pairs of electrons are situated between the carbon center and the hydrogen nuclei. This makes the methane molecule more rare-gas-like when looked at from a distance.

In conclusion we wish to thank Professor R. C. Tolman for the interest he has shown in this research.

Summary

We have measured a critical potential in methane at 14.4–15.2 volts, which we believe to be the ionization potential. Using Eve's rule we have predicted the ionization potential to be 13.7 volts. Special attention has been paid to the possible thermal decomposition of the gas by the hot filament, and it has been avoided. We have also taken care of the effect of mercury vapor in interpreting our current-potential curves.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 174]

ELECTROMOTIVE-FORCE MEASUREMENTS IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID CONTAINING SUCROSE[1]

BY GEORGE SCATCHARD

RECEIVED MARCH 4, 1926 PUBLISHED AUGUST 5, 1926

Solutions of sucrose in water have long occupied a prominent position in the study of the properties of solutions, and particularly in the study of reaction rates. With the correlation of reaction rates with activities, electromotive-force measurements in solutions containing sucrose have become important. All the measurements so far reported, however, have been made in cells containing liquid junctions, and with those junctions made by dipping a small tube containing the lighter liquid into a larger one containing the heavier. Most of them have been made with a hydrogen electrode.

This paper describes an attempt to study the problem in more detail by dividing it into two parts: a study of the effect of sucrose on the liquid-junction potential between hydrochloric acid and saturated potassium chloride, and a study of the effect of sucrose on the potential of the hydrogen electrode. The measurements do not agree with those in the literature, and they disclose three sources of errors which probably account for the discrepancies. They give a more precise knowledge of the ion activities in sucrose solutions, and they comprise the first experimental study, so far as I am aware, of the effect of a non-electrolyte solute on liquid-junction potentials.

---

[1] Reported to the Physical-Inorganic Division of the American Chemical Society at Los Angeles, August 7, 1925. The experimental work was carried out in 1924 during the tenure of a National Research Fellowship.

Cells with Liquid Junctions

The electromotive force at 25° of the cell Hg | HgCl, KCl (satd.) | HCl (c_1), sucrose (c_2), AgCl | Ag was measured in the flowing-junction apparatus previously described,[2] which gives a continuously renewed junction of large cross section but of almost knife-edge thinness, and which also permits a study of the effect on the liquid-junction potential of interdiffusion of the two solutions without the disturbance of turbulent mixing. The concentration of hydrochloric acid was kept constant at 0.1012 mole per liter, while that of sucrose was varied from zero to 700 g. per liter. All weights are reduced to vacuum.

The sucrose had been precipitated with alcohol, dried in a vacuum at 50°, and then in a current of dry air at the same temperature.[3] The other materials were all prepared as for the earlier studies.[2,4] The silver chloride electrodes were all prepared in the solution without sucrose and then washed several times in the solution in which they were to be used. Only two measurements, with a single filling of the apparatus, were made with each solution. Otherwise the procedure was the same as that described in the papers cited.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL Hg | HgCl, KCl (satd.) | HCl (0.1012 *N*), sucrose, AgCl | Ag

Sucrose, g. per liter	*E* flowing	Dev. from mean	*E* maximum	Dev. from mean
0.00	0.0431	0.0000_5	....	....
.00	.0431	$.0000_1$	0.0435	0.0000_4
98.42	.0414	$.0000_3$	.0418	$.0000_3$
99.71	.0410	$.0000_4$	.0412	....
200.66	.0390	$.0000_6$	.0394	....
301.13	.0368	$.0000_5$	.0376	....
406.88	.0344	$.0000_5$	.0351	....
489.86	.0303	$.0000_3$	.0312	....
605.67	.0251	$.0002_3$	.0265	....
700.38	.0195	$.0002_7$	.0224	$.0001_9$

The measurements with a flowing junction are given in the second column of Table I, and the maximum values after the flow is stopped in the fourth column. It was noted in the earlier paper that the electromotive force of a similar cell, but with no sucrose, increases 0.3 mv. when the flow is stopped, and that the amount of this change is independent of the acid concentration.[5] When sucrose is added to the acid this difference increases to 3.0 mv. for the solution containing 700 g. per liter, and the

---

[2] Scatchard, THIS JOURNAL, **47**, 696 (1925).

[3] I wish to thank Professor H. A. Fales of Columbia University for the gift of the sugar used.

