

Its chemical properties are similar to those of the oxychloride. In liquid form, above 42°, it is a powerful solvent, deporting itself in general as an oxidizing and brominating agent.

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THE EFFECT OF SUCROSE ON THE ACTIVITIES OF THE CHLORIDE AND HYDROGEN IONS

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I. The Effect of Sucrose on the Activity of the Chloride Ion in Tenth and Half Normal Solutions of Potassium Chloride

In recent years, the measurement of the individual activity of an ion has been rendered possible by certain assumptions, first made by MacInnes.¹

The first postulate was that the activities of the anion and cation in the same solution of an electrolyte may differ from one another; the second, that in solutions of potassium chloride, the activities of the anion and cation are equal; and the third, that in solutions of univalent chlorides of the same concentrations, the chloride ion has the same activity in every case. The second and third assumptions have been shown by Harned,² to be true experimentally.

Noyes and MacInnes³ have utilized the values of the e.m.f.'s of the cells with and without transport containing potassium chloride, obtained by MacInnes and Parker,⁴ to calculate the activities of potassium chloride in solutions of different concentration, varying from 0.001 to 0.5 *M*. As a basis for the calculation of these relative activities the assumption was made that the activity coefficient was identical with the conductivity-viscosity ratio in very dilute solutions, and on this basis the activities in solutions up to 0.5 *N* potassium chloride were computed. By means of the second postulate of MacInnes, the activities of potassium chloride become identical with those of the chloride ion.

The present investigation consists of measurements of the activity of the chloride ion when the environment is changed by the use of sucrose solutions of different concentrations as solvent in place of pure water. The reason for the use of sucrose is that it is proposed to extend the measurements of the activities of ions, when the environment is changed, to the

¹ MacInnes, *THIS JOURNAL*, **41**, 1086 (1919).

² Harned, *ibid.*, **42**, 1808 (1920).

³ Noyes and MacInnes, *ibid.*, **42**, 239 (1920).

⁴ MacInnes and Parker, *ibid.*, **37**, 1445 (1915).

case of the hydrogen ion and to compare results with those obtained by means of another type of cell, in which sucrose has been used. Also, because much work has been done with sucrose in connection with the inversion process, a large amount of data with reference to sucrose solutions is available.

The type of cell used is almost identical with that used by MacInnes and Parker,⁴ *i. e.*, the cell with transport, namely, Ag | AgCl | KCl (I) | KCl + sucrose (II) | AgCl | Ag, in which the liquid-liquid potential difference is not annulled. The e.m.f. of this cell is given by the expression

$$E = 2n_K \cdot \frac{RT}{F} \log \frac{Cl_I}{Cl_{II}}$$

where n_K is the transport number of the potassium ion and has the value 0.495, and Cl_I and Cl_{II} represent the activities of the chloride ion.

The assumptions made by MacInnes are adhered to and further, for the present, to make calculations possible, it is assumed that the transport number of the potassium ion is the same in the presence of sucrose as in pure aqueous solutions. The latter is a rather bold assumption to make at this stage, but it is confirmed by the general nature of the results obtained.

Experimental

The potassium chloride and sucrose had already been used for exact e.m.f. work. The electrical instruments consisted of a Cambridge-Paul potentiometer, a sensitive mirror galvanometer, and a standard cell having an e.m.f. of 1.0183 volt at 20° with a decrease of 0.00004 volt per degree rise in temperature. A constant temperature of 25° ± 0.05° was attained by means of an electrically regulated thermostat, which was earthed. In order to eliminate external electrical effects, the potentiometer, galvanometer and accumulator rested on sheets of glass which were separated from a piece of sheet iron by means of paraffin wax. This piece of sheet iron was connected to earth.

The cell and electrodes were made as described by MacInnes and Parker,⁴ the electrode vessels being adapted according to the instructions of Cumming and Gilchrist⁵ in order to minimize diffusion at the liquid junctions.

