

The results are in harmony with the hypothesis that the reaction proceeds in two stages; a rapid electrochemical reaction consisting in the discharge of hydrogen ions to atoms, followed by a much slower combination to form molecules, and similarly for the reverse reaction.

The deviations from the theoretical equation have been discussed and certain possible causes eliminated. An empirical equation to represent the data has been formulated.

The equation used by Haber and Russ to represent their results on the polarization of the quinone-hydroquinone electrode has been shown to be unsatisfactory in that it is incapable of giving both positive and negative polarizations with a single equation. A more satisfactory equation has been proposed, and it has been suggested that the intermediate hydrogen mechanism for the quinone reduction is incorrect.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## THE INFLUENCE OF GELATIN ON THE TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID

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RECEIVED AUGUST 25, 1923

### Introduction

In a previous article<sup>1</sup> by Alfred L. Ferguson in co-authorship with one of us it has been shown that gelatin in the presence of sulfuric acid results in an increase in the transference number of the anion. Over a concentration range of 0 to 20% of gelatin the anion transference number undergoes a change of from 0.187 to 0.685. As a result of these measurements together with conductivity measurements the opinion was expressed that "the action of gelatin and sulfuric acid results in the formation of a single dissociable product in which the H<sup>+</sup> ion loses its identity." It was with a view of substantiating this opinion that the present investigation of the influence of gelatin on the transference numbers of hydrochloric acid was undertaken.

Since the appearance of the above-mentioned paper, but two investigations of a similar nature have been published, one by Rene Audbert<sup>2</sup> who used gelatin in concentration cells of the type, AgI-AgNO<sub>3</sub>, and found a lowering of the electromotive force which he explained as selective adsorption of the silver ion by the gelatin added; the other by J. W. Corran<sup>3</sup> who measured the influence of various concentrations of sucrose, 0 to 70%, on concentration cells of potassium chloride with and without transference.

<sup>1</sup> Ferguson and France, *THIS JOURNAL*, **43**, 2161 (1921).

<sup>2</sup> Audbert, *Compt. rend.*, **176**, 838 (1923).

<sup>3</sup> Corran, *THIS JOURNAL*, **45**, 1627 (1923).

Corran found that the transference number of the potassium ion was constant up to 50% sucrose concentration, and that at higher concentrations, it increased slightly.

### Theoretical Part

In this investigation the concentration-cell method was employed. This involves the measurement of the potentials of a concentration cell without diffusion,

$$E = \frac{2RT}{F} \ln \frac{C_1}{C_2} \quad (1)$$

a concentration cell with diffusion and reversible with respect to the cation,

$$E_H = 2N_a \frac{RT}{F} \ln \frac{C_1}{C_2} \quad (2)$$

and a concentration cell with diffusion reversible with respect to the anion,

$$E_{Cl} = 2N_o \frac{RT}{F} \ln \frac{C_1}{C_2} \quad (3)$$

Equation 3, the expression for the electromotive force for a concentration cell with transference, divided by Equation 1, the expression for the electromotive force without transference, gives,

$$\frac{E_{Cl}}{E} = N_o \quad (4)$$

which expresses the transference number of the cation in terms of  $E_{Cl}$  and  $E$ . In a similar way the expression

$$\frac{E_H}{E} = N_a \quad (5)$$

is obtained from Equations 1 and 2.

In this work the gelatin was introduced into the boundary between the acid concentration solutions and its effect on the boundary potential was calculated by the following equation.

$$E_B = \frac{E_{Cl} E_H}{2} = (1 - 2N_o) \frac{RT}{F} \ln \frac{C_1}{C_2} \quad (6)$$

The preceding equations are correct only when the mean activities of the ions of hydrogen chloride are substituted for the molal concentrations  $C_1$  and  $C_2$  in the term  $\ln \frac{C_1}{C_2}$ . The values for the mean activities of 0.1 *M* and 0.01 *M* hydrochloric acid used in the calculations following are those given by Lewis and Randall.<sup>4</sup>

### Apparatus and Materials

The potential measurements were made with an imported 15,000-ohm potentiometer, using two Weston certified cells, one as a check on the other. A commercial "analyzed" mercurous chloride was used. Since it was found impossible to purify tank hydrogen satisfactorily, the hydrogen used was generated by electrolyzing 5 *N* sodium hydroxide solution in a generator of the Bodenstein and Pohl type.<sup>5</sup> The hydrogen electrodes were

<sup>4</sup> Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 336.

