions saturated with Ca (HCO₃)₂ Bjerrum and Gjaldbaek [1919] calculated the "reaction constant" of calcium carbonate as

$$\log K = -5.02 \text{ at } 18^\circ.$$

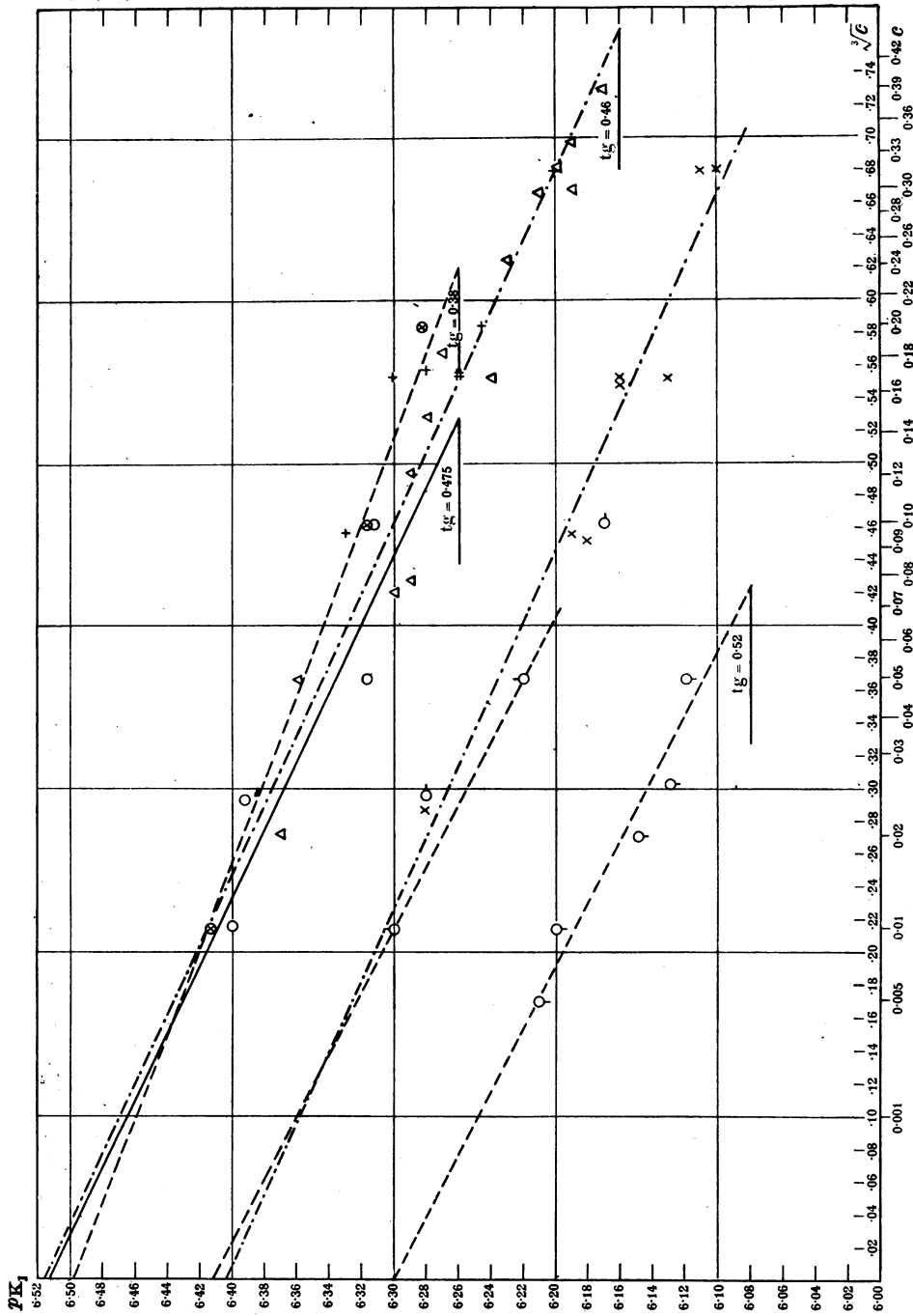


Fig. 13.

This experimental determination they compared with a calculation of the reaction constant by means of the following equation, Bjerrum and Gjaldbaek's equation (28),

$$\log K = \log K_1 + \log Kp - \frac{1}{2} \log K', \dots\dots\dots(144)$$

where K_1 is the first dissociation constant of carbonic acid ($\log K_1$ is therefore equal to $-\rho_{K_1}$), Kp is the "solubility" constant of CO_2 which is estimated as

$$\log Kp = -1.38,$$

and K' is a constant, which we shall shortly consider a little more closely, the value used by Bjerrum and Gjaldbaek being

$$\log K' = -5.68.$$

Bjerrum and Gjaldbaek employed the mean of Walker and Cormack's and Kendall's determinations, namely -6.51 , as the value for $\log K_1$, from which they obtained

$$\log K = -5.05,$$

a figure which therefore was only 0.03 less than that determined directly.

Now it will be seen that equation (144) reversed can be used for the calculation of $\log K_1$ if $\log K'$ is known, and that by substituting the value found, namely $\log K' = -5.02$, we obtain

$$\log K_1 = -6.48.$$

This value agrees extremely well with that previously obtained from Walker and Cormack's and Kendall's experiments, and with those I myself determined, but it will be shown the agreement can be made still better.

The constant K' determines the following equilibrium, Bjerrum and Gjaldbaek's equation (15),

$$\frac{a_{Ca^{++}} \cdot a_{HCO_3^-}^2}{P_{CO_2}} = K' \cdot 1. \dots\dots\dots(145)$$

Apropos of this they write:

"The ionic activity (a) can be calculated by multiplying the ionic concentration (c) by the ionic activity coefficient (F_a). For the monovalent bicarbonate ion the activity coefficient is approximately given by

$$\log F_a = -0.3 \sqrt[3]{c_{Ion}},$$

and for the divalent calcium cation it is given by

$$\log F_a = -2 \times 0.3 \sqrt[3]{c_{Ion}},$$

c_{Ion} standing for the ionic normality of the solution. (145) now assumes the following form:

$$\frac{C_{Ca^{++}} \cdot C_{HCO_3^-}^2}{P_{CO_2}} = K' \cdot 10^{1.2 \sqrt[3]{c_{Ion}}}. \dots\dots\dots(146)$$

If we call the equivalent concentration of the calcium carbonate which Schlösing² found dissolved C , we have

$$C_{Ca^{++}} = \frac{1}{2}C, C_{HCO_3^-} = C, C_{Ion} = C.$$

¹ Bjerrum and Gjaldbaek substitute ρ_{CO_2} for my P_{CO_2} , and naturally their numbering of equations is different from that given here.

² Cited from Bjerrum and Gjaldbaek [1919].

By substitution and taking logarithms (146) becomes

$$3 \log C - \log P_{\text{CO}_2} - 1.2 \sqrt[3]{c} - \log 2 = \log K'. \dots\dots(147)''$$

Bjerrum and Gjaldbaek calculate the values of $\log K'$ with the help of (147) from Schlösing's¹ experiments on the solubility of calcium carbonate at different CO_2 tensions, and their results are recorded in Table XLV in the first three columns. It will be noted they have calculated the activity of the bicarbonate ion from the equation

$$\log F_a(\text{HCO}'_3) = -0.30 \sqrt[3]{C}, \dots\dots\dots(148)$$

but as we have previously found the value 0.3 is too low their tables have been recalculated with the equation

$$3 \log C - \log P_{\text{CO}_2} - 1.52 \sqrt[3]{c} - \log 2 = \log K', \dots\dots(149)$$

having assumed that the constant in the equation for calculating the activity coefficient of the bicarbonate ion in calcium carbonate solutions is the same as in sodium salt solutions (see above). The values obtained have been put in the fourth column of Table XLV. $\log K'$ becomes -5.709 and it will be observed that the agreement between the individual experiments is better calculated in this way than by Bjerrum and Gjaldbaek's method. Schlösing's¹ experiments were carried out at 16° and Bjerrum and Gjaldbaek therefore convert the values to 18° using a temperature coefficient derived from experiments of R. C. Wells¹. Correcting the constant in the same way we obtain

$$\log K' = -5.749 \text{ at } 18^\circ.$$

Now it appears that Bjerrum and Gjaldbaek's "reaction constant" for calcium carbonate can be used without conversion if we confine ourselves to the experiments they signify as best suited for the calculation (0.1 and $0.02n$ CaCl_2), because a recalculation using 0.46 instead of 0.30 gives no difference in the second decimal place. Calculated by (144) p_{K_1} becomes

$$p_{K_1} = 6.515 \text{ at } 18^\circ,$$

which is in surprisingly good agreement with Walker and Cormack's, Kendall's and my own determinations.