In order to make certain that the cell was working correctly, several concentration cells of potassium chloride in aqueous solution were set up and the e.m.f.'s observed were compared with those obtained by other workers. The potassium chloride solutions were in all cases saturated with silver chloride before being used. The results of these measurements are shown in Table I.

⁵ Cumming and Gilchrist, *Trans. Faraday Soc.*, 9, 174 (1913).

TABLE I

MEASUREMENTS WITH CONCENTRATION CELLS OF POTASSIUM CHLORIDE

C_1	C_2	$E_{\text{obs.}}$	E_1	E_2
0.5	0.05	0.0535	0.0531	0.0536 (M. — P.)
0.5	0.1	0.0368	0.0369	0.0369 (F. — M.)
1.0	0.1	0.0529	0.0527	0.0529 (F. — M.)
2.0	0.5	0.0328	0.0325	0.0320 (F. — M.)

C_1 and C_2 represent the concentrations of salt, expressed in gram-equivalents of salt per liter of solution. Under $E_{\text{obs.}}$ are the results obtained by means of the present cell. E_1 represents the values of the e.m.f.'s calculated from the activities of potassium chloride given in the table of Noyes and MacInnes,³ while under E_2 are the values obtained by other observers. M. — P. is an abbreviation for MacInnes and Parker, while F. — M. stands for Fales and Mudge.⁶ The latter observers found the following potentials for different calomel half elements.

Conc. of KCl (molar)..	0.1	0.5	1.0	2.0	3.0
Electrode p. d.....	0.6177	0.5808	0.5648	0.5488	0.5377

From these results E_2 (F. — M.) are found by difference. As $E_{\text{obs.}}$ was found to agree very well with E_1 and E_2 , it was concluded that the cell was working satisfactorily.

A series of cells was now set up in which the concentrations of potassium chlorides in the two compartments were respectively 0.5 *N* and 0.1 *N* (moles of potassium chloride per liter of solution). Into the latter compartment were introduced various amounts of sucrose, varying from 0 to 70%. The e.m.f.'s of these cells were measured at 25°.

The activity of the chloride ion in 0.5 *N* potassium chloride solution was taken to be 0.324.⁷ Hence the expression used for the computation of activities from the observed e.m.f.'s becomes

$$E = 0.99 \times 0.059 \log_{10} \frac{0.324}{a_{\text{Cl}_{0.1}}}$$

where $a_{\text{Cl}_{0.1}}$ is the required activity.

In Table II, the values of the e.m.f.'s observed are given, and in the last column are the activities of the chloride ion in the 0.1 *N* solution in the presence of sucrose.

It will be observed that the e.m.f. of the cell decreases up to 50% sucrose solutions by a fairly constant amount, after which it decreases by a rather larger amount. The effect of the sucrose is to increase the activity of the chloride ion from 0.0760 when no sucrose is present, to 0.126 when there is 70% of sucrose present.

⁶ Fales and Mudge, *THIS JOURNAL*, **42**, 2434 (1920).

⁷ Ref. 3. Noyes and MacInnes expressed their KCl concentrations as moles per 1000 g. of water, whereas in the present investigation concentrations are expressed as moles per 1000 cc. of solution. Due allowance has been made for the change in units.

TABLE II
ACTIVITIES OF CHLORIDE ION IN TENTH NORMAL SOLUTION IN THE PRESENCE OF SUCROSE

Sucrose per 100 cc. of solution G.	E.m.f. obs. (volts)				Av.	$a_{\text{Cl}_{0.1}}$
0	0.0368	0.0368	0.0368	0.0368	0.0368	0.0760
10	0.0353	0.0351	0.0352	0.0352	0.0352	0.0809
20	0.0336	0.0334	0.0335	0.0334	0.0335	0.0865
30	0.0315	0.0318	0.0319	0.0319	0.0319	0.0921
40	0.0298	0.0300	0.0302	0.0301	0.0300	0.0993
50	0.0279	0.0281	0.0283	0.0281	0.0281	0.1070
60	0.0254	0.0260	0.0264	0.0262	0.0261	0.1158
70	0.0234	0.0242	0.0244	0.0240	0.0240	0.1258

The cell was also used to determine the change in activity of the chloride ion in 0.5 *N* solutions of potassium chloride caused by the presence of sucrose. The value of the activity in 0.1 *N* solution was taken to be 0.0760, whence the expression from which the activities were determined becomes

$$E = 0.99 \times 0.059 \log \frac{a_{\text{Cl}_{0.5}}}{0.0760}$$

where $a_{\text{Cl}_{0.5}}$ is the required activity. In Table III are the values of the observed e.m.f.'s, together with the activities of the chloride ion calculated from these values.