<sup>5</sup> *Z. Elektrochem.*, 11, 375 (1905).

of the ordinary foil type coated with platinum black. The mercury used was washed with a dilute solution of mercurous nitrate and distilled five times in a Hulett mercury still. Ash-free gelatin as prepared by Ada M. Field<sup>6</sup> was used throughout this investigation. The acid solutions were prepared from commercial c. p. hydrochloric acid and conductivity water.

All measurements were made with the Weston standard cells and the concentration cells contained in an electrically-heated and regulated oil thermostat, which was maintained at a temperature of  $25^\circ \pm 0.01^\circ$ .

The arrangement of the cells and the location of the potentials are shown in Fig. 1. The procedure followed in making measurements is described by Ferguson and France.<sup>7</sup>

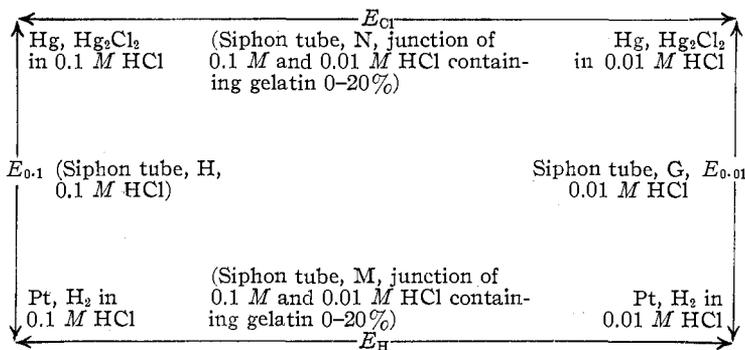


Fig. 1

As a preliminary step in the investigation it was necessary to determine the transference number of the anion of hydrochloric acid for 0.1 *M* and 0.01 *M* solutions. The transference number of the anion was found to be  $0.1699 \pm 0.0018$ , which agrees favorably with the value 0.1708 corrected to  $25^\circ$ , obtained by Noyes and Sammet.<sup>8</sup>

### The Influence of Gelatin on the Transference Numbers of Hydrochloric Acid

The gelatin was introduced into the concentration cells as shown in Fig. 1 and as described by Ferguson and France.<sup>9</sup> Measurements were made with concentrations of gelatin varying from 0.5 to 20%. In all, 28 runs were made, the results of which are summarized in Table II. Table I is given as an example of an individual run.

In Table I, the column headed  $E_H$  contains the potentials of the hydrogen concentration cell with diffusion,  $Pt_{H_2} | 0.1 M HCl | 0.01 M HCl | Pt_{H_2}$ ; in the column headed  $E_{Cl}$ , those of the chloride concentration cell with diffusion,  $Hg | Hg_2Cl_2, 0.01 M HCl | 0.1 M HCl, Hg_2Cl_2 | Hg$ ; in the column headed  $E_{0.1}$ , the potentials of the cell  $Pt_{H_2} | 0.1 M HCl, Hg_2Cl_2 | Hg$ ; and in the column headed  $E_{0.01}$ , the potentials of the cell  $Pt_{H_2} | 0.01 M HCl, Hg_2Cl_2 | Hg$ . The column headed "*E* by  $E_H + E_{Cl}$ " contains the sums of the values recorded in columns  $E_H$  and  $E_{Cl}$ . The column headed "*E* by  $E_{0.01} - E_{0.1}$ " contains the differences between the values recorded in the columns headed  $E_{0.01}$  and  $E_{0.1}$ .

<sup>6</sup> Field, THIS JOURNAL, 43, 668 (1921).

<sup>7</sup> Ref. 1, p. 2153.

<sup>8</sup> Noyes and Sammet, THIS JOURNAL, 24, 944 (1902).

<sup>9</sup> Ref. 1, p. 2162.

