

THE ELECTRICAL CONDUCTIVITY OF URINE IN RELATION TO ITS CHEMICAL COMPOSITION.

[SECOND PAPER.]

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THE CONDUCTIVITY OF MIXED SOLUTIONS.

IN an earlier paper¹ I gave some illustrations of the variations in the conductivity of the urine through a period of several days, the urine being collected and examined at definite short intervals. As this conductivity depends mainly on the sum of the inorganic constituents present and as sodium chloride is the most abundant of these, the determination in itself has but a limited importance. In some cases the value of the conductivity would be merely a rough measure of the salt consumed with the food, and the salt consumption is extremely variable.

Nearly all the other substances found in the urine have a significance very different from that of the salt. The latter is consumed and excreted as such, while the other important urinary constituents are products of metabolism, that is, of the breaking down of the digested and absorbed food materials. The organic products of metabolism are practically non-electrolytes or bodies with a very low conducting power; indeed the conductivity of a weak salt solution is materially lowered by the addition of urea and the effect of the purin bodies is practically in the same direction. Aside from the chlorides, the inorganic salts of the urine are mainly phosphates and sulphates of the alkali or alkali-earth metals and these are made up largely from the oxidation of sulphur and phosphorus of protein foods. We consume a certain amount of complex phosphoric and sulphuric acids in organic combination, in the lecithins and chondroitins for example, and small amounts of mineral sulphates and phosphates are also found in some of our foods, but these amounts are not large enough to vitiate the truth of the general proposition that the sulphuric and phosphoric acids as detected in the urine are results of certain kinds of metabolism. Now the conductivity measures the combined effect of these products of oxidation and, if it could be determined apart from the effect of the chlorides, a factor of considerable practical importance would be secured. In my

¹ This Journal, 24, 996 (1902).

previous paper I indicated how that may be done approximately and below I wish to present further data bearing on the matter.

Approximately, the conductivity due to metabolic products may be found by subtracting from the observed conductivity that due to sodium chloride in the same solution. The chlorine may be accurately determined and calculated as chloride: then from tables the conductivity for a solution of this concentration may be found and used as a correction to be taken from the total observed conductivity, leaving the desired residual or metabolic conductivity. In this plan, however, an error is involved, because the conductivity of the chloride taken from the tables directly is that found in pure aqueous solution in absence of other salts, and is larger than the true conductivity of the chloride as it exists in the urine. It is necessary, therefore, to use as a correction the value of the salt conductivity, not in aqueous solution, but in a solution of a concentration corresponding to that of urine.

Several attempts have been made to measure the conductivity of mixtures of electrolytes and formulate the results. Most of the experiments have been made with dilute solutions and can not be used well in cases like the present one. The literature of the more important older determinations is given by Kohlrausch and Holborn,¹ while the more important recent discussions of the subject are those of Barmwater² and Wolf.³ While the experimental data of these papers is not available for use in what follows, some of the suggestions of a theoretical nature were found of interest.

The non-electrolytes have some effect also, especially urea. The effect of urea on the conductivity of sodium chloride has been considered in a paper by Hantzsch,⁴ but the solutions used were much less concentrated than is urine, and the results, besides, somewhat irregular. I have therefore made some new experiments in this direction which will be detailed first.

CONDUCTIVITY OF SODIUM CHLORIDE WITH UREA.

The conductivity of a pure urea solution is very low. Most of the data given are for very dilute solutions. For $\tau = 32$ Trübs-

¹ "Leitvermögen der Elektrolyte," p. 109.

² Barmwater: *Ztschr. phys. Chem.*, **28**, 424.

³ Wolf: *Ibid.*, **40**, 222.

⁴ Hantzsch: *Ztschr. anorg. Chem.*, **25**, 332.

bach¹ gives $\Delta = 0.08$, which is probably high. From a much stronger solution, 5 grams to 100 cc., or $v = 1.2$, I find $\kappa = 0.000012$ or $\Delta = 0.0144$. The urea used for this purpose was a product of great purity and the determination was made with fresh distilled water carefully prepared and stored to avoid outside contamination. This value is probably only a maximum. The work of Trübsbach shows a remarkable dissociation change or increase in the conductivity in his dilutions. Between $v = 32$ and 256 liters the Δ change is from 0.08 to 0.28. It will be seen below that such small values may be neglected in comparison with the conductivity of the other important urinary constituents.