TABLE III
ACTIVITIES OF CHLORIDE ION IN HALF NORMAL SOLUTION IN THE PRESENCE OF SUCROSE

Sucrose per 100 cc. of solution G.	E.m.f. obs.				Av.	$a_{\text{Cl}_{0.5}}$
0	0.0368	0.0368	0.0368	0.0368	0.0368	0.0324
10	0.0385	0.0384	0.0384	0.0384	0.0384	0.3452
20	0.0401	0.0401	0.0402	0.0401	0.0401	0.3692
30	0.0417	0.0418	0.0418	0.0418	0.0418	0.3950
40	0.0435	0.0433	0.0434	0.0435	0.0435	0.4222
50	0.0453	0.0454	0.0456	0.0454	0.0454	0.4551
60	0.0471	0.0475	0.0475	0.0474	0.0474	0.4925
70	0.0500	0.0495	0.0497	0.0495	0.0496	0.5370

The fractional increase in the activity of the chloride ion in 0.5 *N* solution, as shown by Table III, is almost identical with that in the case of 0.1 *N* solution.

Discussion of Results

The question of the cause of the increase in activity of the chloride ion in the presence of sucrose at once arises. In the first place the presence of sucrose means that there will be a decrease in the total amount of water in the solution, since the concentration of salt is expressed as moles per

liter of solution. This decrease in the total amount will certainly affect the activity, as the effective concentration of the potassium chloride will be increased. In addition to the decrease in the total water, there will be a decrease in the free water due to the hydration of sucrose. A sucrose molecule possesses, on the average, 4 molecules of water of hydration, a result obtained by Moran and Lewis in this laboratory.⁸

The point to be settled is whether the rise in activity of the chloride ion in sucrose solutions can be accounted for by means of one or both of these effects. In order to do this, the compositions of the solutions by weight were found and from these compositions the number of mols of potassium chloride per 1000 g. of total water and free water were determined in each case. From the tables of Noyes and MacInnes, the activity coefficients corresponding to these effective concentrations were obtained, whence the activities were calculated by multiplying activity coefficients by effective concentrations.

Table IV shows the total water and free water per 1000 cc. of sucrose solutions containing 0.1 mol of potassium chloride. Table IVa contains the effective concentrations, that is, the number of moles of salt per 1000 g. of water, calculated in terms of total water, together with the corresponding activities of the chloride ion. Table IVb gives the same quantities, calculated in terms of free water. In Table IVc, a comparison of the observed and calculated activities is made.

Tables V, Va, Vb, Vc show the corresponding data for 0.5 *N* solutions.

It will be noticed that no allowance has been made for the hydration of potassium chloride itself.

The following tables show that the values of a_1 , that is, the activities calculated on the assumption that the water of hydration of sucrose is not available as solvent for the potassium chloride, diverge from a_{obs} , as the concentration increases, being about 33% greater in the case of 70% sucrose solutions.

TABLE IV

COMPOSITIONS OF 1000 CC. OF SOLUTION CONTAINING 0.1 MOL OF POTASSIUM CHLORIDE

Sucrose G.	Total water G.	Water of hydration G.	Free water G.
0	995.05	0	995.05
100	933.0	21	912.0
200	871.6	42	829.6
300	809.5	63	746.5
400	748.0	84	664.0
500	681.7	105	576.7
600	618.8	126	492.8
700	554.1	147	407.1

⁸ As yet unpublished.