TABLE I

DATA FOR AN INDIVIDUAL RUN WITH 5% GELATIN

Set up 10:30 P.M., May 8, 1923; boundaries were put in 7:30 P.M., May 9

Time P.M. May 9	Bar. Mm.	$E_H$	$E_{Cl}$	$E_{0.1}$	$E_{0.01}$	$E$ by $E_H + E_{Cl}$	$E$ by $E_{0.01} - E_{0.1}$
3:15	735.3	...	...	0.39656	0.51101	...	...
				656	101		
5:00	736.9	...	...	665	122	..	...
				665	122		
7:00	738.6	...	...	665	103	...	...
				665	103		
7:30	739.2	0.07444	0.04015	667	121	0.11459	0.11454
		444		667	121		
10:00	739.2	422	3989	688	122	411	423
		422		690	122		
12:00	739.9	420	980	722	125	400	403
		420		722	125		
May 10							
1:30	741.3	462	899	735	147	361	412
		462		735	147		
		Av. .07437	.03971	.39703	.51129	.11408	.11426

TABLE II

SUMMARY OF POTENTIALS AND TRANSFERENCE NUMBERS WITH GELATIN

1	2	3	4	5	6	7	8	9
$E_H$	$E_{Cl}$	$E_H + E_{Cl}$	$E_{0.01} - E_{0.1}$	$\frac{N_a}{E_H}$	$\frac{N_c}{E_H}$	$\frac{N_c}{E_{Cl}}$	$\frac{N_c}{E_{0.1}}$	$\frac{N_a + N_c}{\text{Cols.}}$
				$\frac{E_H + E_{Cl}}$	$\frac{E_{0.01} - E_{0.1}}$	$\frac{E_H + E_{Cl}}$	$\frac{E_{0.01} - E_{0.1}}$	6 + 8
				0.0%				
0.01947	0.09612	0.11462	0.11463	0.16994	0.16991	0.82998	0.82988	0.99979
				0.5%				
.02259	.09145	.11403	.11404	.19811	.19808	.80198	.80190	.99998
.02258	.09145	.11403	.11405	.19802	.19798	.80198	.80182	.99980
.02259	.09145	.11403	.11405	.19806	.19803	.80198	.80186	.99989
				0.75%				
.02530	.08867	.11397	.11403	.22199	.22187	.77801	.77710	.99947
.02566	.08833	.11399	.11400	.22511	.22456	.77488	.77447	.99903
.02548	.08850	.11398	.11402	.22355	.22321	.77644	.77604	.99925
				1.0%				
.02891	.08539	.11430	.11428	.25293	.25297	.74706	.74720	1.00017
.02731	.08686	.11417	.11397	.23920	.23963	.76079	.76214	1.00187
.02757	.08645	.11402	.11402	.24180	.24180	.75820	.75820	1.00000
.02754	.08655	.11409	.11400	.24138	.24161	.75861	.75921	1.00081
.02784	.08631	.11416	.11407	.24388	.24400	.75617	.75669	1.00071
				2.0%				
.04476	.06930	.11406	.11408	.39216	.39236	.60757	.60747	0.99983
.04237	.07167	.11404	.11393	.37153	.37189	.62846	.62967	1.00096
.04667	.06661	.11329	.11305	.41196	.42827	.58796	.58921	1.01748
.04646	.06660	.11306	.11305	.41093	.41097	.58907	.58911	1.00008
.04507	.06854	.11381	.11370	.39664	.40087	.60327	.60371	1.00458

2.5%								
.05151	.06189	.11321	.11311	.45499	.45539	.54492	.54539	1.00078
.05153	.06187	.11320	.11317	.45521	.45533	.54479	.54493	1.00026
3.0%								
.05152	.06168	.11321	.11314	.45510	.45536	.54486	.54516	1.00052
5.0%								
.05635	.05786	.11421	.11416	.49339	.49273	.50662	.50683	0.99956
.05593	.05793	.11386	.11394	.49121	.49087	.50878	.50843	.99929
.05614	.05790	.11404	.11405	.49230	.49180	.50770	.50763	.99943
10.0%								
.07437	.03971	.11408	.11426	.65191	.65088	.34808	.34754	.99842
.07459	.03973	.11432	.11430	.65247	.65264	.34753	.34762	1.00026
.07448	.03972	.11420	.11428	.65219	.65176	.34781	.34758	0.99934
15.0%								
.08150	.03186	.11336	.11344	.71895	.71756	.28105	.28085	0.99841
.08159	.03206	.11365	.11368	.71789	.71772	.28209	.27207	.98974
.08636	.02496	.11332	.11353	.77973	.77823	.22026	.21976	.99804
.08817	.02496	.11332	.11320	.77806	.77888	.22008	.22040	.99928
.09043	.02313	.11356	.11367	.77631	.79554	.20368	.20348	.99902
.08844	.02515	.11360	.11305	.77852	.78231	.22139	.22247	.99821
.08641	.02702	.11347	.11343	.76158	.76171	.23926	.23651	.99821
20.0%								
.08960	.02412	.11376	.11350	.78762	.78942	.21202	.21251	1.00193
.08833	.02544	.11377	.11360	.77693	.77755	.22361	.22394	1.00149
.08897	.02476	.11377	.11355	.78228	.78349	.21782	.21823	1.00171
.08860	.02502	.11362	.11347	.77978	.78082	.22021	.22059	1.0014
.08793	.02581	.11374	.11367	.77309	.77354	.22691	.22707	1.00061
.08827	.02582	.11368	.11357	.77449	.77718	.22356	.22383	1.00101