[4] Scatchard, THIS JOURNAL, **47**, 641 (1925).

[5] See correction, *ibid.*, **47**, 3107 (1925).

time required to reach the maximum value is not changed. Although this effect makes the readings with the solutions flowing more erratic and sensitive to the rate of flow, it is not difficult to fix the average value to 0.1 mv., as the small deviations from the mean values show. However, since the difference between the potentials at two types of junction changes, one at least of the potentials must also change. It is probable that both potentials change in the same direction, perhaps by several millivolts, but there is no indication of the direction of this change. Since one millivolt in the potential of this cell corresponds to a 4.5% change in activity, it is apparent that the uncertainty in activity values determined with the use of a liquid junction must be large.

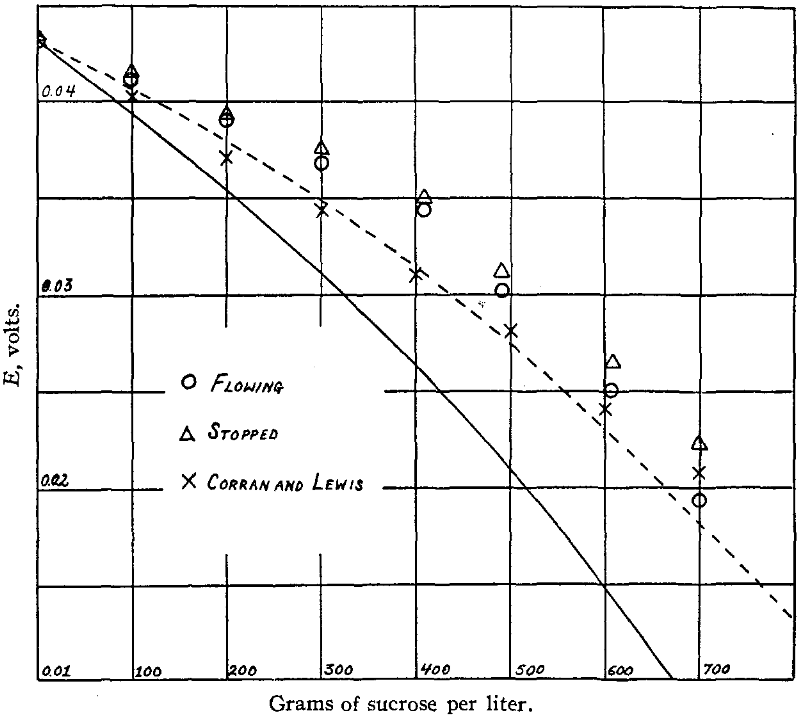

Fig. 1.—Hg | HgCl, KCl (satd.) | HCl (0.1012 *N*), sucrose, AgCl | Ag. Broken line, $\sqrt{A_H \times A_{Cl}}$. Full line, $\sqrt{A_K \times A_{Cl}}$.

In Fig. 1 the values of the electromotive force with flowing junction are represented by circles, and the maximum values without flow by triangles. The measurements of Corran and Lewis[6] on the cell Ag | AgCl, HCl (0.5 *N*) | KCl (satd.) | HCl (0.1 *N*), sucrose, AgCl | Ag, plus a constant to give agreement in the solution without sucrose, are represented by the crosses. The curves in this figure will be discussed in a later section.

---

[6] Corran and Lewis, THIS JOURNAL, **44**, 1673 (1922).

Part of the difference between my measurements and those of Corran and Lewis may be attributed to the fact that their saturated potassium chloride bridge contained sucrose in concentration about half that in the acid solution.

It is probable that the electromotive force of this cell, as of those to be discussed later, changes somewhat as the sucrose is inverted. The effect should be small during the short time required for measurement, and not greater than the deviation from the mean of the individual values. It is probably responsible for the fact that the deviations are larger for the last two solutions, but no attempt was made to study it quantitatively, or to correct the measured values for it.

Cells Without Liquid Junction

The electromotive force at 25° of the cell Pt, H_2 | HCl (c_1), sucrose (c_2), AgCl | Ag was measured with the Clark type rocking hydrogen electrode previously described.[4] The solutions and silver chloride electrodes were prepared with those used in the cells with liquid junction. On each solution two measurements were made with different hydrogen electrodes but with the same silver chloride electrode. For reasons to be discussed below it was necessary to continue the rocking of the hydrogen electrode while the measurements were made. Otherwise the technique was the same as that described in the earlier paper. Measurements were also taken after the rocking had ceased for a definite time, and in some cases ith the electrode stationary but with hydrogen bubbling through the solution.