Now as to the influence of the urea on these conductivities. In the paper by Hantzsch, referred to above, the molecular conductivity given for mixtures of sodium chloride with increasing amounts of urea are so irregular as to lead to the conclusion that the urea employed could not have been pure but must have contained some inorganic salts, as is usually the case. The first effect is, apparently, an increase in conductivity with addition of urea, followed by a decrease, which, however, is not marked. I have made several determinations with solutions of different urea strengths, with the following results. A standard salt solution was made containing 18 grams in 500 cc. This solution was made and used with precautions to secure the greatest accuracy. All the tests given below are based on this or similar solutions. 50 cc. of this solution diluted to 100 cc. gave, at 20°, as a mean of many close tests,

$$\kappa = 0.027315$$

Two dilutions were made with 50 cc. of the standard solution, 2.5 grams of urea being added in each case, and the volume diluted to 100 cc. At 20° I found

(1).....	$\kappa = 0.02683$
(2).....	$\kappa = 0.02684$
Mean	$= 0.026835$

The decrease in κ is here 0.000480. With a solution containing the same amount of salt and 1 gram of urea in 100 cc., I found

(1).....	$\kappa = 0.027126$
(2).....	$\kappa = 0.027128$
Mean	$= 0.027127$

¹ Trübsbach: *Ztschr. phys. Chem.*, 16, 708.

The loss for the gram of urea is here 0.000188. The influence of the urea is therefore marked, the decrease in conductivity for the stronger urea solution being 1.76 per cent. and for the weaker 0.68 per cent. For 1 gram of urea and 2.5 grams of sodium chloride in 100 cc. the decrease in conductivity is about 0.00019, the results for the two solutions agreeing closely.

CONDUCTIVITY OF SODIUM CHLORIDE WITH OTHER SALTS.

To find the effect of other salts on the conductivity of the sodium chloride, I have taken as illustrations ammonium sulphate and sodium phosphate. A sulphate solution containing 9 grams in 500 cc. was prepared and the conductivity of this first determined in a cell having a capacity $C = 8.368$. The conductivities were found in a number of dilutions of this ammonium sulphate, a cell having a capacity $C = 2.835$ being used for the weaker solutions, the final volume of the dilution being always 100 cc. by addition of pure water. Then in a second series of tests a constant volume of sodium chloride solution was used, from the solution with 18 grams to 500 cc., along with the ammonium sulphate, the salt amounting in each case to 1.8 grams in the final volume of 100 cc. The table below gives the composition of the mixtures and the conductivities found. Some further determinations were made with stronger sulphate solutions, the results being necessary for the calculation finally required. The Kohlrausch method was followed. A large bridge with wire corrections known, was used throughout and a standard temperature of 20° maintained.

TABLE I.—SODIUM CHLORIDE AND AMMONIUM SULPHATE.

		NaCl solution = 18 grams to 500 cc.		(NH ₄) ₂ SO ₄ solution = 9 grams to 500 cc.	
(NH ₄) ₂ SO ₄ solution. cc.	NaCl solution. cc.	Water cc.	κ_{20} observed.	Δ_{20} .	Sum of conduc- tivities.
5	..	95	0.001604	117.6
10	..	90	0.003023	111.0
20	..	80	0.005694	104.6
30	..	70	0.008100	99.1
40	..	60	0.01056	96.9
50	..	50	0.01275	93.6
5	50	45	0.02839	..	0.02892
10	50	40	0.02935	..	0.03033
20	50	30	0.03151	..	0.03300
30	50	20	0.03350	..	0.03541
40	50	10	0.03560	..	0.03787
50	50	0	0.03742	..	0.04006
..	50	50	0.027315

With stronger ammonium sulphate solutions I have found the following data:

TABLE Ia.—AMMONIUM SULPHATE.