In Table II the headings of Columns 1, 2, 3 and 4 have the same significance as those given for Table I; Cols. 5, 6, 7 and 8 contain the transference numbers calculated from the values in Cols. 1, 2, 3 and 4 as indicated in the headings. Col. 9 contains the sum of the  $N_a$  and  $N_c$  values as given in Cols. 6 and 8, and should be equal to unity.

The accuracy with which the potentials  $E_H$  and  $E_{Cl}$  can be duplicated in the presence of gelatin is shown by the closeness with which the averages of

TABLE III  
SUMMARY OF POTENTIALS AND TRANSFERENCE NUMBERS

% Gel.	$E_H$	$E_{Cl}$	$N_a$	$E_B$
0.0	0.01947	0.09612	0.16991	0.03783
0.5	.02259	.09145	.19083	.03560
0.75	.02548	.08850	.22321	.03187
1.0	.02784	.08631	.24400	.02948
2.0	.04507	.06854	.40087	.01290
2.5	.05152	.06168	.45536	.00514
3.0	.05614	.05790	.49180	.00094
5.0	.07448	.03972	.65176	— .01748
10.0	.08641	.02702	.76171	— .03014
15.0	.08897	.02478	.78349	— .03264
20.0	.08827	.02542	.77718	— .03192

the table of the same concentrations agree. The lower concentrations of gelatin show a closer agreement than the higher ones. Table III contains a summary of the transference numbers contained in Table II, together with the boundary potentials in the presence of gelatin.

An inspection of values recorded in Table III shows that the values of  $N_a$  increase with increase in gelatin concentration. The relation between the transference number of the anion and the gelatin concentration is shown in Fig. 2. The transference numbers are plotted as ordinates and the concentrations of gelatin as abscissas. The change in transference number is rapid at low gelatin concentrations. It is gradual between 3 and 5%. Then it slowly rises to a maximum value between 5 and 10%. Above