Since the completion of these experiments Taylor and Bomford[7] and Pennycuick[8] have noted that the electromotive force of the cell with a hydrogen electrode and a saturated potassium chloride bridge changes during the inversion of sucrose in the direction indicating an increasing activity of the hydrogen ion. The electromotive force of this cell changes similarly. The change was studied only with the solution containing 700 g. per liter. In the other solutions the change is much smaller and negligible for the short times between the mixing of the solutions and the measurements.

For the most concentrated solution the change for complete inversion is about 10 mv. From the rate of inversion measured by Moran and Lewis[9] this should give a change of about 0.01 mv. per minute at the start of the reaction. The measurements during the course of the reaction and the calculated values at the time of mixing are given in Table II.[10] Part of

[7] Taylor and Bomford, *J. Chem. Soc.*, **125,** 2016 (1924).

[8] Pennycuick, THIS JOURNAL, **48,** 6 (1926).

[9] Moran and Lewis, *J. Chem. Soc.*, **121,** 1613 (1922).

[10] The values at the time of mixing depend somewhat upon the assumption as to the functional relationship between the electromotive force and the fraction of the sugar inverted. If the change in electromotive force is due to a change in the total number of moles, the activity of the ions should be (approximately) a linear function of the

the irregularity shown in the table may be due to the fact that the temperature, except at the time of the electromotive-force measurements, was not accurately controlled.

TABLE II

EFFECT OF REACTIONS ON POTENTIAL IN SOLUTIONS CONTAINING 700 G. OF SUCROSE PER LITER

Expt.	Time, min.	% Inverted	Reading, volts	Average variation from mean	Reading corr. to zero time
A	102–114	13.9	0.3044	0.0000_1	0.3059
	116[a]	..	.3032	....	....
B	164–179	21.2	.3017	$.0000_2$	.3044
	447–460	46.6	.2997	$.0000_1$	.3054
C	505–517	50.6	.3003	$.0000_0$	.3064
	1500–1512	87.5	.2964	$.0000_4$	.3054
	1515[a]	..	.2957	....	....
				Av.	.3055

[a] Rocking stopped immediately after last reading.

The measurements indicate that another chemical action is taking place at the hydrogen electrode. When the shaking was stopped the electromotive force decreased at the rate of 0.1–0.7 mv. per minute. The rate of decrease appeared nearly independent of the sucrose concentration, but varied greatly with some factor not controlled in these experiments. It was always many times the change due to inversion. When the shaking was resumed the electromotive force rose rapidly to its former value. Bubbling hydrogen around the electrode without shaking gave a steady value somewhat lower than that obtained when the cell was shaken. This behavior indicates clearly a reaction that uses up hydrogen and keeps the solution at the electrode unsaturated. The degree of unsaturation depends upon a balance between the rate of this reaction and the rate of diffusion to the electrode, and therefore upon the thickness of the diffusion layer. With the rocking electrode the diffusion layer is so thin that the error is probably small. The thicker diffusion layer with a bubbling electrode leads to a lower electromotive force. In either case the diffusion layer remains so nearly constant that the disturbance could not be detected with a single type of electrode. With neither bubbling nor rocking, the diffusion layer thickens continually as the reaction progresses so that the electromotive force is not constant. Examples of the change when the rocking is stopped are given by the rows marked *a* in Table II.

The most probable reaction that would use up hydrogen is the hydrogenation of sucrose or of the products of its inversion catalyzed by the platinum black of the electrode. A disturbance due to this reaction has

fraction inverted; if the change is due to a change in the dielectric constant, the electromotive force should be a linear function. These two assumptions lead to average values which differ by about 1 mv. Probably both factors are operating. The values given in the table are averages for the two assumptions.

not previously been recorded, probably because all the earlier measurements have been made with bubbling electrodes only. I can find no record of a chemical study of this reaction, although the reaction of the sugars with oxygen in the presence of platinum black has long been known.