TABLE IV_a
CONCENTRATION OF POTASSIUM CHLORIDE IN TERMS OF TOTAL WATER PRESENT

Sucrose %	Total water per liter of solution	KCl per 1000 g. of water	Activity calculated
	G.	Mols	a_2
0	995.05	0.1005	0.0749
10	933.0	0.1072	0.0795
20	871.6	0.1147	0.0850
30	809.5	0.1235	0.0909
40	748.0	0.1337	0.0981
50	681.7	0.1467	0.1068
60	618.8	0.1616	0.1168
70	554.1	0.1805	0.1289

TABLE IV_b
CONCENTRATION OF POTASSIUM CHLORIDE IN TERMS OF FREE WATER PRESENT

Sucrose %	Free water per liter of solution	KCl per 1000 g. of water	Activity calculated
	G.	Mols	a_1
0	995.05	0.1005	0.0749
10	912.0	0.1096	0.0815
20	829.6	0.1205	0.0892
30	746.5	0.1339	0.0981
40	664.0	0.1506	0.1095
50	576.7	0.1734	0.1240
60	492.8	0.2029	0.1431
70	407.1	0.2456	0.1683

TABLE IV_c
COMPARISON OF CALCULATED AND OBSERVED ACTIVITIES

Sucrose %	a_1 , in terms of free water	a_2 , in terms of total water	$a_{obs.}$
0	0.0749	0.0749	0.0760
10	0.0815	0.0795	0.0809
20	0.0892	0.0850	0.0865
30	0.0981	0.0909	0.0921
40	0.1095	0.0981	0.0993
50	0.1240	0.1068	0.1070
60	0.1431	0.1168	0.1158
70	0.1683	0.1289	0.1258

TABLE V
COMPOSITIONS OF 1000 CC. OF SOLUTIONS CONTAINING 0.5 MOL OF POTASSIUM CHLORIDE

Sucrose	Total water	Water of hydration	Free water
	G.	G.	G.
0	983.1	0	983.1
100	921.1	21	900.1
200	859.0	42	817.0
300	796.9	63	733.9
400	734.4	84	650.4
500	670.0	105	565.0
600	606.5	126	480.5
700	543.5	147	396.5

TABLE Va

CONCENTRATION OF POTASSIUM CHLORIDE IN TERMS OF TOTAL WATER PRESENT

Sucrose %	Total water per liter of solution	KCl per 1000 g. of water	Activity calculated
	G.	Mols	a_2
0	983.1	0.5085	0.3239
10	921.1	0.543	0.3441
20	859.0	0.582	0.3667
30	796.9	0.627	0.3919
40	734.4	0.681	0.4222
50	670.0	0.746	0.4576
60	606.5	0.824	0.5007
70	543.5	0.920	0.5520

TABLE Vb

CONCENTRATION OF POTASSIUM CHLORIDE IN TERMS OF FREE WATER PRESENT

Sucrose %	Free water per liter of solution	KCl per 1000 g. of water	Activity calculated
	G.	Mols	a_1
0	983.1	0.5085	0.3239
10	900.1	0.555	0.3510
20	817.0	0.612	0.3837
30	733.9	0.681	0.4222
40	650.4	0.769	0.4699
50	565.0	0.885	0.5337
60	480.5	1.040	0.6136
70	396.5	1.260	0.7402

TABLE Vc

COMPARISON OF CALCULATED AND OBSERVED ACTIVITIES

Sucrose %	a_1 , in terms of free water	a_2 , in terms of total water	$a_{\text{obs.}}$
0	0.3239	0.3239	0.3240
10	0.3510	0.3441	0.3452
20	0.3837	0.3667	0.3692
30	0.4222	0.3919	0.3950
40	0.4699	0.4222	0.4222
50	0.5337	0.4576	0.4551
60	0.6136	0.5007	0.4925
70	0.7402	0.5520	0.5370

On the other hand, a_2 , the values calculated on the assumption that the activity of the chloride ion is only affected by decrease in the total water, agrees satisfactorily with the observed activities. The values for 70% sucrose show about 2% difference, but this is probably due to experimental error. There is a possibility that this difference is due to a change in the transport number of the potassium ion in the presence of 70% sucrose, due only to the presence of sucrose, for Washburn⁹ has shown that