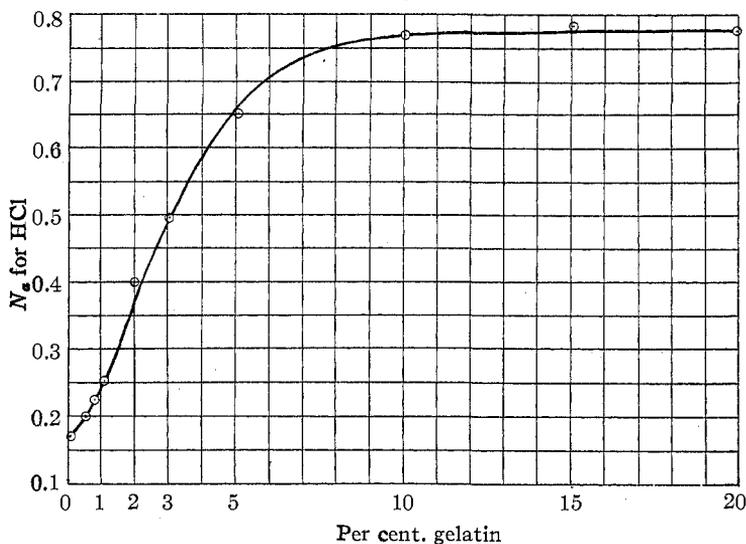


Fig. 2

10% it remains constant. If this represents an actual increase in the migration velocity of the anion, then there must be a corresponding decrease in the boundary potential ( $E_B$ ). The values given in columns headed  $N_a$  and  $E_B$  indicate such changes. It was shown in the theoretical development that the boundary potential opposes the electrode potentials in the hydrogen concentration cell ( $E_H$ ), and in the chloride concentration cell ( $E_{Cl}$ ) it is in the same direction as the electrode potentials. If a decrease takes place in  $E_B$  there should be an increase in  $E_H$  and a corresponding decrease in  $E_{Cl}$ . The values in columns  $E_H$  and  $E_{Cl}$  indicate that such a change takes place.

It has been shown (Equation 6) that the boundary potentials depend on the transference numbers of the ions and the ratio of their concentration in the two solutions. Therefore, a change in  $E_B$  would result from a change in concentration or a change in transference number.

From theoretical considerations the value of  $E_B$  would be reduced by making the concentrations of the solutions approach equality. When  $E_B$  is equal to zero and when the concentrations of the solutions became less than 0.01 M solution, the direction would be reversed.

**Influence of Gelatin on the Hydrogen-Ion Concentration of Hydrochloric Acid Solutions**

In order to determine whether or not concentration changes are produced by the addition of gelatin, concentration cells of the type,  $Pt_{H_2} |$

TABLE IV  
INFLUENCE OF GELATIN ON THE HYDROGEN-ION CONCENTRATION OF 0.1 M AND 0.01 M HYDROCHLORIC ACID SOLUTIONS

Gelatin %	0.1 M		0.01 M	
	$C_1$	$E_x$	$C_2$	$E_z$
0	0.09170	.....	0.00975	.....
1	.08791	.00217	.00442	0.03946
2	.08500	.00391	.00143	.09754
3	.08178	.00588	.00095	.12057
4	.07864	.00789	.00087	.12421 <sup>a</sup>

<sup>a</sup> Due to the foaming of the gelatin solution this value could not be accurately obtained.

0.1 M HCl | M KCl | 0.1 M HCl + gelatin |  $Pt_{H_2}$ ;  $Pt_{H_2} |$  0.01 M HCl | M KCl | 0.01 M HCl + gelatin |  $Pt_{H_2}$ , were used. The data obtained from these measurements are given in Table IV.

The first column contains the percentage of gelatin in the acid in one half the cell. The columns  $E_x$  and  $E_z$  contain the measured potentials of the cells  $E_x$  and  $E_z$  when 0.1 M and 0.01 M solutions were used. The hydrogen-ion concentrations  $C_1$  and  $C_2$  calculated for the concentrations of gelatin used show that gelatin produces a relatively small decrease of the hydrogen-ion concentration in 0.1 M solution and a much larger relative decrease in 0.01 M solution.

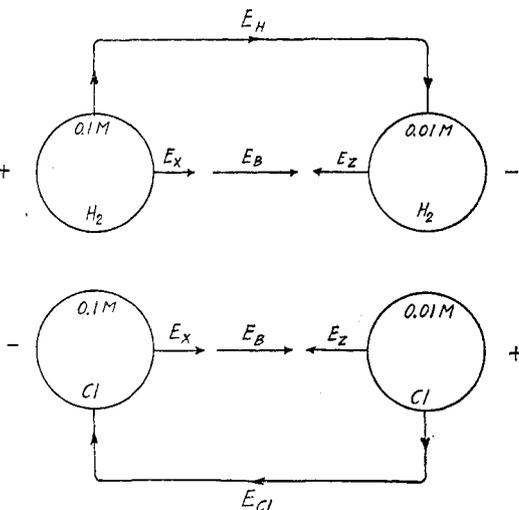


Fig. 3

Since the hydrogen-ion concentration of the 0.1 M solution is always greater than that of the 0.01 M solution, the reverse of the boundary potential  $E_B$  cannot result from concentration changes produced by the gelatin.