At 18° the first dissociation exponent is therefore according to

Knox	6.426	Kendall	6.507
Walker and Cormack	6.512	Bjerrum and Gjaldbaek	6.515
Hasselbalch	6.420	Warburg ²	6.514

Of these values Knox's was obtained with a relatively indifferent technique. In view of what was said in chapter IV Hasselbalch's experiments may very well have a systematic error; all the other determinations give values which approximate closely to 6.51 . Therefore

$$K_1 = 3.1 \times 10^{-7} (18^\circ).$$

T. H. Milroy [1917] has carried out electrical determinations at 37.5° with pure $0.2n$ sodium bicarbonate solution and the same diluted with $0.2n$ sodium chloride solution from which $p_{K'_1}$ at the concentration $0.2n$ can be calculated.

¹ Cited from Bjerrum and Gjaldbaek [1919].

² Sodium salts.

I have gone over Milroy's experiments and the technique is hardly as good as could be wished. The dispersion is rather large and p_{K_1} has a lower value than would be expected, being not as much as 6.00 on an average. J. F. McClendon, A. Shedlov and W. Thomson [1917] have also made measurements in salt solutions containing bicarbonate but they have only published their results graphically so that it is impossible to adjudicate upon the accuracy of the determinations.

Lastly L. Michaelis and P. Rona [1914] have made some measurements in sodium bicarbonate solutions but as Hasselbalch has shown they are subject to a technical error which makes them very doubtful.

The osmotic coefficient of the bicarbonate can be calculated with equation (44),

$$1 - f_0 = k \sqrt[3]{c},$$

where k is determined by (46),

$$\log_e f_a = -4k \sqrt[3]{c}.$$

By substituting the value 2.303×0.46 for $4k$ we get

$$f_0 (\text{HCO}'_3) = 1 - 0.26 \sqrt[3]{c}. \dots\dots\dots(150)$$

According to (136) $f_\mu (\text{NaHCO}_3) = 1 - 0.51 \sqrt[3]{c}$,

and from (143) we have

$$\log f_a (\text{HCO}'_3) = (\log F_a (\text{HCO}'_3)) = -0.46 \sqrt[3]{c}.$$

With the help of these equations the deviation coefficients for the bicarbonate ion have been calculated and the results recorded in Table XLVI and graphically displayed in Fig. 14.

When one compares the deviation coefficients given here with those valid for KCl which are recorded in chapter I, Table III one cannot help thinking the marked depression of the activity of the bicarbonate ion and the relatively low conductivity coefficient are an indication that the salt is not completely dissociated as we previously supposed.

It would be of great interest to compare the deviation coefficients of a considerable number of salts with one another and with the dissociation constant of the corresponding acid, but such an investigation lies outside the scope of this work and it is to be hoped it will soon be undertaken by someone more expert in that branch of the subject. It may however be put forward that the fact that the activity of the bicarbonate ion can be determined with (143) over a large range of concentration does not at all well fit in with the idea of an incomplete dissociation of sodium bicarbonate. If we assume that equation (143) only represents the relation between the bicarbonate concentration and the activity of its ions, while the relation between the ionic concentration and activity of bicarbonate and sodium is given by

$$-\log F_a = 0.25 \sqrt[3]{c}, \dots\dots\dots(\text{I})$$

we can construct the following equation:

$$c\gamma \cdot 10^{-0.25 \sqrt[3]{c}\gamma} = c \cdot 10^{-0.46 \sqrt[3]{c}}, \dots\dots\dots(\text{II})$$

and therefore

$$\log \gamma = \sqrt[3]{c} (0.46 - 0.25 \sqrt[3]{\gamma}). \dots\dots\dots(\text{III})$$

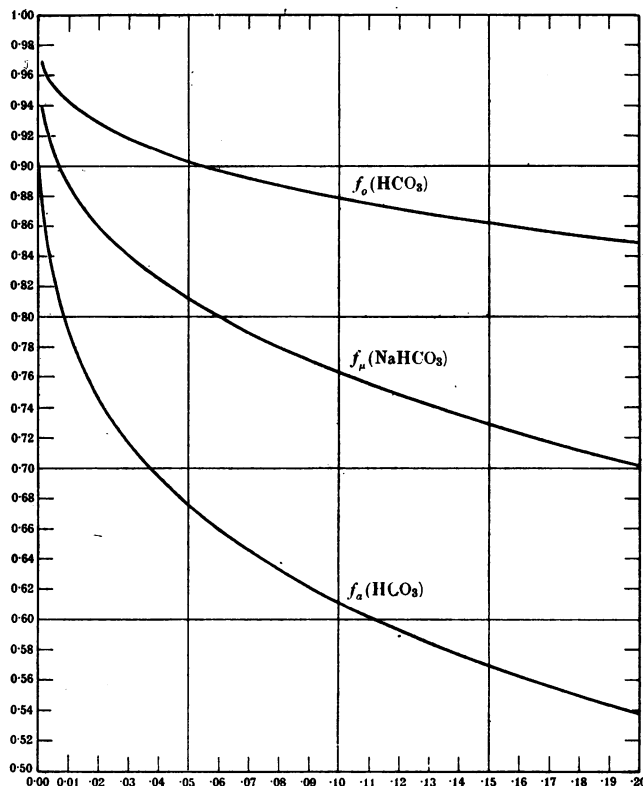


Fig. 14. Deviation coefficients of sodium bicarbonate solutions.

According to the mass action law the following holds:

$$\frac{C_{\text{Na}^+} \cdot F_a(\text{Na}^+) \cdot C_{\text{HCO}_3^-} \cdot F_a(\text{HCO}_3^-)}{C_{\text{NaHCO}_3} \cdot F_a(\text{NaHCO}_3)} = K. \quad \text{.....(IV)}$$

If we put $F_a(\text{NaHCO}_3) = 1$ we get

$$\frac{c\gamma \cdot 10^{-0.5} \sqrt[3]{c\gamma}}{1-\gamma} = K. \quad \text{.....(V)}$$

If now equation (III) is solved by successive approximations and the values found are substituted in (V) we obtain

c	γ	K
0.001	0.952	1.7×10^{-2}
0.01	0.897	6.1×10^{-2}
0.1	0.790	1.8×10^{-1}

The example given shows therefore that "the constant" in (V) must increase with the salt concentration and that the mass action law cannot therefore be satisfied if the salt is incompletely dissociated, provided that an equation for the relation between the concentration and ionic activity of the form of (143) holds good.

In Table XLVII are given determinations of p_{K_1} in solutions which contain small amounts of phosphate in addition to NaCl and NaHCO₃. It

is probable that $p_{K'_1}$ allowing for experimental error is identical with the constant one might expect if phosphate was substituted by chloride.

In Table XLVIII are recorded two series of estimations carried out in about 0.01*n* sodium bicarbonate solutions which were at the same time 0.501*m* as regards cane sugar.

The solutions were prepared by making stock solutions double the strength of those used in the experiments. These were kept on ice. Equal parts of sodium bicarbonate and cane sugar solutions were measured with Geissler pipettes and mixed half an hour before saturation was commenced during which time they were in the laboratory at room temperature.

The potential established itself—in contrast to the pure salt solutions—not immediately, but only when the electrode had been rocked 10–25 times. The first series of measurements belongs to series A and was performed late in this series so that $p_{K'_1}$ is too low. It shows that the relative absorption coefficient is about 0.835 and γ is therefore 16.5. The second series of measurements was carried out with E III and E VI simultaneously with the experiments previously noted as technically the best. It gives $p_{K'_1} = 6.461$ (18°). As $p_{K'_1}$ in the corresponding pure NaHCO₃ solution is 6.413, it appears that the addition of cane sugar increases the constant. If now we regard the depression of solubility of CO₂ as an expression of the amount of water the cane sugar has appropriated (we assume that CO₂ and NaHCO₃ are insoluble in hydrated cane sugar), and correct the calculations for this we obtain

$$p_{K'_1} - \log F_a(\text{CO}_2) = 6.383,$$

and at the same time the solution may be regarded as 0.012*n* with respect to bicarbonate, which corresponds to

$$p_{K'_1} = 6.402.$$

The difference between 6.383 and 6.402 does not lie outside the experimental error for certain, so much the more so because of the peculiarity in the establishment of the potential in cane sugar solutions, just referred to.