(NH ₄) ₂ SO ₄ . Grams per liter.	κ_{20} observed.	Δ_{20} .
15.0	0.01965	86.5
20.0	0.02600	85.6
25.0	0.03140	82.9
30.0	0.03651	80.3
33.0	0.03950	79.0
35.0	0.04150	78.3

The conductivity found for the mixtures is seen to be considerably below the sum of the conductivities observed separately. The same is true for the next mixtures containing sodium chloride and phosphate. Here the same chloride solution was employed containing 18 grams to 500 cc., the dilution, by mixing, giving therefore always resultant products with 1.8 gram to 100 cc., or 18 grams to the liter. The phosphate solution was made with 20 grams of the ordinary salt, HNa₂PO₄.12H₂O, twice purified by crystallization, dissolved to make 500 cc. The volumes of this taken gave finally in the mixtures made 2, 4, 6, 8 grams, and so on, to the liter. Some stronger phosphate solutions were also investigated as the data were needed for certain reductions to follow. These figures are not given in the Kohlrausch tables quoted above.

TABLE II.—SODIUM CHLORIDE AND SODIUM PHOSPHATE.

NaCl solution = 20 grams to 500 cc.

HNa₂PO₄.12H₂O solution = 18 grams to 500 cc.

HNa ₂ PO ₄ . 12H ₂ O. solution. cc.	NaCl solution. cc.	Water. cc.	κ_{20} observed.	Δ_{20} .	Sum of conductivities.
5	..	95	0.000925	82.8	...
10	..	90	0.00175	78.3
15	..	85	0.00251	75.1
20	..	80	0.00323	72.4
25	..	75	0.00394	70.5
30	..	70	0.00462	68.9
40	..	60	0.00590	66.0
50	..	50	0.00720	64.4
5	50	45	0.02779	...	0.02824
10	50	40	0.02825	...	0.02906
15	50	35	0.02869	...	0.02982
20	50	30	0.02921	...	0.03054
25	50	25	0.02977	...	0.03125
30	50	20	0.03011	...	0.03193
40	50	10	0.03111	...	0.03321
50	50	0	0.03199	...	0.03451
..	50	50	0.027315

With the stronger phosphate solutions I found the following values:

TABLE IIa.—SODIUM PHOSPHATE.

$\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ Grams per liter.	κ_{20} observed.	Δ_{20} .
25.0	0.00880	63.0
37.5	0.01245	59.4
50.0	0.01567	56.1
62.5	0.01868	53.5
75.0	0.02152	51.4
100.0	0.02650	47.4

Having found the effect of certain weights of urea, sodium phosphate and ammonium sulphate, mixtures were made containing the three substances at the same time with sodium chloride. Two solutions were used, one with 18 grams of the chloride to 500 cc., and the other with 9 grams of ammonium sulphate, 20 grams of sodium phosphate and 25 grams of urea to 500 cc. This in the table below is described as "mixture." Certain volumes of these solutions were then taken to make 100 cc. as shown in the tables, and the conductivities found.

TABLE III.—SODIUM CHLORIDE AND MIXTURE.

NaCl solution = 18 grams in 500 cc.						
$(\text{NH}_4)_2\text{SO}_4$ $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ CON_2H_4						
} mixture = { 9 grams in 20 grams in 25 grams in } 500 cc.						
Mixture. cc.	NaCl Sol. cc.	Water. cc.	κ_{20} observed.	Sum of conductivities, salt and mixture.	Sum of conductivities taken separately.	
5	..	95	0.00234	
10	..	90	0.00436	
15	..	85	0.00622	
20	..	80	0.00797	
30	..	70	0.01136	
40	..	60	0.01441	
50	..	50	0.01733	
5	50	45	0.02873	0.02965	0.02984	
10	50	40	0.03031	0.03167	0.03209	
15	50	35	0.03170	0.03353	
20	50	30	0.03309	0.03528	0.03624	
30	50	20	0.03559	0.03867	0.04003	
40	50	10	0.03811	0.04172	0.04377	
50	50	0	0.04052	0.04464	0.04726	
..	50	50	0.027315	

Expressed as grams per liter, the solutions finally used contained as follows:

Mixture. cc.	NaCl. Grams per liter.	NH ₄ .SO ₄ . Grams per liter.	HNa ₂ PO ₄ .12H ₂ O. Grams per liter.	CON ₂ H ₄ . Grams per liter.
5	18	0.9	2	2.5
10	18	1.8	4	5.0
15	18	2.7	6	7.5
20	18	3.6	8	10.0
30	18	5.4	12	15.5
40	18	7.2	16	20.0
50	18	9.0	20	25.0

