

T H E S I S

BY

H. DARWIN KIRSCHMAN

THE VAPOR PRESSURE OF HYDROGEN CHLORIDE

ABOVE ITS AQUEOUS SOLUTION

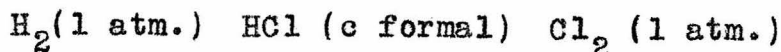
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Introduction

The free energy of formation of hydrogen chloride gas may be calculated most readily by the aid of electromotive force data and of vapor pressure measurements. From the electromotive force of the cell



may be calculated the free energy of HCl in a c formal solution. By adding to this the free energy increase attending the change in state from the pressure at which the hydrogen chloride is in equilibrium with its c formal solution to a pressure of one atmosphere, the free energy of formation of hydrogen chloride gas is obtained.

The necessary electromotive force data have been determined with a considerable degree of accuracy; but, as pointed out by Ellis¹, the existing data for the vapor pressure of hydrogen chloride above its aqueous solutions at 25° are not at all consistent. This investigation was undertaken with the object of securing the necessary vapor pressure data.

Previous Determinations of Vapor Pressure.

A comparison of the values determined by Gahl² and Dolezalek³ for the vapor pressure of hydrogen chloride above its aqueous solutions indicate inaccuracy in the methods of one or both of these investigators.

1. Ellis, J. Am. Chem. Soc. 38, 737. (1916)
2. Zeit. Phy. Chem. 33, 178. (1900)
3. Zeit. Phys. Chem. 26, 334. (1898)

Linhart¹ has calculated from Dolezalek's vapor pressure data at 30° the vapor pressure at 25°. Thus for a concentration of 6.75 mol of HCl per 1000 grams of water he calculates the value of 0.27 mm. At this concentration Gahl gave the vapor pressure as 0.08 mm.

Dolezalek's method was to pass a mixture of hydrogen and oxygen generated by the electrolysis of a potassium hydroxide solution through saturators filled with the hydrochloric acid solution and then through an apparatus for absorbing the hydrogen chloride and the water vapor. The volume of the gas passed was calculated from the difference in weight of the generating apparatus before and after a run. The hydrogen chloride was absorbed in standard potassium hydroxide solution and its amount determined by titrating back with acid. Eight to 10 liters of gas were passed in from 5 to 8 hours. In this way he determined the vapor pressure at 30° of hydrochloric acid gas over hydrochloric acid solutions from 5 to 12 normal.

Although Dolezalek's measurements are of considerable accuracy, the fact that they were made at 30° renders them less valuable for free energy calculations, since but few physical chemical measurements have been made at this temperature and since the necessary electromotive force data for calculating the free energy of formation of hydrogen chloride in solution at this temperature are not available.

1. J. Am. Chem. Soc 39 2601 (1917)

Gahl investigated the vapor pressure at 25° of hydrogen chloride in equilibrium with its solutions from 1 to 6 normal. He passed a mixture of hydrogen and oxygen generated by the electrolytic decomposition of a potassium hydroxide solution through saturators filled with the hydrochloric acid solutions and then through a conductivity cell containing 1 cc. of water. The volume of gas passed was calculated from the quantity of electricity used in decomposing the potassium hydroxide solution. The gas was bubbled through saturators consisting of spiral tubes about 1 cm. in diameter. The amount of hydrogen chloride taken up by the water in the cell was determined by measuring the conductivity of the resulting solution. It is difficult to point out specific defects in the method employed because Gahl neglects to give such details as the volume of gas passed through the apparatus, the rate of flow of gas, the size of saturators employed, their efficiency, or the constancy of values obtained. As already pointed out, Ellis found that Gahl's vapor pressure measurements did not agree with the electromotive force data. A large error is doubtless due to the type of cell used to absorb the the hydrogen chloride gas. Condensation of evaporation of even a small amount of water would appreciably change the concentration of the solution in it; it is, moreover, doubtful whether the water completely absorbed the hydrogen chloride gas.