The result of this small series of experiments is that the activity of the bicarbonate ion is not affected with any certainty by the cane sugar molecules when a correction for the hydration is made.

RÉSUMÉ.

I. The first dissociation constant of carbonic acid has been recalculated from the best experiments in the literature, and it has been determined afresh by the electrical potential method at 18° and 38°.

II. The apparent activity coefficient of the bicarbonate ion has been determined in sodium and potassium solutions up to 0.4*n*.

III. The apparent osmotic coefficient of the bicarbonate ion has been calculated from the apparent activity coefficient.

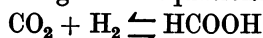
IV. The apparent conductivity coefficient of the bicarbonate ion has been recalculated.

V. It has been rendered probable that the alkaline bicarbonates are completely dissociated.

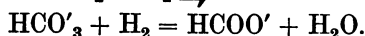
ADDENDUM

After this chapter was completed a paper by C. Lovatt Evans appeared (*J. Physiol.* 1921, **54**, pp. 353-366) which necessitates a certain amount of criticism. The author himself is rather cautious, as he writes: "Although perhaps some doubt still remains as to the finality of the conclusions which will be presented here etc...."

The object of the paper was to prove that electrical determinations of the reaction of bicarbonate solutions give too acid values (too low $p_{\text{H}'}$) and that correct results can be obtained by the colorimetric method. The explanation of the reaction being found too acid by potential measurements is given by the author as a consequence of the formation of formic acid in sufficient quantity to set up a reduction potential by the catalytic action of the platinum black on the electrode, according to the equations



and



(1) It can very easily be shown that the combined CO_2 in an alkali bicarbonate solution does not decrease when the solution is treated for half an hour (or one hour) with hydrogen in the presence of platinum black. I have myself carried out over 50 such experiments. However it would be very probable that the combined amount of CO_2 would decrease if a reduction potential was set up as Evans suggests.

(2) If such a process took place $p_{\text{K}'_1}$ would be dependent upon the CO_2 tension and HCO_3' concentration and not, as has been shown, practically only upon the cation concentration.

(3) The calculation of $p_{\text{K}'_1}$ from Bjerrum and Gjaldbæk's and from my own experiments would give lower values than from conductivity determinations if the formation of formic acid took place.

(4) The agreement between the calculated amount of combined CO_2 and that found experimentally in the phosphate experiments in chapter XI would be bad if Evans was right in his conclusions.

The most important of Evans' experiments are the following ($p_{\text{K}'_1}$ calculated by the author):

mm. Hg CO_2	Neutral red		Phenol red		Electrically	
	$p_{\text{H}'}$	$p_{\text{K}'_1}$	$p_{\text{H}'}$	$p_{\text{K}'_1}$	$p_{\text{H}'}$	$p_{\text{K}'_1}$
	0.02 <i>n</i> NaHCO_3 20°					
8.93	8.23	(6.59)	8.04	6.40	7.96	(6.33)
21.8	7.70	6.45	7.42	6.17	7.55	6.30
33.3	7.57	6.51	7.28	6.22	7.34	6.28
46.0	7.37	6.45	7.17	6.25	7.16	6.24
68.9	7.19	6.34	6.97	6.12	7.07	6.22
	Mean	6.44	Mean	6.19	Mean	6.26
	0.02 <i>n</i> NaHCO_3 + 0.18 <i>n</i> NaCl 20°					
6.5	8.13	(6.36)	—	—	—	—
11.5	7.77	6.25	—	—	—	—
13.9	7.66	6.22	7.67	6.23	7.60	6.16
18.8	—	—	—	—	7.34	6.06
26.0	7.48	6.31	—	—	—	—
30.5	7.33	6.23	7.34	6.24	7.15	6.05
42.8	7.23	6.28	—	—	—	—
44.0	7.21	6.27	—	—	—	—
46.1	—	—	—	—	7.08	6.16
57.2	7.11	6.28	—	—	—	—
58.5	—	—	—	—	6.88	6.10
65.4	7.04	6.27	—	—	—	—
	Mean	6.26	Mean	6.235	Mean	6.11

From the determinations made in the preceding chapter pK'_1 in the first series is 6.38 and in the second series 6.23 at 20°.

The reason Evans did not obtain agreement between the electrical and colorimetric results is probably the fact that his electrode vessel is of an unsuitable type. As far as I can judge it must be almost impossible with his electrode to avoid the O₂ error. Evans himself writes: "Definitive potentials were obtained almost at once provided the gas was free from oxygen; when this was not the case, there was first a somewhat lower potential than that finally obtained after one or two hundred inversions."

The colorimetric determinations of the reaction in salt solutions seem from the above to be rather good (agreement between pK'_1 in each series), but the curves of the reaction of the blood indicate too alkaline a reaction possibly because the blood was saturated at body temperature, the dialysis and colorimetry however being performed at room temperature.

The reactions of salt solutions which are "saturated" with smaller CO₂ tensions than 10 mm. are more alkaline than would be expected as Evans himself has noted. He ascribes this to hydrolysis which is incorrect as hydrolysis at the reactions of the experiments is negligible in this connection (it is of the same order as $\alpha_{OH'}$). The strongly alkaline reactions probably arise from equilibrium not being reached during the "saturation" at the low CO₂ tensions (cf. chapter XI).

I shall not enter further into a discussion of the theory of the "degree of dissociation" of the bicarbonate here but refer the reader to the preceding chapters.

Table XXX. Conductivity determinations in bicarbonate solutions.

V	c	$\frac{V}{c}$	μ_v	
12.1	0.0826	0.436	77.3	Kendall NaHCO ₃ 25°
24.2	0.0413	0.346	81.7	
48.4	0.0207	0.275	85.3	
96.8	0.0103	0.217	88.2	
193.6	0.00516	0.173	90.6	
387.2	0.00258	0.137	92.4	
774.4	0.00129	0.109	93.8	
1548.8	0.000646	0.0864	94.8	
3097.6	0.000323	0.0686	95.5	
—	0	0	99.2	
32.0	0.0313	0.315	69.8	Walker and Cormack NaHCO ₃ 18°
64.0	0.0156	0.250	72.9	
128.0	0.00782	0.198	75.6	
256.0	0.00391	0.158	78.6	
512.0	0.00195	0.125	80.8	
—	0	0	88.1	
64.0	0.0156	0.250	83.3	Kendall 1/2 CaCO ₃ 25°
128.0	0.00782	0.198	88.8	
256.0	0.00391	0.158	93.4	
512.0	0.00195	0.125	96.7	
1024.0	0.000977	0.0992	102.0	
2048.0	0.000488	0.0787	107.7	
—	0	0	?	

Table XXXI. Determinations of the first dissociation constant of carbonic acid calculated from Walker and Cormack's and from Kendall's experiments.

V	μ_n	γ	$K_1 \times 10^{-7}$	
31.25	1.104	0.00310	3.09	Walker and Cormack 18° CO ₂ from marble
62.5	1.570	0.00441	3.13	
93.7	1.916	0.00539	3.11	
125.0	2.218	0.00623	3.12	
∞	355.8		Mean 3.11	
			pK_1 6.507	
27.5	1.033	0.00291	3.07	Walker and Cormack 18° CO ₂ from carbonic acid snow
55.0	1.454	0.00409	3.05	
82.5	1.754	0.00502	3.05	
110.0	2.052	0.00577	3.04	
∞	355.8		Mean 3.05	
			pK_1 6.516	
25.4	0.631	0.00237	2.23	Kendall 0°
38.3	0.770	0.00290	2.20	
50.0	0.880	0.00331	2.20	
76.3	1.081	0.00407	2.18	
99.8	1.242	0.00468	2.21	
152.6	1.548	0.00584	2.24	
∞	265.6		Mean 2.21	
			pK_1 6.656	
30.9	1.100	0.00309	3.11	Kendall 18°
42.0	1.281	0.00360	3.11	
61.2	1.550	0.00437	3.14	
83.4	1.792	0.00504	3.06	
∞	355.8		Mean 3.11	
			pK_1 6.507	
36.4	1.403	0.00355	3.47	Kendall 25°
51.3	1.659	0.00320	3.44	
72.8	1.977	0.00500	3.45	
102.4	2.341	0.00592	3.44	
145.5	2.820	0.00713	3.54	
∞	395.5		Mean 3.47	
			pK_1 6.460	

Table XXXII. Calculation of pK'_1 in pure sodium bicarbonate solutions from K. A. Hasselbalch's experiments, *Biochem. Zeitsch.* 78, p. 119.