Since it has been shown that gelatin produces changes in the hydrogen concentration, new potentials are produced at the boundaries between the solutions in the wicks and the gelatin. The direction of the boundary potentials  $E_B$ ,  $E_X$  and  $E_Z$  together with  $E_H$  and  $E_{C1}$  are shown diagrammatically in Fig. 3. The potentials  $E_X$ ,  $E_B$  and  $E_Z$  which result from the presence of the gelatin can be calculated from the data in Table IV. These calculations are shown in Table V.  $E_B$  represents the potential within the siphon, that is, the potential considered thus far,  $E_X$  and  $E_Z$  represent the potentials at the contact of the solutions in the reservoirs,  $E_H$  and  $E_{C1}$  are the measured potentials and are the algebraic sum of the potentials at the electrodes and the boundary potentials  $E_X$ ,  $E_B$  and  $E_Z$ .

TABLE V  
BOUNDARY POTENTIAL CALCULATIONS

% Gel.	$E_H$	$E_{C1}$	$E_B$	$E_X$	$E_Z$	$E_Z - E_X$	$E'_B$	$E'_B - 0.03783$
1	0.02784	0.08631	0.02948	0.00071	0.01298	0.01228	0.04908	0.01125
2	.04507	.06864	.01090	.00129	.03219	.03090	.06761	.02978
3	.05614	.05790	.00094	.00194	.03968	.03774	.07464	.03681
4	.....	.....	.....	.00259	.04087	.03828	.07509	.03726 <sup>a</sup>

<sup>a</sup> The values in line 4 do not check because the 4% gelatin solution foamed so much when hydrogen was bubbled through it that consistent values for the e.m.f. could not be obtained.

The boundary potentials  $E'_B$ ,  $E'_X$  and  $E_Z$  were calculated by means of the boundary potential formula,  $E_B = (1 - 2N_a) \frac{RT}{F} \ln \frac{C_1}{C_2}$ . The total potentials  $E'_B$  should be considered as composed of the original potentials plus the potentials caused by the alteration of the acid concentration due to the presence of the gelatin. This change in potential should be equal to the total potential  $E'_B$  less the original boundary potential and is given in the column designated  $E'_B - 0.03783$ . Fig. 3 shows that  $E_X$  and  $E_Z$ , the potentials between the gelatin solutions and the solutions in the wicks, are directed in opposition to each other. If the values of  $E_Z$  and  $E_X$  are due to concentration changes, then  $E_Z - E_X$  should be equal to  $E'_B - 0.03783$ . Since they agree satisfactorily, this eliminates the possibility that changes observed in the boundary potential are due to concentration changes produced by the addition of gelatin.

### Conductivity of Hydrochloric Acid Solutions of Gelatin

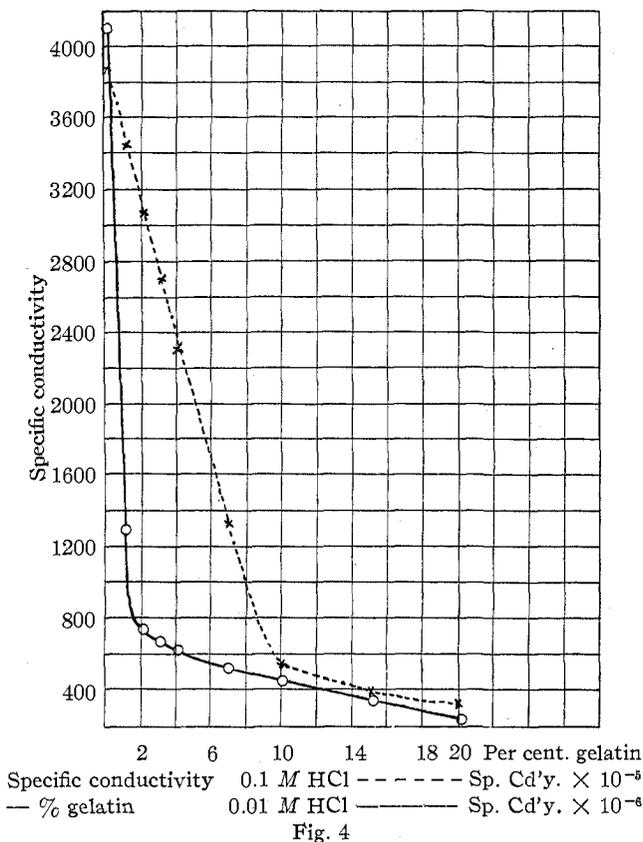
Any change in the mobility and number of the ions affects the conductivity of a solution; therefore it was thought that conductivity measurements would give some information as to the nature of the changes caused by the addition of gelatin. Measurements were made of the conductivity of 0.1 *M* and 0.01 *M* hydrochloric acid solutions, in which the concentration of gelatin varied from 0 to 20%. A correction was applied for con-

ductivity of gelatin solutions of water over the same range of concentrations. These results are shown in Table VI.