Outling of Method Employed.

The method employed in this investigation was to bring a volume of air into equilibrium with a hydrochloric acid solution, determine the hydrogen chloride contained in this air, and compare this with the amount of water vapor which the same air contained when in equilibrium with pure water at the same temperature. From a knowledge of the vapor pressure of water at this temperature the vapor pressure of hydrochloric acid gas can then be computed. This method avoids the rather difficult determination of the volume of air passed through the apparatus.

The air under a slight pressure was first passed thru a pressure regulator, then washed by bubbling thru a preliminary saturating apparatus which consisted of three tubes containing glass beads and partially filled with a solution of hydrochloric acid of the same concentration as that used in the saturator. From these tubes the air was led into the saturator. This was of the type designed by Berkley and Hartley¹ with the modifications made by Washburn and Gordon². The chief advantage of this type of saturator is that the air does not bubble through the solution, but passes over it and past the walls of the vessel which are being continually wet with the solution. In this way more complete saturation is obtained than by the air bubbling method and danger of spray being carried over into the absorber is eliminated.

1. Proc. Roy. Soc. London. 77, 156, (1906)

2. H.B.Gordon, Univ. of Ill. Thesis, 1912

The total length of path over which the air traveled in passing thru the saturating apparatus was about 140 cm. Each of the first five limbs of the saturator was about one third filled by placing in it 30 cc. of the acid; the last limb contained but 10 cc.

The hydrogen chloride was absorbed by passing the air from the saturator over tenth normal sodium hydroxide in an absorber similar in construction to the saturator, but of smaller size, and having but two limbs. This absorber contained 10 cc. of the alkaline solution in each limb.

After the absorption of the hydrogen chloride, the air already almost saturated with water vapor, was completely saturated by passing it thru a saturator of the same type and size as that used for the hydrogen chloride gas saturation. The water was then absorbed from this air by four U tubes, the first containing calcium chloride and the rest broken pumice moistened with string sulphuric acid. The amount of water absorbed was found from the gain in weight of the U tubes.

The saturators and hydrogen chloride absorber were placed in a thermostat, and mounted on a rocking device which oscillated about 30 times a minute. The U tubes were outside the thermostat. To avoid condensation of water the tube connecting the last saturator to the U tubes was kept warmer than 25° by passing a small current thru a wire wound around it.

A roughly calibrated gas meter was placed at the end of the last U tube to indicate approximately the rate of flow of air through the apparatus.

Description of a Determination

From 70 to 100 liters of air per determination were passed thru the system at a rate of 8 to 10 liters per hour. At the end of a run the water absorbers were immediately removed and weighed. The solution in the absorber for hydrogen chloride gas was poured into a beaker and the absorber rinsed out with five 10 cc. portions of water. The chlorine content was determined by the Volhard method modified as follows by Rosanoff and Hill¹. An excess of 0.05 normal silver nitrate solution was added. The precipitate of silver chloride was coagulated by heating and filtered into a weighed Gooch crucible. The filtrate was allowed to cool and the excess silver nitrate was titrated against thiocyanate solution. In this way were obtained two determinations of the chlorine content of the solution in the absorber. The normality of the acid in the saturator was determined by titration against a weighed amount of sodium carbonate before and after each run. In the latter case samples were taken from both the first and the last limbs of the saturator.

Reagents Used.

The hydrochloric acid used was prepared by the distillation. J. Am. Chem. Soc. 29, 269 (1907)

tion of C. P. 6 normal acid, the first and last portions of the distillate being rejected. This constant boiling distillate which was approximately 6 normal was diluted with conductivity water to the desired concentration. For concentrations above 6 normal C.P. concentrated acid was diluted. The silver nitrate solution was prepared from the pure salt by weight. The ammonium thiocyanate solution was prepared from Kahlbaum's salt and standardized against the silver nitrate solution by the Volhard method. The sodium carbonate used was Kahlbaum's "Zur Analyse". The dilute alkali solution and the ferric alum indicator were made up from Baker's C.P. analyzed chemicals. Conductivity water was used for all solutions and washings. All reagents were tested for chlorides and found to be free from them.