⁹ Washburn, THIS JOURNAL, 31, 322 (1909).

the transport number of potassium in potassium chloride solutions has a constant value up to 1.3 *N* solutions, whereas the highest effective concentration reached in the present case is 0.920 mol per 1000 g. of water. It is proposed in a later publication to compare the present results with those obtained by means of a cell without transport.⁴

Neglecting the small differences which exist, it is improbable that the close agreement between a_2 and a_{obs} is merely a coincidence. It means that, besides being soluble in the free water, the chloride and potassium ions are also soluble in the water of hydration of sucrose. That is, beyond taking up space previously occupied by water, the sucrose behaves as an inert substance with respect to these ions.

Apart from these direct conclusions, the close agreement between a_2 and a_{obs} furnishes justification for certain assumptions that have been made. The first is that the activity of the potassium ion is equal to that of the chloride in the presence of sucrose as well as in pure aqueous solutions. In view of the fact that the sucrose merely appears to take up space in the solution, its effect on the potassium and chloride ions will be the same. Hence, the extension of MacInnes' assumption to sucrose solutions is admissible.

Similarly, justification is furnished for the assumption of the constancy of the transport number of the potassium ion. Sucrose solutions have a much greater viscosity than water, and increasing viscosity affects the absolute velocity of the ions. Therefore, it follows that if the transport numbers are constant, the sucrose has the same effect on the mobilities of the potassium and chloride ions.

Green¹⁰ has found that in solutions of potassium chloride in the presence of sucrose, the following relation is true, $\Lambda \cdot \eta^{0.7} = \text{a constant}$, where Λ is the equivalent conductivity and η is the viscosity of the solution. In view of the constancy of the transport numbers of the potassium and chloride ions in the presence of sucrose, it follows that the product $n_{\text{Cl}} \cdot \Lambda \cdot \eta^{0.7}$ is a constant, where n_{Cl} represents the transport number of the chloride ion. MacInnes¹¹ has found that this product is a constant when the solvent is pure water and the solute is potassium chloride. Hence, one is able to extend MacInnes' relation to the case in which the solvent consists of sucrose solutions.

II. The Effect of Sucrose on the Activity of the Hydrogen Ion in Tenth Normal Solutions of Hydrochloric Acid

As already mentioned, MacInnes¹ has made the assumption that in solutions of univalent chlorides of the same concentration, the activity of the chloride ion has the same value in every case, irrespective of the associated cation. Harned² verified this assumption experimentally.

¹⁰ Green, *J. Chem. Soc.*, 93, 2023 (1908).

¹¹ MacInnes, *THIS JOURNAL*, 43, 1217 (1921).

By using the cell with transport, similar to that used in Part I, but substituting hydrochloric acid for potassium chloride, it is possible to measure the activity of the hydrogen ion, knowing that of the chloride ion. The e.m.f. of the cell, $\text{Ag} \mid \text{AgCl} \mid \text{HCl (I)} \mid \text{sat. KCl} \mid \text{HCl (II)} \mid \text{AgCl} \mid \text{Ag}$, is given by the expression

$$E = \frac{RT}{F} \log \frac{\sqrt{H_I \times Cl_I}}{\sqrt{H_{II} \times Cl_{II}}}$$

where H_I and Cl_I are the hydrogen and chloride ion activities, respectively, in Solution I and H_{II} and Cl_{II} the activities in Solution II, the liquid-liquid potential difference being annulled by means of saturated potassium chloride solution.¹²

Knowing the value of the geometric mean of the activities of the hydrogen and chloride ions in one of the solutions, the e.m.f. of the cell determines the other value for the geometric mean. A knowledge of the chloride-ion activity in the latter case enables one to calculate the hydrogen-ion activity.