Concentration	mm. CO ₂	pH'		pK'_1	
		Uncorrected		Corrected for decreased H ₂ pressure	
0.05 <i>n</i>	47.2	7.47	6.19	7.48	6.20
$\sqrt{c}=0.368$	403.2	6.53	6.18	6.68	(6.33) ¹
18°	74.0	7.28	6.20	7.30	6.22
Mark \diamond	147.7	6.97	6.19	7.01	6.23
		Mean	6.19	Mean	6.22
0.01 <i>n</i>	54.3	6.82	6.29	6.83	6.30
$\sqrt{c}=0.215$	134.3	6.42	6.28	6.46	6.32
18°	101.8	6.51	6.25	6.54	6.29
Mark \diamond	84.5	6.59	6.25	6.61	6.27
	68.8	6.73	6.30	6.75	6.32
	92.4	6.59	6.29	6.62	6.32
		Mean	6.28	Mean	6.30

¹ Not included in the mean value.

Table XXXII (continued)

Concentration	mm. CO ₂	Uncorrected		Corrected for decreased H ₂ pressure	
		pH'	pK' ₁	pH'	pK' ₁
0.05 <i>n</i>	168.9	7.02	6.06	7.08	6.12
$\sqrt[3]{c}=0.368$	247.8	6.87	6.08	6.97	(6.18) ¹
38°	52.6	7.55	6.09	7.57	6.11
Mark ϕ	717.0	6.40	6.07	?	?
		Mean	6.08	Mean	6.12
0.03 <i>n</i>	40.6	7.48	6.12	7.49	6.13
$\sqrt[3]{c}=0.311$	80.7	7.15	6.09	7.18	6.12
38°	135.0	6.92	6.09	6.96	6.13
Mark ϕ	96.9	7.08	6.10	7.11	6.13
		Mean	6.10	Mean	6.13
0.02 <i>n</i>	123.3	6.83	6.13	6.87	6.17
$\sqrt[3]{c}=0.271$	36.7	7.33	6.11	7.34	6.12
38°	62.8	7.13	6.14	7.15	6.16
Mark ϕ		Mean	6.13	Mean	6.15
0.01 <i>n</i>	85.0	6.70	6.14	6.73	6.17
$\sqrt[3]{c}=0.215$	218.6	6.33	6.18	6.40	6.25
38°	137.4	6.51	6.16	6.55	6.20
Mark ϕ	189.2	6.40	6.19	6.46	6.23
	119.8	6.57	6.16	6.61	6.20
	149.0	6.44	6.13	6.48	6.17
		Mean	6.16	Mean	6.20
0.005 <i>n</i>	23.5	7.02	6.21	7.03	6.22
$\sqrt[3]{c}=0.171$	41.35	6.75	6.18	6.76	6.19
Mark ϕ	71.8	6.53	6.20	6.55	6.22
		Mean	6.20	Mean	6.21

¹ Not included in the mean value.Table XXXIII. Determinations of pK'₁ for 18° in sodium bicarbonate solutions carried out with the small saturator electrode. Series A. Mark Δ .

Concentration	Temp.	mm. Hg		pH'	pK' ₁ 18°
		CO ₂	O ₂		
<i>T</i> = 8.88	16.0	240.2	0.6	5.84	6.37
0.00399 <i>n</i> HCO' ₃	16.5	118.6	0.2	6.19	6.42
0.00399 <i>n</i> Na'	16.5	41.6	0.2	6.56	6.33
	16.5	15.2	0.2	7.04	6.37
	16.5	5.8	0.2	7.45	6.37
				Mean	6.37
<i>T</i> = 17.52	19.5	543.4	0.3	5.80	(6.37)
0.00786 <i>n</i> HCO' ₃	19.5	141.0	0.5	6.38	6.37
0.00786 <i>n</i> Na'	19.5	55.2	0.5	6.82	6.40
	19.5	18.0	0.5	7.29	6.38
	20.0	7.1	0.3	7.70	6.39
	20.0	4.2	0.3	8.05	(6.51)
				Mean	6.38
<i>T</i> = 55.5	19.5	486.5	0.7	6.35	6.37
0.0249 <i>n</i> HCO' ₃	19.0	124.4	0.5	6.95	6.38
0.0249 <i>n</i> Na'	19.0	51.0	0.5	7.33	6.37
	19.0	30.9	0.3	7.51	6.35
	19.0	11.3	0.3	8.01	6.40
				Mean	6.37

 $\sqrt[3]{c}=0.273$

Table XXXIII (continued)

Concentration	Temp.	mm. Hg.		p_{H^+}	$p_{\text{K}'_1}$ 18°	
		CO ₂	O ₂			
$T = 110.0$	20.5	538.0	0.6	6.60	(6.37)	$\sqrt[3]{c} = 0.367$
0.0494 <i>n</i> HCO ₃ '	20.0	267.0	0.5	6.91	6.37	
0.0494 <i>n</i> Na'	20.0	67.2	0.5	7.50	6.36	
	20.0	25.2	0.2	7.91	6.35	
	20.0	9.2	0.2	8.36	6.37	
				Mean	6.36	
$T = 221.9$	19.5	126.3	0.5	7.44	6.28	$\sqrt[3]{c} = 0.464$
0.0997 <i>n</i> HCO ₃ '	19.5	37.5	0.5	8.00	6.32	
0.0997 <i>n</i> Na'	19.5	14.7	0.3	8.39	6.31	
	19.0	58.8	0.3	7.80	6.31	
	17.0	193.4	0.2	7.28	6.31	
	17.0	85.3	0.9	7.63	6.31	
	17.0	25.1	1.2	8.08	6.33	
	17.0	50.1	0.7	7.88	6.32	
	17.0	130.1	0.5	7.41	6.27	
	17.0	56.6	0.3	7.81	6.32	
				Mean	6.31	

Table XXXIV. Determinations of $p_{\text{K}'_1}$ for 18° in sodium bicarbonate solutions with the addition of 0.42 % NaCl (0.0718*n*). Carried out with the small saturator electrode. Series A. Mark Δ.

Concentration	Temp.	mm. Hg		p_{H^+}	$p_{\text{K}'_1}$ 18°	
		CO ₂	O ₂			
$T = 8.88$	18.5	245.8	0.6	5.78	6.31	$\sqrt[3]{c} = 0.421$
0.00399 <i>n</i> HCO ₃ '	19.0	29.5	0.6	6.70	6.31	
0.0718 <i>n</i> Cl'	19.0	40.7	0.6	6.56	6.30	
0.07479 <i>n</i> Na'	19.0	63.8	0.4	6.23	6.28	
				Mean	6.30	
$T = 17.52$	19.0	395.5	1.0	5.86	6.31	$\sqrt[3]{c} = 0.429$
0.00786 <i>n</i> HCO ₃ '	19.0	108.9	0.4	6.42	6.28	
0.0718 <i>n</i> Cl'	19.5	34.5	0.2	6.91	6.29	
0.07966 <i>n</i> Na'	19.5	6.0	0.2	7.68	6.30	
	19.5	14.4	0.2	7.31	(6.31)	
				Mean	6.29	
$T = 55.5$	20.0	36.7	6.6	7.34	(6.24)	$\sqrt[3]{c} = 0.459$
0.0249 <i>n</i> HCO ₃ '	20.0	119.2	1.2	6.86	6.27	
0.0718 <i>n</i> Cl'	20.0	106.2	0.7	6.93	6.29	
0.0967 <i>n</i> Na'	20.0	7.3	0.5	8.10	6.30	
	20.0	512.0	0.6	6.22	(6.25)	
	20.0	126.7	0.3	6.85	6.29	
	20.0	36.1	0.2	7.40	6.29	
	20.0	3.1	0.2	8.46	(6.31)	
				Mean	6.29	
$T = 110.0$	21.0	144.2	0.2	7.10	6.29	
0.0494 <i>n</i> HCO ₃ '	21.0	48.3	0.2	7.57	6.29	
0.0718 <i>n</i> Cl'	21.0	34.7	0.2	7.72	6.29	
0.1212 <i>n</i> Na'	20.5	7.7	0.2	8.36	6.29	
	20.5	3.8	0.2	8.77	(6.43)	
				Mean	6.29	
$T = 221.9$	17.0	476.4	1.5	6.76	(6.18)	$\sqrt[3]{c} = 0.556$
0.0997 <i>n</i> HCO ₃ '	17.5	122.5	0.8	7.41	6.23	
0.0718 <i>n</i> Cl'	17.0	58.2	0.3	7.77	6.28	
0.1715 <i>n</i> Na'	17.0	23.3	0.3	8.15	6.27	
	17.5	22.2	0.3	8.17	6.27	
				Mean	6.26	

Table XXXV. Determinations of pK'_1 for 18° in sodium bicarbonate solutions with the addition of 0.85 % sodium chloride (0.145*n*). Carried out with the small saturator electrode. Series A. Mark Δ .