TABLE III

ELECTROMOTIVE FORCE OF THE CELL Pt, H_2 | HCl (0.1012 *N*), sucrose, AgCl | Ag

Sucrose, g. per liter	*E* meas.	Dev. from mean	*E* calcd.	d_4^2	a_w without acid	Dielectric constant
0.00	0.3516	0.0001_1	0.3518	0.9986	1.0000	78.8
.00	.3518	$.0000_1$	.3518	.9986	1.0000	78.8
98.42	.3466	$.0001_3$	.3473	1.0364	0.9944	76.3
99.71	.3461	$.0002_3$	.3472	1.0369	.9943	76.3
200.66	.3412	$.0000_5$	.3413	1.0752	.9874	74.3
301.13	.3352	$.0000_2$	.3350	1.1131	.9789	72.3
406.88	.3283	$.0000_0$	.3276	1.1526	.9676	70.1
489.86	.3222	$.0000_8$	.3211	1.1846	.9565	68.3
605.67	.3129	$.0001_0$	.3110	1.2245	.9363	65.7
700.38	.3055	$.0005_5$	.3018	1.2623	.9143	63.4

The results for the cells without liquid junction are given in the second column of Table III, and are shown graphically by the circles in Fig. 2.

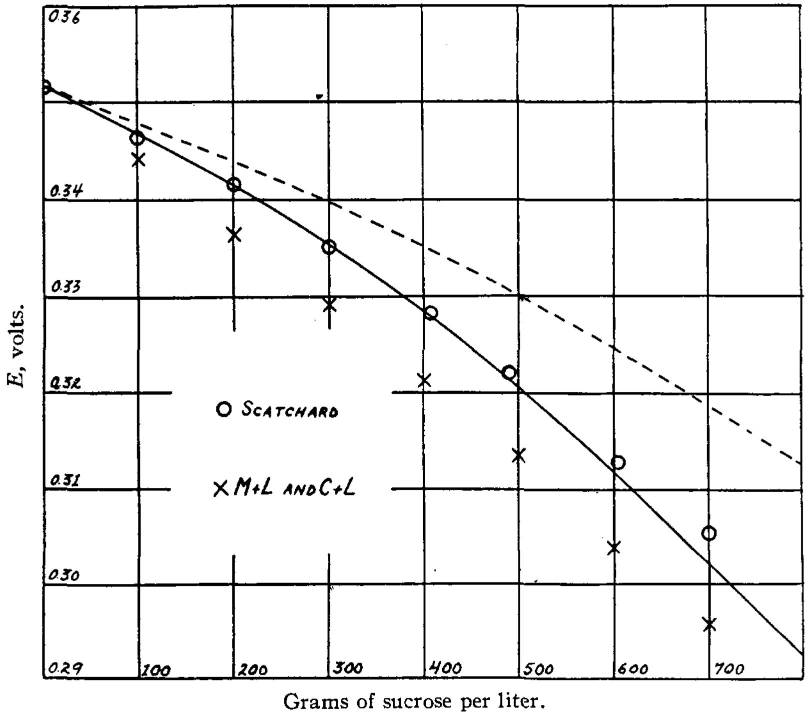

Fig. 2.—Pt, H_2 | HCl (0.1012 *N*), sucrose, AgCl | Ag. Broken line, no hydrate; full line, hydrate.

No attempt was made to correct any but the last for the effect of inversion, but the error from this cause should not be greater than twice the deviation from the mean given in the third column. The sum of the measurements of Corran and Lewis[6] on the cell Ag, AgCl, HCl (0.5 *N*) | KCl (satd.) | HCl (0.1 *N*), sucrose, AgCl | Ag and those of Moran and Lewis[9] on the cell Pt, H_2 | HCl (0.1 *N*), sucrose | KCl (satd.) | KCl (1.0 *N*), HgCl | Hg should give the same change on the addition of sucrose as the cell without liquid junction if their liquid junctions are reproducible. Their results, with a constant added to give agreement for the solution without sucrose, are represented by the crosses in Fig. 2. The discrepancy is several millivolts.

Theoretical Interpretation

The electromotive force of the cell Pt, H_2 | HCl, AgCl | Ag in any solvent mixture whose average molecular weight, dielectric constant and vapor pressure of water are known may be calculated from the Debye theory of electrolytic solutions. The methods of calculation and the necessary assumptions are given elsewhere.[11] The water activity was determined by interpolating for concentration the values already interpolated for temperature[12] from the measurements of Berkeley, Hartley and Burton.[13] The dielectric constants were determined by interpolation from a smooth curve drawn through the values of Debye and Sack,[14] assuming that for each solution the ratio of the dielectric constant to that of water is the same at 25° as at 18°. These results agree excellently with those of Harrington[15] on dilute solutions if the latter are multiplied by 1.027 to make his dielectric constant of water agree with that of other observers. The measurements of Drude[16] at higher concentrations do not agree so well, and those of Fürth[17] are very different throughout the whole concentration range.[18] The density, water activity in the solution without acid and the dielectric constant for each solution are given in Table III.