In the present case, the concentrations of hydrochloric acid used in the cell are 0.5 *N* and 0.1 *N*, respectively. In the compartment containing 0.1 *N* acid, the solvent consists of solutions of sucrose in water ranging from 0 to 70%, as in the previous case. The value for the geometric mean of the hydrogen- and chloride-ion activities in the case of 0.5 *N* aqueous solution of hydrochloric acid was taken to be 0.3911⁷. Hence the expression from which the activities of hydrochloric acid were calculated becomes

$$E = 0.059 \log \frac{0.3911}{a_{\text{HCl}}}$$

where a_{HCl} represents the geometric mean of the hydrogen- and chloride-ion activities in the 0.1 *N* solution. The liquid-liquid potential difference was annulled by means of saturated potassium chloride solution and when sucrose was present in one side, some was added to the saturated potassium chloride such that the concentration of sucrose in the bridge was about half of what it was in the cell itself.

Experimental

The apparatus was similar to that already described.

In Table VI are given the values for the e.m.f.'s of the cells with various concentrations of sucrose. The measurements were carried out at 25° as were the previous measurements. In the last column of Table VI are given the geometric means of the activities of the two ions, as calculated from the observed e.m.f. values by means of the above expression. In Table VII, the activities of the chloride ion in the solutions are shown in Col. 2, the geometric-mean activities in Col. 3, while in Col. 4 are given the hydrogen-ion activities, calculated from the values in Cols. 2 and 3.

¹² Fales and Vosburgh, *THIS JOURNAL*, **40**, 1291 (1918).

TABLE VI
 ELECTROMOTIVE-FORCE VALUES

Sucrose %	E. m. f. in volts				Av.	Smoothed values	Geometric- mean activities
0	0.0406	0.0408	0.0409	0.0407	0.0408	0.0408	0.0796
10	0.0381	0.0380	0.0380	0.0380	0.0380	0.0888
20	0.0353	0.0346	0.0348	0.0349	0.0349	0.1002
30	0.0326	0.0323	0.0322	0.0323	0.0320	0.1121
40	0.0292	0.0288	0.0288	0.0288	0.0289	0.1266
50	0.0263	0.0266	0.0256	0.0260	0.0257	0.1434
60	0.0220	0.0226	0.0218	0.0222	0.0220	0.0222	0.1644
70	0.0186	0.0190	0.0186	0.0185	0.0186	0.0186	0.1892

TABLE VII

Sucrose %	a_{Cl}	Geometric- mean activities	a_H
0	0.0760	0.0796	0.0834
10	0.0809	0.0888	0.0974
20	0.0865	0.1002	0.1161
30	0.0921	0.1121	0.1367
40	0.0993	0.1266	0.1614
50	0.1070	0.1434	0.1923
60	0.1158	0.1644	0.2335
70	0.1258	0.1892	0.2847

The values for the geometric-mean activities show that both the hydrogen-ion activities and the geometric-mean activities are increased by the addition of sucrose, but that the increase in the case of the hydrogen ion is much more pronounced.

Discussion of Results

In the computation of hydrogen-ion activities by the direct method, that is, by means of the cell $Hg | Hg_2Cl_2 | KCl N | KCl sat. | HCl | H_2$, the assumption is generally made that the hydrogen electrode measures the hydrogen-ion activity and not the geometric mean of the hydrogen- and chloride-ion activities. Such an assumption needs experimental verification.

A comparison of results obtained by means of the silver-silver chloride concentration cell, shown in Table VII, with those obtained by the direct method, in which solutions of hydrochloric acid in the presence of sucrose have been used, furnishes a convenient method of verifying this assumption. Measurements by means of the direct method have been carried out in this laboratory by Mr. T. Moran, the solvent being solutions of sucrose, and the solute hydrochloric acid of 0.1 *N* concentration. The value for the normal calomel electrode was taken to be 0.5648 volt at 25°. The activity, assumed to be hydrogen-ion activity, was calculated by means of the expression

$$E = E_0 + 0.059 \log a_H$$

where E was the observed potential of the hydrogen electrode and E_0 was the potential when the hydrogen-ion activity was unity.