TABLE VI  
CORRECTED SPECIFIC CONDUCTIVITIES OF GELATIN AND WATER

Gelatin and water $\times 10^{-6}$	Gelatin %	Corr. value 0.01 M HCl and gelatin $\times 10^{-8}$	Corr. value 0.10 M HCl and gelatin $\times 10^{-8}$	Gelatin and water $\times 10^{-6}$	Gelatin %	Corr. value 0.01 M HCl and gelatin $\times 10^{-8}$	Corr. value 0.10 M HCl and gelatin $\times 10^{-8}$
1.00	0	4093.0	38687.3	114.74	4	629.16	23371.0
40.09	1	1315.41	34445.2	171.19	7	542.5	13278.7
67.10	2	750.3	30722.3	206.62	10	455.28	5558.4
90.76	3	675.16	26969.6	246.37	15	348.43	3939.7
...	..	.....	.....	260.60	20	365.60	3092.7

Fig. 4 shows the effect of gelatin on the conductivity of 0.1 M and 0.01 M solutions of hydrochloric acid. The specific conductivities are plotted



as ordinates and the concentrations of gelatin as abscissas. These curves show that the gelatin produces a greater relative change in the specific conductivity of the 0.01 M than in the 0.1 M solutions. This fact is also

substantiated by the data in Table IV which shows that the addition of 3 to 4% of gelatin reduces the hydrogen-ion concentration to not far from zero. From Fig. 4, it is seen that 10% of gelatin reduces the conductivity of the 0.1 *M* solution almost to zero. A similar change occurs in the 0.01 *M* solution at 2 to 3% concentration of gelatin. This indicates that not only is the hydrogen-ion concentration reduced by the addition of gelatin but also that the acid is removed as a whole.

### Discussion of Results and Conclusions

Two main theories have been evolved to account for the action of gelatin on electrolytes. One assumes that a highly dissociable compound is formed either by chemical union or molecular adsorption while the other assumes that the ions of the electrolyte are specifically adsorbed by the gelatin.

This investigation has shown that gelatin exerts a definite influence on the transference number of the anion of hydrochloric acid. A summary of the data obtained is given in Table III. It shows that the boundary potential has been changed from 0.03783 to -0.03192. Corresponding to this decrease in boundary potential there is an increase in the potential of the hydrogen concentration cell ( $E_H$ ) from 0.01947 to 0.08827 while there is a decrease in the potential of the chloride concentration cell ( $E_{Cl}$ ) from 0.09612 to 0.02542. The transference number of the anion has apparently been increased from 0.1699 to 0.7772. This observed effect of a decrease in the boundary potential would be given by any factor which would numerically increase the value of  $E_H$  and decrease that of  $E_{Cl}$ . This factor would also account for the apparent increase found in the transference number of the anion.

The data given in Table IV show that this factor cannot be the result of the change in the concentration of the acid solution when the gelatin is added. If this increase were caused by a change of concentration, then the concentration of the hydrogen ions would have to be less in the 0.1 *M* than in the 0.01 *M* solutions of gelatin. The recorded data show that this is contrary to the facts. It was also shown that the boundary potentials  $E'_B - 0.03784$ ,  $E_X$  and  $E_Z$  which result from concentration changes, neutralize one another. Therefore, this effect is not due to concentration changes caused by the addition of the gelatin. This decrease in the boundary potential could be caused by any one of three factors: a decrease in the concentration of the 0.1 *M* solution such that it became less than in the 0.01 *M* solution; a change in the transference number; or a change in the kind of ions present. The data recorded in Table V eliminate the first of these factors, because they show that such concentration changes are impossible. This indicates that the decrease in boundary potential can only be due to the other factors.