If the mole fraction of the ions be calculated on the assumption that the sucrose and water do not react chemically, the agreement between the theory and measurements is poor. The curve for this case is shown by the broken line in Fig. 2. It has been shown,[19] however, that the vapor

[11] Scatchard, This Journal, **47**, 2098 (1925).

[12] Scatchard, *ibid.*, **45**, 1580 (1923).

[13] Berkeley, Hartley and Burton, *Phil. Trans.*, **218A**, 295 (1919).

[14] Private communication.

[15] Harrington, *Phys. Rev.*, **8**, 581 (1916).

[16] Drude, *Z. physik. Chem.*, **23**, 267 (1897).

[17] Fürth, *Ann. Physik*, **70**, 63 (1923); *Physik. Z.*, **25**, 676 (1924).

[18] Recent measurements of Kackel [*Ann. Physik*, **77**, 417 (1925)] are generally somewhat lower, with a maximum difference of 1% from the values quoted.

[19] Scatchard, This Journal, **43**, 2406 (1921).

pressure of aqueous sucrose solutions may be simply and accurately explained by assuming that there is hydrate formation and that the vapor pressure of water is proportional to the mole fraction of the uncombined water. With these assumptions the number of moles of water per liter is equal to the number of moles of sucrose multiplied by the activity of the water and divided by one minus this activity. The values calculated with this assumption are represented by the full curve of Fig. 2 and are given in Col. 4 of Table III. The agreement between measurement and theory is very much better. The deviations in concentrated solutions increase regularly and are in the direction to be expected from the fact that the theory neglects the effect of the acid on the equilibrium between sucrose and water.

The theory includes four reasons why the electromotive force should change with a change in the concentration of sucrose: the change in mole fraction due to the change in the total number of moles per liter; the change in the free-energy increase of the reaction $H_3O^+ = H^+ + H_2O$ due to the change in the activity of the water; the effect of the change in dielectric constant on the activity at infinite dilution; and the effect of the change in dielectric constant on the activity coefficient. Table IV shows the magnitude of each of these effects for the most concentrated solution, and shows also the effect of the two assumptions regarding the total number of moles.

TABLE IV

FACTORS IN EFFECT OF SUCROSE ON ELECTROMOTIVE FORCE (700 G. PER LITER)

	HCl		KCl	
Factor	Hydrate	No hydrate	Hydrate	No hydrate
Mole fraction	−0.0429	−0.0263	−0.0429	−0.0263
Water activity	− .0023	− .0023	.0000	.0000
E_N (inf. dil.)	− .0088	− .0088	− .0327	− .0327
Activity coeff.	+ .0040	+ .0040	+ .0052	+ .0052
Total change	− .0500	− .0334	− .0704	− .0538

The electromotive force of the cell Ag | AgCl, KCl (0.1012 *N*) | K, Hg | KCl (0.1012 *N*), sucrose (*c*), AgCl | Ag was calculated in an exactly similar way, and the effects of the four factors for the most concentrated solution are shown in Table IV. If the addition of sucrose affected the activity of the potassium and chloride ions to an equal extent and did not change the liquid-junction potential, the change in electromotive force of the cell Hg | HgCl, KCl (satd.) | HCl (0.1012 *N*), sucrose (*c*), AgCl | Ag would be half the electromotive force of the above cell. This corresponds to the full curve of Fig. 1. The assumption of equal effect on the potassium and chloride ions demands a change in the liquid-junction potential of more than ten millivolts, which seems improbable. The measurements are fitted much better by assuming that the change in activity of the chloride ion is equal to the change in the mean activity of the ions of hydrochloric acid, represented by the broken line in Fig. 1. These results confirm the conclusions drawn from measurements on alcohol-water mixtures[11] that the effect of changing dielectric constant on activity cannot be the same for the potassium and the chloride ions, but the uncertainty as to the liquid-junction potential prevents more precise conclusions.