In the last mixtures we have a complex case in which the conductivities of each of the four constituents are modified by the presence of all of the others. The resultant observed conductivities are the sums of the modified individual conductivities. It will be noticed that in the stronger mixtures the observed conductivities are about 10 per cent. lower than are the sums of the "mixture" and chloride conductivities taken alone. In the weaker mixtures, the discrepancies are naturally less. If we compare the observed values for the complete mixtures with the sums of the separate conductivities, the differences become very pronounced. For the strongest solution, the sum of the individual conductivities is over 15 per cent. greater than the value actually found for the mixture. This is in accord, of course, with what is well known about the conductivity of mixtures. The molecular or equivalent conductivity of a salt decreases with the number of molecules dissolved and this change follows in nearly the same proportion whatever the character of the salts, as long as they exhibit approximately the same dissociation and do not act on each other chemically. In expressing the conductivity of a mixture as made up of the sum of component conductivities, we can use a formula of this kind:

$$k = p_1\eta_1\Delta_1 + p_{11}\eta_{11}\Delta_{11} + p_{111}\eta_{111}\Delta_{111} + \text{etc.},$$

in which p_1 , p_{11} , p_{111} are factors containing the effects of dissociation and viscosity in modifying the normal Δ values. Δ here represents the equivalent (or molecular) conductivity and η the concentration. In the case in hand, and probably for many similar cases, a simpler method of calculation leads to good results as the following will show. This is based on the assumption that in diminishing the conductivity of sodium chloride the addition of a relatively small amount of ammonium sulphate or sodium phosphate has the same effect as the addition of the same number

of sodium chloride molecules, and on this assumption I have calculated the modified conductivities in the following manner: If, using the Kohlrausch symbols, Δ is always the derived equivalent conductivity, κ any observed conductivity and η the corresponding concentration in gram-molecules per cubic centimeter, then we have:

$$\Delta = \frac{\kappa}{\eta};$$

or, if we take Δ from the tabulated results as known,

$$\kappa = \eta \Delta.$$

In the formula η corresponds to a given Δ , since Δ is calculated from a given η always. I have used the relation arbitrarily in a somewhat different way and have calculated κ from a given η and a Δ corresponding to a greater η . This use of Δ amounts, of course, to using a modifying factor, but a simple one. To illustrate, assume the following relation which I have found experimentally for two salt solutions:

Sol.	η .	Δ_{20} .
A or A ₁	0.00005	99.92
B	0.00010	96.07

We may consider the second solution, B, as made up of two solutions, A and A₁ with $\eta = 0.00005$ for each. To find the conductivity of A in presence of A₁, we have, following the assumption referred to above,

$$\kappa = 0.00005 \times 96.07.$$

and for the conductivity of A₁ in presence of A, we have the same

$$\kappa = 0.00005 \times 96.07.$$

The sum of these gives the conductivity of B, or:

$$\kappa = 0.0001 \times 96.07 = 0.009607.$$

Consider in general two substances A and B in concentrations given below under η .

Substance A,	η .	Δ .
	C	P
	C + a	P ₁
	C - b	P ₁₁
	C + c	P ₁₁₁
Substance B,	R	ρ
	R ₁	ρ_1
	R ₁₁	ρ_{11}
	R ₁₁₁	ρ_{111}
	R _m	ρ_m
	R _n	ρ_n
	R _v	ρ_v

a , b and c represent the equivalent concentrations R , R_1 , R_{11} , expressed in terms of C , so that $C + a$ represents a concentration of substance A equal to the sum of $C + R$. The conductivity of substance A of concentration C in presence of substance B of concentration R is given by $\kappa = \eta \Delta = C P_1$. In presence of B of concentration R_1 we have $\kappa = C P_{11}$ and so on.