Preliminary Experiments

Preliminary experiments were made to determine the efficiency of the saturator and of the absorber. The efficiency of the absorber was shown by the fact that when 60 liters of air were passed thru the apparatus at a rate twice as great as that actually used in the final experiments, no determinable amount of chlorine was found in a second absorber. The water in the second saturator was tested twice during the course of the final determinations and in each case was found to yield less than 0.1

milligram of silver chloride, thus further indicating the efficiency of the absorber. To test the degree of saturation of the air with hydrogen chloride three runs were made. In each run about 100 liters of air were passed thru the system at rates of five, ten, and twenty liters per hour. The vapor pressure thus found agreed with one another to within 2 per cent. To further test the saturation the preliminary saturating device was removed and a test run made. The value obtained was within 1 per cent of that previously found. The experiments of Gordon and Heuse¹ show that the method of saturating the air with water vapor is efficient and reliable. They passed air through similar saturators at a much faster rate than that used in this investigation and obtained equilibrium conditions². The last U tube in the water absorbing device usually increased in weight about 3 milligrams as compared with a total weight of water absorbed of one and a half grams, which shows that they were sufficiently efficient.

1. J. Am. Chem. Soc. 37, 309 (1915)

2. This in one experiment air was passed at a rate of 27 liters per hour. The difference between the vapor pressure of water as given by 2 such saturators in series was .02 per cent. Heuse, loc. cit. P. 14

To determine the pressure difference between parts of the system, differential manometers were used. One was placed between the first saturator and the first absorber; and one between the water saturator and the U tubes which absorbed the water. It was found that these pressure differences were less than one tenth of a millimeter of mercury. There was thus no appreciable change in total pressure as the air passed from one part of the apparatus to another. In the final experiments the manometers were not used.

Results.

The experimental data and the calculated results are given in Table 1.

Table 1.

c	M	$E_1 \times 10^3$	$E_1 \times 10^3$	W	P	D
4.008	4.369	0.132	0.127	2.329	0.0240	+10.0
4.646	5.137	0.168	0.161	1.413	0.0498	-10.6
5.103	5.703	0.361	0.367	1.459	0.1079	+ 3.8
5.458	6.150	0.534	0.549	1.490	0.1574	- 3.0
5.458	6.150	0.698	0.697	1.773	0.1702	+ 4.9
5.588	6.313	0.600	0.586	1.432	0.1793	- 5.5
5.588	6.313	0.661	0.665	1.577	0.1819	- 4.1
5.866	6.669	-----	1.259	2.084	0.2617	- 1.5
6.656	7.714	2.282	2.268	1.440	0.6855	+ 1.0
7.921	9.468	7.267	7.267	1.120	2.8169	<u>0.0</u>

4.5 = Mean

In this table c is the concentration in mols per litre of the acid employed, M is the same concentration expressed as mols per 1000 grams of water, E_1 and E_2 are equivalents of chloride found in the absorber by the gravimetric and volumetric methods respectively, W is the weight in grams of the water absorbed by the U tubes, P is the pressure in millimeters of hydrogen chloride above its solutions, and D is the percentage deviation from the smooth curve obtained by plotting values of $\log p$ against corresponding values of c (Fig. 1)

By the aid of the curve in Fig. 1 values of the vapor pressure were interpolated to round concentrations. The results expressed both as mols per 1000 grams of water and as mols per litre of solution are given in Table 11.

Table 11.

Concentration mols per 1000 g.	Pressure mm.	Concentration mols per litre	Pressure mm.
4.0	0.0138	4.0	0.0213
5.0	0.0471	5.0	0.0832
6.0	0.139	6.0	0.316
7.0	0.378	7.0	1.00
8.0	0.861	8.0	3.07
9.0	1.93	---	-----
10.0	4.29	---	-----

The vapor pressures here given are two or three times as great as those determined by Gahl¹ at the same temperature but agree well with the values which Linhart² calculated for 25° from Dolezalek's¹ experimental results at 30°.