Concentration	Temp.	mm. Hg		pH'	pK'_1 18°	
		CO ₂	O ₂			
<i>T</i> = 8.88	19.0	238.4	0.9	5.78	6.30	
0.00399 <i>n</i> HCO' ₃	19.0	111.6	0.0	6.10	6.29	$\sqrt[3]{c} = 0.530$
0.145 <i>n</i> Cl'	19.0	30.1	0.3	6.64	6.26	
0.1490 <i>n</i> Na'	19.0	12.2	0.3	7.03	6.26	
	19.0	63.7	0.3	6.33	6.27	
	19.0	12.6	0.3	7.02	6.27	
				Mean	6.28	
<i>T</i> = 17.52	20.0	587.6	0.7	5.60	(6.20)	
0.00786 <i>n</i> HCO' ₃	19.5	149.5	0.3	6.24	6.26	$\sqrt[3]{c} = 0.535$
0.145 <i>n</i> Cl'	19.0	43.9	0.5	6.76	6.24	
0.1529 <i>n</i> Na'	19.0	14.3	0.4	7.23	6.22	
	19.0	6.3	0.4	7.61	6.24	
	19.0	3.6	0.4	7.87	(6.26)	
				Mean	6.24	
<i>T</i> = 55.5	21.0	152.0	0.4	6.72	6.22	
0.0249 <i>n</i> HCO' ₃	20.5	47.6	0.4	7.24	6.24	$\sqrt[3]{c} = 0.554$
0.145 <i>n</i> Cl'	21.0	14.6	1.6	7.77	6.26	
0.1699 <i>n</i> Na'	20.5	2.7	0.4	8.55	(6.25)	
	19.5	598.0	1.1	6.13	(6.24)	
	19.5	411.7	0.5	6.27	6.22	
				Mean	6.24	
<i>T</i> = 110.0	19.5	60.9	0.2	7.44	6.27	
0.0494 <i>n</i> HCO' ₃	19.5	26.5	0.2	7.81	6.28	$\sqrt[3]{c} = 0.569$
0.145 <i>n</i> Cl'	19.5	7.7	0.2	8.34	6.29	
0.1844 <i>n</i> Na'	20.5	565.0	1.4	6.42	(6.25)	
	20.5	142.0	0.6	7.06	6.23	
	20.5	27.7	0.6	7.79	6.28	
				Mean	6.27	
<i>T</i> = 221.9	17.0	460.5	0.6	6.73	(6.14)	
0.0997 <i>n</i> HCO' ₃	17.0	161.2	0.6	7.24	6.19	$\sqrt[3]{c} = 0.625$
0.0997 <i>n</i> Cl'	17.0	49.1	0.2	7.79	6.23	
0.2447 <i>n</i> Na'	17.0	15.5	0.2	8.28	6.23	
	17.0	67.9	0.2	8.64	6.25	
	19.0	45.0	0.6	7.83	6.22	
	19.0	90.9	0.7	7.56	6.26	
	19.0	32.8	0.6	8.00	6.25	
				Mean	6.23	

Table XXXVI. Determinations of pK'_1 for 18° in sodium bicarbonate solutions with the addition of 1.7 % NaCl (0.291*n*). Carried out with the small saturator electrode. Series A. Mark Δ .

Concentration	Temp.	mm. Hg		pH'	pK'_1 18°	
		CO ₂	O ₂			
<i>T</i> = 8.88	18.5	243.4	0.4	5.69	6.22	
0.00399 <i>n</i> HCO' ₃	19.0	115.5	0.4	6.00	6.20	$\sqrt[3]{c} = 0.666$
0.291 <i>n</i> Cl'	19.0	36.1	0.4	6.52	6.22	
0.2950 <i>n</i> Na'	19.5	11.7	0.4	7.00	6.21	
	19.5	16.1	0.4	6.85	6.19	
				Mean	6.21	
<i>T</i> = 17.52	18.5	529.3	1.1	5.57	(6.13)	
0.00786 <i>n</i> HCO' ₃	18.5	149.5	0.8	6.17	6.19	$\sqrt[3]{c} = 0.669$
0.291 <i>n</i> Cl'	18.5	46.2	0.2	6.67	6.18	
0.2989 <i>n</i> Na'	19.0	15.3	0.2	7.17	6.19	
				Mean	6.19	

Table XXXVI (continued)

Concentration	Temp.	mm. Hg		pH'	pK'_1 18°	
		CO ₂	O ₂			
$T=55.5$	19.5	602.7	1.1	6.08	(6.20)	
0.0249 <i>n</i> HCO ₃ '	19.5	416.2	0.5	6.27	6.23	
0.291 <i>n</i> Cl'	19.5	131.1	0.6	6.73	6.19	$\sqrt[3]{c}=0.681$
0.3159 <i>n</i> Na ⁺	19.0	62.0	0.5	7.09	6.23	
	19.0	17.2	0.5	7.61	6.18	
	19.0	6.0	0.5	8.08	6.19	
	19.0	2.8	0.5	8.48	(6.19)	
				Mean	6.20	
$T=110.0$	20.0	518.9	0.4	6.50	(6.25)	
0.0499 <i>n</i> HCO ₃ '	20.0	139.1	0.4	7.01	6.19	
0.291 <i>n</i> Cl'	20.5	48.4	0.4	7.50	6.21	$\sqrt[3]{c}=0.699$
0.3409 <i>n</i> Na ⁺	20.0	16.2	0.4	7.94	6.19	
				Mean	6.19	
$T=221.9$	17.0	442.1	0.6	6.76	6.15	
0.0997 <i>n</i> HCO ₃ '	17.0	40.0	0.4	7.84	6.19	
0.291 <i>n</i> Cl'	17.0	20.7	0.4	8.09	6.15	
0.3907 <i>n</i> Na ⁺	17.0	40.1	0.4	7.83	6.18	$\sqrt[3]{c}=0.731$
	17.0	14.5	0.4	8.23	6.14	
	18.0	95.2	0.6	7.50	6.18	
	18.0	106.4	0.6	7.39	6.15	
	18.0	365.2	0.7	6.86	6.17	
	18.0	26.1	0.4	8.04	6.19	
				Mean	6.17	

Table XXXVII. Determinations of pK'_1 for 18° in sodium bicarbonate solutions with the addition of varying quantities of KCl. Carried out with the small saturator electrode. Series A.