Discussion

In spite of the difficulties of measurement it is believed that the measurements on the cell without liquid junction are accurate to a few tenths of a millivolt when the sucrose concentration is not greater than 500 g. per liter, and to a few millivolts for higher concentrations. This corresponds to an accuracy in the measurement of the mean activity of the ions of hydrochloric acid of about 0.5% below 500 g. per liter, and to a few per cent. above. The agreement with the theory is not quite so close, but it is as good as should be expected from the simplifying assumptions which were made.

The measurements with the cell with flowing junction are reproducible to the same precision, but their interpretation in terms of activities are uncertain to several millivolts on account of the lack of knowledge of the effect of sucrose on the liquid junction potential. Moreover, in this case theory gives no definite values with which the measurements might be checked. So the values of single ion activities in solutions containing sucrose are uncertain to many per cent., and it is evident that this uncertainty cannot be reduced without some radical improvement in experimental technique or in theoretical knowledge.

The values previously reported in the literature for the activity of the hydrogen ion in sucrose solutions are even more uncertain because they are probably not free from error due to irreproducible liquid-junction potentials and to the effect of the hydrogenation reaction on the potential at a bubbling hydrogen electrode. The new experimental evidence is thus directly contradictory to the conclusions which I drew elsewhere[12,20] that these values might be accepted as accurate.

This uncertainty as to the activity of the hydrogen ion in solutions containing sucrose makes inconclusive the attempts made by myself,[12,21] and others[9,22] to determine the mechanism of the inversion process by fitting the rates of reaction quantitatively with formulas containing this hydrogen activity. Even the difference between the change of liquid junction potential with flowing and with stationary junction amounts to 11% in the hydrogen activity between 0 and 700 g. of sucrose per liter, while the change in water activity in this range is less than 9%. Obviously the number of moles of water that enter into the reaction cannot be accurately determined.

---

[20] Scatchard, THIS JOURNAL, **45,** 1716 (1923).

[21] Scatchard, *ibid.*, **43,** 2387 (1921).

[22] Jones and Lewis, *J. Chem. Soc.*, **117,** 1120 (1920).

Summary

The electromotive forces of the cell Hg | HgCl, KCl (satd.) | HCl, sucrose, AgCl | Ag with flowing junction and of the cell Pt, H_2 | HCl, sucrose, AgCl | Ag have been measured at 25° with 0.1012 *N* acid and sucrose concentrations ranging from 0 to 700 g. per liter.

The potentials at both hydrogen and silver-chloride electrodes change during the process of inversion. The potential at the hydrogen electrode is also affected by a hydrogenation of sucrose or of the products of its inversion. The liquid-junction potential appears to be considerably changed by the addition of sucrose.

This last phenomenon, and to a smaller extent the second one, introduces a large uncertainty into the measurement of single-ion activities in these solutions, and therefore into the determination of the mechanism of the inversion process.

The values of the second cell are interpreted by theory, and some theoretical implications of the measurements with the first cell are discussed.

CAMBRIDGE, MASSACHUSETTS

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

A STUDY OF THE INFLUENCE OF THE ELECTRODES ON THE FORMATION OF OZONE AT LOW PRESSURES IN THE ELECTRICAL DISCHARGE

BY PHILIP T. NEWSOME[1]

RECEIVED MARCH 13, 1926 PUBLISHED AUGUST 5, 1926

The electrolysis of gases constitutes a field of investigation which is important because it connects ionization with chemical reaction. Lind[2] has pointed out that electrolysis in solution is a special case of electrolysis, and that it is simpler than the electrolysis of gases. In solution, all the chemical reaction occurs at the surface of the electrodes, and there is a simple relation between the number of molecules reacting and the number of electrons passing through the circuit. This relation finds expression in Faraday's law, which is one of the most exact laws in science.

In the case of gases, chemical reaction is brought about partly in the gas space between the electrodes by ions that combine before they can reach the electrodes. Under these conditions the number of electrons, *n*, recorded by the ammeter in the circuit is considerably less than the total number of ions, *N*, involved, and less than the number of molecules, *M*, reacting.

---

[1] This communication is based on a thesis presented in 1926 at the University of Wisconsin for the degree of Doctor of Philosophy. The investigation was carried out under the direction of Farrington Daniels.

[2] Lind, *Trans. Am. Electrochem. Soc.*, **44**, 63 (1923).