Next consider the conductivity of substance B in varying proportions in presence of A in concentration C . R_m expresses the concentration of the sum of the substances considered in terms of R and is, of course, equivalent to $C + a$. The equivalent conductivity of substance B of this concentration is not, however, P_1 but some other quantity as p_m . The conductivity of B in concentration R in presence of A in concentration C is therefore $R \times p_m$. In the same way $R_1 \times p_n$ expresses the conductivity of B in concentration R_1 in presence of C , and $R_{11} \times p_o$ the conductivity of R_{11} in presence of C . We have then for the total conductivity the sum of these modified conductivities, or,

$$\begin{aligned} \kappa = & CP_1 + R p_m \\ & CP_{11} + R_1 p_n \\ & CP_{111} + R_{11} p_o, \\ & \dots \dots \end{aligned}$$

while the simple sums of the conductivities would be

$$\begin{aligned} & CP + R p \\ & CP + R_1 p_1 \\ & CP + R_{11} p_{11}, \\ & \dots \dots \end{aligned}$$

Similar relations will obtain for other mixtures of A and B.

In the following table are given the calculated conductivities of mixtures of sodium chloride and ammonium sulphate similar to those employed in the experiments recorded, the method of calculation being that just suggested. In the column headed " m sum" we have the values of C , $C + a$, $C + b$, etc., and under " Δ sum" we have the equivalent conductivities, P , P_1 , P_{11} , etc.

TABLE IV.—CONDUCTIVITY OF NaCl IN PRESENCE OF $(NH_4)_2SO_4$.

NaCl. Grams per liter.	$(NH_4)_2SO_4$. Grams per liter.	Sum as NaCl.	m for NaCl. $m=1000 \eta$.	m for sum. $m=1000 \eta$.	Δ for sum as NaCl.	κ from η of NaCl and Δ of sum.
18	0.0	18.00	0.3077	0.3077	88.7	0.027315
18	0.9	18.80	0.3214	88.2	0.02714
18	1.8	19.60	0.3350	87.7	0.02698
18	3.6	21.19	0.3623	87.2	0.02683
18	5.4	22.79	0.3895	86.7	0.02668
18	7.2	24.38	0.4168	86.1	0.02650
18	9.0	25.95	0.4441	85.6	0.02634

Table V is analogous to the above, but gives the conductivities of the sulphate in presence of the chloride by the same method of calculation.

TABLE V.—CONDUCTIVITY OF $(\text{NH}_4)_2\text{SO}_4$ IN PRESENCE OF NaCl.

NaCl. Grams per liter.	$(\text{NH}_4)_2\text{SO}_4$. Grams per liter.	Sum as $(\text{NH}_4)_2\text{SO}_4$.	m for $(\text{NH}_4)_2\text{SO}_4$. $m=1000 \eta$.	m for sum. $m=1000 \eta$.	Δ for sum as $(\text{NH}_4)_2\text{SO}_4$.	κ from η of $(\text{NH}_4)_2\text{SO}_4$ and Δ of sum.
0.0	0.9	0.90	0.013636	0.013636	117.6	0.001604
18	0.9	21.21	0.013636	0.3214	85.0	0.00116
18	1.8	22.11	0.02727	0.3350	84.5	0.00230
18	3.6	23.91	0.05454	0.3623	83.5	0.00455
18	5.4	25.71	0.08182	0.3895	82.6	0.00675
18	7.2	27.51	0.10909	0.4168	81.5	0.00888
18	9.0	29.31	0.13636	0.4441	80.6	0.01099

By adding the separate κ values, we obtain the values for the mixed solutions as calculated. These are shown in Table VI.

TABLE VI.—CALCULATED AND OBSERVED CONDUCTIVITIES OF MIXED NaCl AND $(\text{NH}_4)_2\text{SO}_4$.

NaCl. Grams per liter.	$(\text{NH}_4)_2\text{SO}_4$. Grams per liter.	κ calculated.	κ observed.	Difference.
18	0.9	0.02830	0.02839	0.00009
18	1.8	0.02928	0.02935	0.00007
18	3.6	0.03138	0.03151	0.00013
18	5.4	0.03343	0.03350	0.00007
18	7.2	0.03538	0.03560	0.00022
18	9.0	0.03733	0.03742	0.00009

The differences are very low and are within the limits of errors of experiment. Similar observations made with mixed chloride and phosphate solutions are given in the tables following:

TABLE VII.—CONDUCTIVITY OF NaCl IN PRESENCE OF HNa_2PO_4 .