Concentration	Temp.	mm. Hg		pH'	pK'_1 18°
		CO ₂	O ₂		
$T=44.3$	20.0	80.4	0.3	6.98	6.32
0.0199 <i>n</i> HCO ₃ '	20.0	132.0	0.3	6.79	6.34
0.54 % KCl (0.0718 <i>n</i>)	20.0	15.4	0.6	7.71	6.33
				Mean	6.33
$T=110.0$	18.0	58.6	0.5	7.48	6.28
0.0494 <i>n</i> HCO ₃ '	18.0	98.7	1.7	7.26	6.29
0.54 % KCl (0.0718 <i>n</i>)	18.0	21.2	0.5	7.92	6.29
				Mean	6.29
$T=44.3$	19.0	130.3	0.6	6.72	6.27
0.0199 <i>n</i> HCO ₃ '	19.0	37.1	0.8	7.27	6.28
1.08 % KCl (0.145 <i>n</i>)	19.5	13.8	0.6	7.69	6.26
	19.5	56.2	0.6	7.09	6.27
				Mean	6.27
$T=44.3$	19.0	64.3	0.5	6.98	6.22
0.0199 <i>n</i> HCO ₃ '	20.0	95.3	0.7	6.84	6.24
2.16 % KCl (0.291 <i>n</i>)	20.0	30.1	0.7	7.34	6.25
	19.5	39.3	0.7	7.20	6.23
				Mean	6.24
$T=55.5$	17.0	132.2	0.5	6.76	6.20
0.0249 <i>n</i> HCO ₃ '	17.0	55.0	0.4	7.14	6.23
2.16 % KCl (0.291 <i>n</i>)	17.0	18.1	0.6	7.61	6.22
				Mean	6.22
$T=111.0$	18.0	58.6	0.6	7.40	6.21
0.0494 <i>n</i> HCO ₃ '	18.0	98.7	1.7	7.17	6.21
2.16 % KCl (0.291 <i>n</i>)	18.0	21.2	0.5	7.85	6.22
				Mean	6.21

Table XXXVIII. Determinations of $p_{K'_1}$ for 18° in sodium bicarbonate solutions with the addition of 0.145*n* NaCl or KCl. Carried out with the small saturator electrode. Series A.

Concentration	Temp.	mm. Hg		NaCl		KCl	
		CO ₂	O ₂	p_{H^+}	$p_{K'_1}$	p_{H^+}	$p_{K'_1}$ 18°
$T=56.25$	17.0	162.2	0.2	6.66	6.21	6.69	6.24
0.0253 <i>n</i> HCO ₃ '	17.5	59.1	0.7	7.11	6.23	7.16	6.28
				Mean	6.22	Mean	6.26
$T=111.0$	17.0	125.3	0.4	7.07	6.21	7.10	6.25
0.0499 <i>n</i> HCO ₃ '	17.5	34.2	1.7	7.68	6.23	7.70	6.28
	17.5	45.3	0.4	7.54	6.24	7.57	6.28
				Mean	6.23	Mean	6.27

 Table XXXIX. Determinations of $p_{K'_1}$ for 18° in sodium bicarbonate solutions with varying additions of salt. Series A.

<i>T</i>	No salt added	0.0718 <i>n</i>		0.0145 <i>n</i>		0.291 <i>n</i>	
		NaCl	KCl	NaCl	KCl	NaCl	KCl
8.88	(6.37)	6.30	—	6.28	—	6.21	—
17.5	(6.38)	6.29	—	6.24	—	6.19	—
44.3	—	—	6.33	—	6.27	—	6.24
55.5	6.37	6.29	—	6.24	—	6.20	6.22
110.0	6.36	6.29	6.29	6.27	6.27	6.19	—
111.0	—	—	—	—	6.23	—	6.21
221.9	6.31	6.26	—	6.23	—	6.17	—

 Table XL. Determinations of $p_{K'_1}$ for 18° in sodium bicarbonate solutions with the addition of salt. Carried out with the small saturator electrode. Series B. Mark +.

Concentration	Temp.	mm. Hg			$p_{K'_1}$ 18°
		CO ₂	p_{H^+}	$p_{K'_1}$	
$T=45.2$	21.0	50.1	7.18	6.30	$\frac{2}{3}c=0.452$
0.0203 <i>n</i> HCO ₃ '	21.0	8.7	7.90	6.26	
0.42 % NaCl (0.0718 <i>n</i>)	21.0	27.7	7.46	6.32	
0.0718 <i>n</i> Cl'			Mean	6.29	
0.0921 <i>n</i> Na'					
$T=56.5$	15.0	579.4	6.18	6.32	$\frac{2}{3}c=0.458$
0.0254 <i>n</i> HCO ₃ '	15.5	139.0	6.79	6.31	
0.42 % NaCl (0.0718 <i>n</i>)	15.5	30.1	7.50	6.35	
0.0718 <i>n</i> Cl'	19.5	61.8	7.20	6.34	
0.0962 <i>n</i> Na'	19.5	52.0	7.27	6.32	
	19.5	41.6	7.39	6.35	
	20.0	41.6	7.38	6.33	
			Mean	6.33	
$T=45.2$	21.0	51.2	7.16	6.30	$\frac{2}{3}c=0.452$
0.0203 <i>n</i> HCO ₃ '	21.0	36.0	7.30	6.28	
0.42 % NaCl (0.0718 <i>n</i>)			Mean	6.29	
0.0718 <i>n</i> Cl'					
0.0921 <i>n</i> Na'					
$T=55.7$	20.0	36.5	7.42	6.30	$\frac{2}{3}c=0.554$
0.0250 <i>n</i> HCO ₃ '	20.0	23.2	7.55	6.24	
0.85 % NaCl (0.145 <i>n</i>)	20.0	22.2	7.60	6.27	
0.145 <i>n</i> Cl'	21.0	38.4	7.36	6.26	
0.170 <i>n</i> Na'	19.0	142.6	7.76	6.24	
	19.0	53.2	7.22	6.27	
			Mean	6.26	

Table XL (continued)

Concentration	Temp.	mm. Hg		pK' , 18°	$\sqrt[3]{c}$
		CO ₂	pH'		
$T = 56.5$	21.5	579.4	6.13	(6.22)	$\sqrt[3]{c} = 0.558$
0.0254 <i>n</i> HCO ₃ '	21.0	111.3	6.92	6.29	
0.85 % NaCl (0.145 <i>n</i>)	21.0	48.5	7.26	6.27	
0.145 <i>n</i> Cl'	21.0	31.8	7.46	6.29	
0.174 <i>n</i> Na'	21.0	49.0	7.26	6.26	
	21.0	19.7	7.68	6.30	
			Mean	6.28	
$T = 56.5$	19.5	199.8	6.55	6.19	$\sqrt[3]{c} = 0.681$
0.0254 <i>n</i> HCO ₃ '	19.0	81.3	6.97	6.21	
1.7 % NaCl (0.291 <i>n</i>)	19.0	36.8	7.29	6.18	
0.291 <i>n</i> Cl'	19.0	20.0	7.58	6.21	
0.3164 <i>n</i> Na'	19.0	8.4	7.96	6.22	
	19.0	17.1	7.65	6.21	
			Mean	6.20	
$T = 56.5$	19.5	61.8	7.18	6.30	$\sqrt[3]{c} = 0.554$
0.025 <i>n</i> HCO ₃ '	19.5	52.5	7.25	6.31	
1.08 % KCl (0.145 <i>n</i>)	19.5	41.6	7.34	6.30	
0.145 <i>n</i> Cl'	20.0	41.6	7.36	6.30	
0.145 <i>n</i> K'					
0.025 <i>n</i> Na'					
			Mean	6.30	

Table XLI. Determinations of pK'_1 in salt solutions for 18°. Carried out by Höber technique in E VI and E III. Series B. Mark O.

Concentration	Temp.	mm. Hg		pK'_1 , 18°		
		CO ₂	pH'	E VI	E III	
$T = 224.4$	19.0	96.2	7.533	6.247	—	$n/10$ NaHCO ₃
0.1008 <i>n</i> HCO ₃ '	19.0	65.9	7.737	6.287	—	
0.1008 <i>n</i> Na'	19.0	40.7	7.969	6.299	—	
	19.0	31.6	8.051	6.281	—	$\sqrt[3]{c} = 0.464$
	19.0	31.6	8.061	6.292	—	
	19.0	30.7	8.070	6.288	—	
	19.0	32.7	8.026	6.261	—	
			Mean	6.279		
$T = 112.2$	18.0	86.9	7.364	6.340	—	$n/20$ NaHCO ₃
0.05041 <i>n</i> HCO ₃ '	18.0	86.9	7.364	—	6.340	
0.05041 <i>n</i> Na'	18.0	61.5	7.506	6.321	—	
	18.0	61.5	7.497	—	6.323	$\sqrt[3]{c} = 0.369$
	18.0	50.7	7.604	6.346	—	
	18.0	50.7	7.597	—	6.349	
			Mean	6.335	6.337	
				6.335		
$T = 56.49$	18.5	52.7	7.324	6.384	—	$n/40$ NaHCO ₃
0.02538 <i>n</i> HCO ₃ '	20.0	24.8	7.680	6.400	—	
0.02538 <i>n</i> Na'	20.0	14.7	7.890	6.383	—	$\sqrt[3]{c} = 0.294$
	20.0	32.0	7.571	6.402	—	
	19.0	47.8	7.382	6.391	—	
			Mean	6.393		
$T = 22.96$	17.0	104.1	6.644	6.392	—	$n/100$ NaHCO ₃
0.01031 <i>n</i> HCO ₃ '	17.0	104.1	6.636	—	6.385	
0.01031 <i>n</i> Na'	16.5	43.4	7.038	6.416	—	
	16.5	43.4	7.035	—	6.413	$\sqrt[3]{c} = 0.217$
	19.5	82.2	6.742	6.382	—	
	19.5	35.9	7.133	6.413	—	
	19.5	35.9	7.133	—	6.413	
	19.5	37.3	7.090	6.386	—	
			Mean	6.398	6.403	
				6.400		