In the last column of Table VIII are given the values of the activity measured by Moran using the hydrogen electrode, while in Cols. 2 and 3 are shown the geometric means and hydrogen-ion activities, respectively, as recorded in Table VII of the present paper, using the silver-silver chloride concentration cell.

TABLE VIII
COMPARISON WITH MORAN'S VALUES
Geometric-mean activities

Sucrose %	Geometric-mean activities	a_{H}	a_{H} (Moran)
0	0.080	0.083	0.080
10	0.089	0.097	0.096
20	0.100	0.116	0.115
30	0.112	0.137	0.139
40	0.127	0.161	0.167
50	0.143	0.192	0.200
60	0.164	0.234	0.240
70	0.189	0.285	0.288

It is evident from the above results that the activities measured by the hydrogen electrode correspond almost exactly with the individual hydrogen-ion activities obtained from the silver-silver chloride concentration cell, employing MacInnes' postulate regarding the independent activity of the chloride ion in solutions of univalent chlorides of the same concentration. In view of the different methods by which the activities have been computed, one cannot hope for exact agreement. Therefore, the deciding factor lies not so much in the absolute values, although these are distinct enough to make a decision possible, as in the fractional rise in the activity of the presence of sucrose. A glance at the table shows that the hydrogen electrode measures, beyond doubt, the hydrogen-ion activity and not the geometric mean of the activities of the hydrogen ion and the anion.

Summary

1. The effect of sucrose on the activity of the chloride ion in 0.1 *N* and 0.5 *N* potassium chloride solutions has been studied by means of the cell $\text{Ag} \mid \text{AgCl} \mid \text{KCl} (c_1) \mid \text{KCl} (c_2) + \text{Sucrose} \mid \text{AgCl} \mid \text{Ag}$. It has been found that the increase in activity could be accounted for by simply allowing for the decrease in the total water present in the solutions; that is, the potassium and chloride ions are soluble in the water of hydration of the sucrose.

2. The effect of sucrose on the activity of the hydrogen ion in 0.1 *N* hydrochloric acid has also been studied, using the MacInnes assumption of the independent activity of the chloride ion in solutions of chlorides of the same concentration.

3. It was demonstrated by means of a comparison between the hydrogen-ion activities, obtained in the present investigation, and the values obtained with a hydrogen electrode, that the hydrogen electrode measures the hydrogen-ion activity and not the geometric mean of the activities of the hydrogen ion and the accompanying anion.

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LIVERPOOL, ENGLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

TEMPERATURE COEFFICIENT OF ELECTROMOTIVE FORCE OF GALVANIC CELLS AND THE ENTROPY OF REACTIONS

BY ROSCOE H. GERKE

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The third law of thermodynamics in the limited form given by Lewis and Gibson¹ is becoming regarded as an exact law of nature. These authors have calculated the entropy of the elements and compounds,² for which heat-capacity data were available. They also tested the validity of the third law of thermodynamics by comparing the entropy change in a chemical reaction calculated on the one hand from heat-capacity data, and on the other hand from electromotive-force and thermochemical data. The discrepancies found amounted to over two entropy units on the average, but these were no greater than was to be expected, due to the inaccuracy of available calorimetric data.

The purpose of this investigation is to subject the third law of thermodynamics to a more rigorous test through more exact determination of entropy and heat content changes in a number of reactions. Such data can be determined with greater accuracy by a study of electromotive force of galvanic cells and its change with the temperature.

Experimental Considerations

By use of the equation $\frac{dE}{dT} = \frac{\Delta S}{nf}$, and by the Gibbs-Helmholtz equation, $\frac{\Delta H}{nf} = -E + T\left(\frac{dE}{dT}\right)$, the entropy change and the heat content change, respectively, may be calculated.

If the desired accuracy for the entropy change per equivalent is 0.10 calorie per degree, which corresponds to an accuracy of 30.0 calories for the change of heat content, the temperature coefficient of electromotive

¹ Lewis and Gibson, *THIS JOURNAL*, **42**, 1533 (1920).

² Lewis and Gibson, *ibid.*, **39**, 2554 (1917).