NaCl. Grams per liter.	$\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$. Grams per liter.	Sum as NaCl.	m for NaCl. $m=1000 \eta$.	m for sum. $m=1000 \eta$.	Δ for sum as NaCl.	κ from η of NaCl and Δ of sum.
18	2	18.653	0.3077	0.3189	88.3	0.02717
18	4	19.307	0.3300	88.0	0.02708
18	6	19.961	0.3412	87.7	0.02698
18	8	20.614	0.3524	87.3	0.02686
18	10	21.268	0.3636	87.1	0.02680
18	12	21.922	0.3748	86.9	0.02674
18	16	23.229	0.3971	86.4	0.02659
18	20	24.536	0.4194	86.0	0.02646

TABLE VIII.—CONDUCTIVITY OF HNa_2PO_4 IN PRESENCE OF NaCl .

NaCl. Grams per liter.	HNa_2PO_4 . $12\text{H}_2\text{O}$. Grams per liter.	Sum as HNa_2PO_4 . $12\text{H}_2\text{O}$.	m for HNa_2PO_4 . $12\text{H}_2\text{O}$. $m=1000 \eta$.	m for sum. $m=1000 \eta$.	Δ for sum as HNa_2PO_4 . $12\text{H}_2\text{O}$.	κ from η of HNa_2PO_4 . $12\text{H}_2\text{O}$. and Δ of sum.
18	2	57.08	0.01117	0.3189	54.6	0.00061
18	4	59.08	0.02235	0.3300	54.2	0.00121
18	6	61.08	0.03352	0.3412	53.8	0.00180
18	8	63.08	0.04469	0.3524	53.5	0.00239
18	10	65.08	0.05586	0.3636	53.1	0.00297
18	12	67.08	0.06704	0.3748	52.8	0.00354
18	16	71.08	0.08938	0.3971	52.1	0.00466
18	20	75.08	0.11173	0.4194	51.4	0.00574

TABLE IX.—CALCULATED AND OBSERVED CONDUCTIVITIES OF MIXED
 NaCl AND HNa_2PO_4 .

NaCl. Grams per liter.	$\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$. Grams per liter.	κ , sum calculated.	κ observed.	Difference.
18	2	0.02778	0.02771	0.00007
18	4	0.02829	0.02815	0.00014
18	6	0.02878	0.02812	0.00066
18	8	0.02925	0.02911	0.00014
18	10	0.02977	0.02967	0.00010
18	12	0.03028	0.03001	0.00027
18	16	0.03125	0.03101	0.00024
18	20	0.03220	0.03189	0.00031

The results given in the last table show a remarkably close agreement between the observed and calculated values. The variations are not greater than should be expected from calculations in which the Δ values are partly interpolated. In the next tabulation we have the combined effect of chloride, sulphate, phosphate and urea, the results being compared finally with those observed directly.

TABLE X.—EQUIVALENT CONDUCTIVITIES IN THE MIXTURES.

NaCl. Grams per liter.	$(\text{NH}_4)_2\text{SO}_4$. Grams per liter.	HNa_2PO_4 . $12\text{H}_2\text{O}$. Grams per liter.	Sum as NaCl.	Sum as $(\text{NH}_4)_2\text{SO}_4$.	Sum as HNa_2PO_4 . $12\text{H}_2\text{O}$.	Δ for total as NaCl.	Δ for total as $(\text{NH}_4)_2\text{SO}_4$.	Δ for total as HNa_2PO_4 . $12\text{H}_2\text{O}$.
18	0.9	2	19.45	21.95	59.52	87.8	84.6	54.1
18	1.8	4	20.90	23.59	63.96	87.3	83.6	53.2
18	3.6	8	23.80	26.86	72.84	86.6	81.9	51.8
18	5.4	12	26.71	30.13	81.74	85.6	80.2	50.3
18	7.2	16	29.61	33.41	90.61	84.5	78.8	49.0
18	9.0	20	32.52	36.68	99.49	83.2	77.7	47.4

TABLE XI.—COMPARISON OF CALCULATED AND OBSERVED CONDUCTIVITIES.