Treatment of Results

In order to calculate the vapor pressure of hydrogen chloride from the above experimental results, it is necessary to assume that this gas obeys the perfect gas law at the pressures (less than 0.03 atm.) involved; the deviation is certainly less than 0.1 per cent³. The calculations are simplified if it is assumed that the water vapor at 25° and in equilibrium with pure water at this temperature also obeys the perfect gas law. Dynamic¹⁻ and Static²⁻ methods of determining its vapor pressure give results which agree with each other to within 0.2 percent and hence the deviation from the gas law is not greater than this amount.

1. Loc. cit. P. 1

2. Loc. cit. P. 2

3. At 0° and 0.1 atm. pressure the deviation of hydrogen chloride is 0.08%

1- Lincoln and Klein J. Phys. Chem. 11, 318 (1907)

Krauskopf, J. Phys. Chem. 14, 489 (1910)

2- Scheel and Heuse, Ann-d- Phys. (4) 31, 715 (1910)

The pressure of hydrogen chloride p_1 above its solution is given by the expression

$$p_1 v_1 = N_1 RT \quad (1)$$

Here N_1 is the number of mols of hydrogen chloride contained in the volume of air v_1 in equilibrium with the solution; in these experiments v_1 is the volume of air as it passes thru the hydrogen chloride saturator. Similarly for water vapor.

$$p_2 v_2 = N_2 RT \quad (2)$$

Here v_2 is the volume of air passing thru the saturator for water vapor. The volumes v_1 and v_2 are not quite the same, for tho the total pressure in the two saturators is substantially the same (as shown by the differential manometers), the partial pressure of the air is $p_a - p_s - p_1$ as it leaves the hydrogen chloride saturator and $p_a - p_2$ as it leaves the water saturator; here p_a and p_s are the barometric pressure and the vapor pressure of water above the acid solution respectively.

The volumes v_1 and v_2 are, however, in inverse ratio to these pressures; that is:

$$\frac{v_1}{v_2} = \frac{p_a - p_s}{p_a p_s - p_1} \quad (3)$$

From equations (1), (2), and (3) the following expression for p_1 may be derived:

$$p_1 = \frac{p_a - p_s - p_1}{p_a - p_s} \frac{N_1}{N_2} \quad p_2$$

In using this expression p_s , the pressure of water above the acid solutions, was interpolated from the values calculated by Linhart¹; for p_2 the value 23.76 mm. was employed. N_1 and N_2 are the mols of chloride and of water respectively found in the absorbers.

COMPARISON WITH Electromotive Force Data.

The results obtained above may be compared with the electromotive force measurements of Ellis and of Linhart in the following manner. The free energy decrease attending the transfer of HCl from a solution of concentration c molal to one 0.1 molal² is given by the expression

$$-\Delta F = E N F \quad (4)$$

where E is the electromotive force of a cell in which the above change in state takes place. The same free energy decrease may be calculated by means of the equation

$$-\Delta F = RT \log_e \frac{p}{p_{0.1}} \quad (5)$$

where p and $p_{0.1}$ are the vapor pressures of hydrogen chloride above its c molal and 0.1 molal solutions respectively.

1. Loc. cit. p. 2

2. Any other concentration within the range over which the electromotive force data has been accurately determined could be employed in place of 0.1 molal but this concentration offers particular advantages for the calculation of the free energy of formation of hydrogen chloride. (See following section.)