Table XLI (continued)

Concentration	Temp.	mm. Hg CO ₂	pH'	pK' ₁ 18°		
				E VI	E III	
<i>T</i> = 111.4	21.0	28.2	7.803	6.291	—	<i>n</i> /20 KHCO ₃
0.05004 <i>n</i> HCO' ₃	20.5	33.3	7.751	6.308	—	
0.0497 <i>n</i> Cl'	20.5	33.3	7.742	—	6.299	<i>n</i> /20 KCl
0.1000 <i>n</i> K'	20.5	49.8	7.600	6.332	—	
	20.5	49.8	7.593	—	6.323	√ <i>c</i> = 0.464
	22.0	26.2	7.876	6.319	—	
			Mean	6.313	6.312	Mark ⊗
				6.312		
<i>T</i> = 224.4	20.0	83.3	7.621	6.268	—	<i>n</i> /10 NaHCO ₃
0.1008 <i>n</i> HCO' ₃	20.0	83.3	7.618	—	6.265	
0.1012 <i>n</i> Cl'	20.0	41.1	7.911	6.250	—	<i>n</i> /10 KCl
0.1008 <i>n</i> Na'	20.0	41.1	7.911	—	6.260	
0.1012 <i>n</i> K'						√ <i>c</i> = 0.585
0.09965 <i>n</i> Cl'	22.0	91.7	7.586	6.269	—	
0.09965 <i>n</i> K'	22.0	38.3	7.938	6.242	—	
	22.0	38.3	7.931	—	6.235	
<i>T</i> = 222.7	21.5	85.1	7.611	6.271	—	<i>n</i> /10 KHCO ₃
0.1000 <i>n</i> HCO' ₃	21.5	85.1	7.604	—	6.264	
0.1012 <i>n</i> Cl'	21.5	44.5	7.896	6.275	—	<i>n</i> /10 NaCl
0.1000 <i>n</i> K'						
0.1012 <i>n</i> Na'			Mean	6.262	6.256	
				6.260		
<i>T</i> = 2.244	19.5	35.2	6.029	6.310	—	
0.001008 <i>n</i> HCO' ₃	19.5	35.2	6.026	—	6.310	<i>n</i> /1000 NaHCO ₃
0.0994 <i>n</i> Cl'	20.0	47.0	5.904	6.303	—	
0.1004 <i>n</i> Na'	20.0	38.6	5.991	6.298	—	<i>n</i> /10 NaCl
	20.0	38.6	5.991	—	6.298	
	19.0	37.4	6.034	6.334	—	
	19.0	37.4	6.031	—	6.333	
	19.5	39.5	5.987	6.318	—	
	19.5	39.5	5.984	—	6.315	
			Mean	6.313	6.314	
				6.313		
<i>T</i> = 221.45	19.5	44.1	7.929	6.322	—	<i>n</i> /10 KHCO ₃
0.09948 <i>n</i> HCO' ₃	19.5	44.1	7.918	—	6.315	
0.09948 <i>n</i> K'	19.5	29.2	8.101	6.317	—	
	19.5	29.2	8.094	—	6.310	√ <i>c</i> = 0.464
	19.5	60.9	7.799	6.324	—	
	19.5	60.9	7.789	—	6.314	
			Mean	6.321	6.313	Mark ⊗
				6.317		
<i>T</i> = 22.14	19.5	38.9	7.092	6.422	—	
0.009948 <i>n</i> HCO' ₃	19.5	38.9	7.095	—	6.425	<i>n</i> /100 KHCO ₃
0.009948 <i>n</i> K'	19.5	48.4	6.979	6.404	—	
	19.5	48.4	6.979	—	6.404	√ <i>c</i> = 0.215
	19.5	50.2	6.969	6.410	—	
			Mean	6.412	6.415	Mark ⊗
				6.413		
<i>T</i> = 224.4	20.0	57.8	7.737	6.226	—	<i>n</i> /10 NaHCO ₃
0.1008 <i>n</i> HCO' ₃	20.0	57.8	7.737	—	6.226	
0.1002 <i>n</i> Cl'	19.5	41.5	7.906	6.267	—	<i>n</i> /10 NaCl
0.2010 <i>n</i> Na'	19.5	41.5	7.904	—	6.265	
	22.0	81.3	7.623	6.254	—	
	22.0	81.3	7.621	—	6.252	√ <i>c</i> = 0.585
	22.0	29.5	8.048	6.228	—	
	22.0	29.5	8.058	—	6.238	Mark +
	22.5	78.2	7.642	6.249	—	
	22.5	78.2	7.639	—	6.256	
			Mean	6.245	6.247	
				6.246		

Table XLI (continued)

Concentration	Temp.	mm. Hg.		pK'_1 18°		
		CO ₂	pH'	E VI	E III	
$T=112.2$	21.0	75.6	7.411	6.314	—	$n/20$ NaHCO ₃
0.05041 <i>n</i> HCO ₃ '	21.0	75.6	7.408	—	6.311	
0.0501 <i>n</i> Cl'	22.0	24.3	7.889	6.295	—	$n/20$ NaCl
0.1005 <i>n</i> Na'	22.0	24.3	7.871	—	6.277	
	20.0	31.6	7.773	6.300	—	$\sqrt[3]{c}=0.464$
	20.0	31.6	7.761	—	6.288	
			Mean	6.303	6.292	Mark +
				6.297		
$T=222.7$	21.5	80.9	7.647	6.285	—	$n/10$ KHCO ₃
0.1000 <i>n</i> HCO ₃ '	21.5	80.9	7.637	—	6.275	$n/10$ KCl
0.0995 <i>n</i> Cl'	21.5	29.2	8.070	6.276	—	
0.1995 <i>n</i> K'	21.5	29.2	8.068	—	6.274	$\sqrt[3]{c}=0.585$
	21.5	30.4	8.063	6.286	—	
	21.5	30.4	8.063	—	6.296	
			Mean	6.282	6.282	Mark ⊗
				6.282		

Table XLII. Determinations of pK'_1 at 38°; salt solutions. Carried out by Höber technique in E VI. Series B. Mark ◊.

Concentration	mm. Hg		pH'	pK'_1 38°	
	CO ₂	O ₂			
$T=56.3$	465.7	0.2	6.25	(6.02)	$\sqrt[3]{c}=0.681$
0.0253 <i>n</i> HCO ₃ '	108.7	0.2	7.20	6.15	
1.7% NaCl (0.291 <i>n</i>)	44.3	0.2	7.35	6.11	
0.291 <i>n</i> Cl'	17.9	0.3	7.22	6.09	
0.3163 <i>n</i> Na'	40.1	0.3	7.38	6.09	
			Mean	6.11	
$T=56.5$	587.6	0.0	6.21	(6.09)	$\sqrt[3]{c}=0.681$
0.0254 <i>n</i> HCO ₃ '	338.4	0.1	6.45	6.10	
1.7% NaCl (0.291 <i>n</i>)	127.7	0.0	6.89	6.11	
0.291 <i>n</i> Cl'	45.8	0.0	7.44	6.11	
0.3164 <i>n</i> Na'	8.7	0.6	7.04	6.08	
			Mean	6.10	

Table XLIII. Determinations of pK'_1 at 38° in sodium bicarbonate solutions without the addition of salt. Carried out by Höber technique in E VI. Series B. Mark ◊.