The facts are considered from the point of view that a chemical compound which ionizes is formed. If such is the case, there should be a fairly definite relation between the amount of gelatin added and the acid removed. On this basis one would be able to explain the decrease in the hydrogen-ion concentration and in the conductivity which was observed. If such a reaction occurs new compounds are formed and some of the hydrogen ions are replaced by complex gelatin ions which should have a smaller velocity than the hydrogen ions and consequently the transference number of the anion should be increased. This is in agreement with the observed facts. No data from which the exact amount of hydrochloric acid removed by the gelatin could be determined were obtained.

From the conductivity curves, Fig. 4, it appears that the conductivities of the 0.01 *M* and 0.1 *M* hydrochloric acid solutions are reduced definite amounts for each addition of gelatin. If the compound dissociates, then the conductivity curves should tend to flatten at the higher concentrations of gelatin. This agrees with the observed facts. Moreover, such a compound should possess some conductivity, so that for higher concentrations of gelatin the decrease in conductivity would no longer be proportional to the gelatin added. The flattening of the gelatin-hydrochloric-acid curve for higher concentrations of gelatin tends to confirm this view. The sharp bend in the conductivity curve for 0.01 *M* acid solutions occurs at about the same point as the similar bend in the transference number curve, Fig. 2. In a similar way Table IV shows that practically all the hydrochloric acid has been removed from the 0.01 *M* HCl solution for the same concentration of gelatin.

These facts indicate that hydrochloric acid as such is removed by the addition of gelatin to the solution. Therefore, the apparent change in the transference numbers is due not to an actual change in the velocity of the hydrogen and chlorine ions but to the presence of new ions in the solutions resulting from the dissociation of the gelatin chloride compound formed.

It has been definitely shown that gelatin causes an increase in the transference number of the anion of hydrochloric acid. Furthermore, it has also been shown that this increase in the transference number of the anion cannot be due to a change in the effective concentration of the acid solution when the gelatin is added. In view of these facts, the results of this investigation tend to confirm the hypothesis advanced that a single dissociable adsorption complex or definite chemical compound is formed by the action of hydrochloric acid and gelatin. In this reaction the hydrogen ion of the acid loses its identity. It is also further held that in the presence of a base a similar product would result, in which the hydroxyl ion of the base would lose its identity. In conformity with this view no similar action should take place between gelatin and a neutral salt.

The authors desire to express their thanks to Professor Charles H. Skinner of the Department of Physics, Ohio Wesleyan University, for the potentiometer used in this investigation.

### Summary

1. A new determination of the transference numbers of the ions of hydrochloric acid has been made.

2. It has been shown that the addition of gelatin reduces the effective hydrogen-ion concentration of 0.1 *M* and 0.01 *M* hydrochloric acid solutions.

3. The transference numbers of 0.1 *M* and 0.01 *M* hydrochloric acid have been found to be changed by the presence of gelatin.

4. The presence of gelatin alters the conductivity of 0.1 *M* and 0.01 *M* solutions of hydrochloric acid.

5. *Some evidence has been found which apparently substantiates the theory that gelatin reacts with acids to form an adsorption complex or additive chemical compound which dissociates. This is in agreement with the views set forth by Jacques Loeb.*<sup>10</sup>

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

## A CALORIMETER FOR HEATS OF MIXING AT ELEVATED TEMPERATURES<sup>1</sup>

BY BURT H. CARROLL AND J. HOWARD MATHEWS

RECEIVED SEPTEMBER 28, 1923

In the numerous investigations of the properties of liquid mixtures, heat of mixing has received comparatively little attention. Quantitative theoretical treatment has been thus far unsuccessful; the attempt of Kremann<sup>2</sup> to compute heat of formation of a mixture from the constants of the van der Waals equation for the components was not verified by experiment. It is improbable that such calculations can be made until our knowledge of the liquid state is more complete and accurate. However, the work of van der Waals has indicated clearly that heat effects are to be expected, independent of molecular change, when the mixture is non-ideal. In some cases heat of mixing may be definitely, if not quantitatively, ascribed to polarity. A considerable liberation of heat, accompanied by a minimum vapor pressure, is strong evidence for the formation of a

<sup>10</sup> Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., 1922.

<sup>1</sup> This paper constitutes a portion of a thesis presented by Burt H. Carroll to the Graduate School of the University of Wisconsin, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1922.

<sup>2</sup> Kremann, *Monatsh.*, **35**, 1235 (1914); **37**, 11 (1916).