NaCl. Grams per liter.	(NH ₄) ₂ SO ₄ . Grams per liter.	HNa ₂ PO ₄ ·12H ₂ O. Grams per liter.	κ from η of NaCl and total Δ .	κ from η of (NH ₄) ₂ SO ₄ and total Δ .	κ from η of HNa ₂ PO ₄ ·12H ₂ O and total Δ .	Sum of κ values.	κ as found.	Difference. Calculated—found.
18	0.9	2	0.02702	0.00115	0.00060	0.02877	0.02873	0.00004
18	1.8	4	0.02686	0.00228	0.00119	0.03033	0.03031	0.00002
18	3.6	8	0.02665	0.00446	0.00232	0.03343	0.03309	0.00034
18	5.4	12	0.02634	0.00655	0.00337	0.03626	0.03559	0.00067
18	7.2	16	0.02600	0.00860	0.00438	0.03898	0.03811	0.00087
18	9.0	20	0.02560	0.01060	0.00530	0.04150	0.04052	0.00098

Here, as in the simple cases, the calculated conductivity is not far from the observed. For this mixture, the conductivities found are lower throughout than are the calculated values. But in the experiment made a certain amount of urea was present in each case and this, of course, lowers the conductivity. Assuming for calculation that the effect of this falls wholly on the sodium chloride, the following approximate corrections may be made, taking the mixtures in order.

TABLE XII.—FINAL CALCULATED CONDUCTIVITY.

No.	Sum of κ values.	Effect of urea.	κ corrected.	κ found.	Difference. Calculated—found.
1	0.02877	0.00005	0.02872	0.02873	-0.00001
2	0.03033	0.00009	0.03024	0.03031	-0.00007
3	0.03343	0.00019	0.03324	0.03308	+0.00015
4	0.03620	0.00028	0.03598	0.03559	+0.00039
5	0.03898	0.00038	0.03860	0.03811	+0.00049
6	0.04150	0.00047	0.04103	0.04052	+0.00051

It appears, therefore, that a very close approximation to the real conductivity of certain mixtures can be made by the method of calculation as suggested above, a closer approximation, in fact, than is given by some of the more complicated procedures which have been described.

As would naturally be expected, the departures from the observed values increase with the concentration of the solutions mixed. While the experiments were begun as a contribution to the question of the conductivity of urine, it is evident that the results obtained may find general application in cases where mixtures of moderate strength only are considered. The higher concentrations here are greater than are found in normal urine. The chlorine, calculated as sodium chloride, rarely reaches 18

grams per liter and the sulphate, calculated as ammonium sulphate, is usually below 4 grams per liter. The phosphoric acid of the urine as PO_4 , is generally below 3 grams per liter, with the phosphate calculated as $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$, consequently below about 12 grams per liter. These amounts are therefore well within the weights of salts taken in the experiments. In addition the conductivity of the urine is rarely above 0.025 or 0.03 at most. From all this, taken in connection with the results of Table XI, it follows that with the salt of a urine known and the conductivity at 20° accurately determined, the conductivity of the non-chloride constituents may be found with a considerable degree of certainty by diminishing by about 3 per cent. the chloride conductivity as calculated from tables for the given concentration, and subtracting this corrected salt conductivity from the observed urine conductivity. The remainder must give very nearly the true conductivity of the remaining substances in solution and must measure, in a manner, the amount of the electrolytes. The 3 per cent. correction for the chloride conductivity covers the average effect of the other salts present in normal urine. It is not to be supposed that the method would suffice to give a quantitative determination, but as an independent factor the non-chloride conductivity has a bearing and importance of its own, irrespective of the character of the salts which produce it.

NORTHWESTERN UNIVERSITY,
CHICAGO, November, 1903.

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THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD.

BY ROBERT BANKS GIBSON.

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IN a recently published paper by Kutscher and Steudel,¹ the reliability of the Kjeldahl method for estimating nitrogen in various organic compounds of physiological-chemical importance has been called in question. These investigators have failed to obtain satisfactory results in the analysis of such substances as creatine, creatinine, uric acid, lysine and histidine by this widely

¹ Kutscher and Steudel: *Ztschr. physiol. Chem.*, **39**, 12 (1903).