Concentration	mm. Hg		pH'	pK'_1 38°	
	CO ₂	O ₂			
$T=56.5$	54.1	—	7.42	6.27	$\sqrt[3]{c}=0.287$
0.0254 <i>n</i> HCO ₃ '	41.4	—	7.56	6.29	
0.0254 <i>n</i> Na'	43.4	—	7.55	6.30	
	95.7	—	7.19	6.28	
	32.1	—	7.66	6.27	
			Mean	6.28	
$T=224.4$	74.0	—	7.82	6.20	$\sqrt[3]{c}=0.466$
0.101 <i>n</i> HCO ₃ '	59.4	—	7.90	6.18	
0.101 <i>n</i> Na'	90.7	—	7.75	6.22	
	59.5	—	7.87	6.15	
	112.0	—	7.58	6.14	
	50.2	—	7.92	6.14	
			Mean	6.17	

Table XLIV. Determinations of pK'_1 at 38° in sodium bicarbonate solutions with the addition of salt. Carried out with the small saturator electrode. Series B. Mark \times .

Concentration	mm. Hg		pH'	$\frac{pK'_1}{38^{\circ}}$	
	CO ₂	O ₂			
$T = 45.2$	48.8	—	7.31	6.21	$\sqrt{c} = 0.452$
0.0203 <i>n</i> HCO ₃ '	8.7	—	8.01	6.17	
0.42 % NaCl (0.0718 <i>n</i>)	26.5	—	7.56	6.18	
0.0718 <i>n</i> Cl'					
0.0921 <i>n</i> Na'				Mean 6.18	
$T = 56.5$	34.6	0.1	7.55	6.19	$\sqrt{c} = 0.458$
0.0254 <i>n</i> HCO ₃ '	114.0	0.6	7.02	6.19	
0.42 % NaCl (0.0718 <i>n</i>)	52.3	0.3	7.34	6.17	
0.0718 <i>n</i> Cl'	39.3	0.0	7.51	6.21	
0.0962 <i>n</i> Na'				Mean 6.19	
$T = 45.2$	543.5	—	6.15	(6.09)	$\sqrt{c} = 0.549$
0.0203 <i>n</i> HCO ₃ '	62.7	—	7.10	6.11	
0.85 % NaCl (0.145 <i>n</i>)	49.2	0.8	7.26	6.17	
0.145 <i>n</i> Cl'	36.2	0.5	7.41	6.17	
0.1653 <i>n</i> Na'	34.4	0.1	7.43	6.18	
	19.1	0.5	7.66	6.15	
				Mean 6.16	
$T = 56.3$	529.7	0.2	6.28	6.12	$\sqrt{c} = 0.554$
0.0253 <i>n</i> HCO ₃ '	107.6	0.2	7.00	6.15	
0.85 % NaCl (0.145 <i>n</i>)	37.4	0.2	7.44	6.12	
0.145 <i>n</i> Cl'	35.3	0.2	7.47	6.13	
0.1703 <i>n</i> Na'				Mean 6.13	
$T = 56.5$	567.3	0.0	6.27	6.14	$\sqrt{c} = 0.554$
0.0254 <i>n</i> HCO ₃ '	142.0	0.1	6.89	6.16	
0.85 % NaCl (0.145 <i>n</i>)	25.6	0.2	7.61	6.13	
0.145 <i>n</i> Cl'	34.3	0.0	7.53	6.18	
0.1704 <i>n</i> Na'	34.0	0.6	7.54	6.18	
	56.6	0.6	7.30	6.17	
	39.9	0.6	7.45	6.16	
				Mean 6.16	

Table XLV. Conversion of Bjerrum and Gjaldbaek's Table VI.

P_{CO_2}	$c \cdot 10^3$	$\log K'$	$\log K'$ converted
0.000504	1.492	-5.619	-5.666
0.000808	1.700	-5.660	-5.698
0.00333	2.744	-5.677	-5.754
0.01387	4.462	-5.688	-5.741
0.0282	5.930	-5.649	-5.707
0.0501	7.200	-5.661	-5.723
0.1422	10.66	-5.635	-5.705
0.2538	13.27	-5.621	-5.697
0.4167	15.75	-5.630	-5.710
0.5533	17.71	-5.613	-5.697
0.7297	19.44	-5.620	-5.705
0.9841	21.72	-5.616	-5.704
		Mean -5.641	Mean -5.709

Table XLVI. Deviation coefficients of the bicarbonate ion in sodium salt solutions.

C	$\frac{3}{2}c$	f_a	f_o	f_μ (NaHCO ₃)
0.001	0.100	0.900	0.974	0.949
0.005	0.171	0.834	0.955	0.913
0.01	0.215	0.796	0.944	0.890
0.02	0.271	0.751	0.929	0.862
0.03	0.311	0.719	0.919	0.841
0.04	0.342	0.696	0.911	0.827
0.05	0.368	0.677	0.904	0.812
0.06	0.391	0.661	0.898	0.801
0.07	0.412	0.646	0.893	0.790
0.08	0.431	0.634	0.888	0.780
0.09	0.448	0.622	0.884	0.778
0.10	0.464	0.612	0.879	0.764
0.12	0.493	0.593	0.872	0.749
0.14	0.519	0.577	0.865	0.735
0.16	0.543	0.563	0.859	0.723
0.18	0.565	0.550	0.853	0.712
0.20	0.585	0.538	0.848	0.702
0.22	0.604	0.528	0.843	0.692
0.24	0.621	0.518	0.839	0.683
0.25	0.630	0.513	0.836	0.679

Table XLVII. Determinations of $p_{K'_1}$ in salt solutions containing phosphates, for 18°. Carried out with the small saturator electrode. Series A.

Concentration	Temp.	mm. Hg CO ₂	Vols. % CO ₂ combined	pH'	$p_{K'_1}$ 18°	
0.85 % NaCl	19.0	49.3	35.8	7.03	6.26	Y=6
70 cc. NaHCO ₃ (T=43.0)	19.0	156.9	45.9	6.63	6.24	Phosphate
6 cc. KH ₂ PO ₄ (0.066 <i>m</i>)	19.0	48.2	34.8	6.45	6.27	
24 cc. Na ₂ HPO ₄ (0.066 <i>m</i>)	19.0	16.3	28.9	6.41	6.24	
0.02 <i>m</i> phosphate	19.0	38.3	33.6	6.44	6.25	
0.145 <i>n</i> Na ⁺						
0.004 <i>n</i> K ⁺					Mean 6.25	
0.42 % NaCl	18.0	51.5	38.5	7.06	6.28	Y=5
70 cc. NaHCO ₃ (T=43.0)	18.5	28.9	33.4	7.25	6.28	Phosphate
6 cc. KH ₂ PO ₄ (0.066 <i>m</i>)	18.5	53.6	37.5	7.05	6.29	
24 cc. Na ₂ HPO ₄ (0.066 <i>m</i>)	19.0	156.9	48.2	6.66	6.25	
0.02 <i>m</i> phosphate					Mean 6.28	
0.0718 <i>n</i> Cl ⁻						
0.101 <i>n</i> Na ⁺						
0.004 <i>n</i> K ⁺						

Table XLVIII. Determinations of $p_{K'_1}$ for 18° in cane sugar solutions (0.501*m*) with sodium bicarbonate (*circ. m*/100). Carried out with E VI and E III.

Concentration	Temp.	mm. Hg CO ₂	pH'	$p_{K'_1}$	Vols. % CO ₂ combined	
0.501 <i>m</i> saccharose	18.0	519.9	6.03	6.36	27.6	Y=16.5
T=27.7	18.0	117.3	6.66	6.38	28.1	E VI
0.0125 <i>n</i> HCO ₃ '	18.5	28.6	7.29	6.39	27.6	Series A
0.0125 <i>n</i> Na ⁺	19.0	16.9	7.47	6.34	27.6	
	19.5	523.4	6.03	6.40	27.7	
	18.5	34.7	—	(6.31)	27.9	
				Mean 6.38	Mean 27.7	
0.501 <i>m</i> saccharose	20.5	43.9	7.098	6.471	—	Y=16.5
T=22.44	20.5	43.9	7.092	6.465	—	E VI and E III
0.01008 <i>n</i> HCO ₃ '	20.5	41.4	7.102	6.450	—	Series B
0.01008 <i>n</i> Na ⁺	20.5	41.4	7.102	6.450	—	
	20.5	43.6	7.095	6.465	—	
	20.5	43.6	7.095	6.465	—	
				Mean 6.461		