From equations (4) and (5) the relation

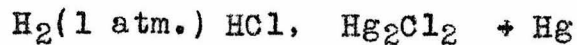
$$ENF = RT \log_e \frac{p}{p_{0.1}}$$

follows, hence

$$\log_{10} p = \log_{10} p_{0.1} + \frac{ENF}{2.303RT} \quad (6)$$

Therefore if $\log_{10} p$ is plotted against E a straight line having the slope $\frac{NF}{2.303 RT}$ should be obtained

The desired value E may be readily calculated from the results of Ellis and of Linhart. Both of these investigators determined the electromotive force at 25° of cells of the type

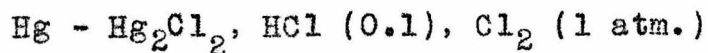


over a considerable concentration range. Evidently by subtracting from the electromotive force of the cell in which the concentration is c formal from that of the similar cell in which the concentration is 0.1 formal, the value E which is to be substituted in equation (6) is obtained. The values of E were thus calculated and plotted against concentrations expressed as mols per 1000 grams of water. (Fig. 2) The results of Ellis and of Linhart agree excellently with each other. From this graph values of E corresponding to the concentrations at which the vapor pressures were experimentally determined were read off and plotted against values of $\log_{10} p$ (Fig. 3) The straight line shown in the figure has the slope required of equation

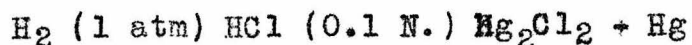
(6) It is evident that the best straight line through the experimental points would have almost but not quite the same slope; the difference between the slopes is about 5 per cent. We were unable to fully account for this diversion which seems larger than can be accounted for by experimental error in either the electromotive force data or the vapor pressure determinations. Of course the hydrochloric acid solutions used for the electromotive force measurements were saturated with calomel, yet the amount which dissolves is so slight¹ that it would not be expected to affect the vapor pressure more than 0.2 percent in 5 N. solutions, and at other concentrations the effect would be smaller.

Free Energy of Formation of Hydrogen Chloride

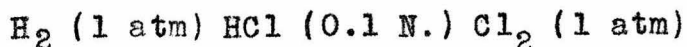
The electromotive force at 25° of the cell



has been determined to be 1.0896 volts² and that of the cell



to be 0.39904 volt³ Hence the electromotive force of the cell



is 1.4886 volts; the probable error of this value is

1. Richards and Archibald Zeit. Phys. Chem 40 391 (1902)
2. Lewis and Rupert. J. Am. Chem Soc 33 299 (1911)
3. Ellis, Ibid. 38, 754. (1916)

about 0.5 millivolt¹. The relation $-\Delta F = ENF$ then gives $-143,650 \pm 50$ joules as the free energy of HCl in 0.1 molal solution. The free energy of formation of hydrogen chloride is obtained by adding to this value the free energy increase which results when the pressure is changed from that which the hydrogen chloride has above its 0.1 molal solution $p_{0.1}$ to a pressure of one atmosphere. This is given by the relation $-\Delta F = RT \log_e \frac{760}{p_{0.1}}$ (7)

The pressure $p_{0.1}$ may be calculated by means of equation (6) from each of the ten experimentally determined values in Table I. The mean of these values thus calculated is 2.22×10^{-6} mm; the average deviation from the mean is 5.9 per cent, hence the probable error is $5.9/\sqrt{10} = 1.9$ per cent. Equation (7) is based upon the assumption that the gas obeys the perfect gas law up to a pressure of one atmosphere. At this pressure the deviation of hydrogen chloride is 0.74 per cent at 0° and it is smaller at 25°. The uncertainty introduced into the value calculated by means of equation (7) by reason of the deviation of the gas from the perfect gas law and the uncertainty in $p_{0.1}$ is thus about one percent. Equation (7) then gives $48,730 \pm 50$ joules as the free energy increase.

The free energy of formation of hydrogen chloride at 25° is hence $-94,920 \pm 75$ joules or $-22,690 \pm 20$ calories

1. See Noyes and Ellis. Ibid 39, 2540, (1917)

Summary.

The vapor pressures at 25° of hydrogen chloride above its aqueous solutions have been determined at concentrations from 4 to 9 normal.

By the aid of electromotive force data the free energy of formation of hydrogen chloride at 25° is found to be -22,690 calories.

Fig. 1.

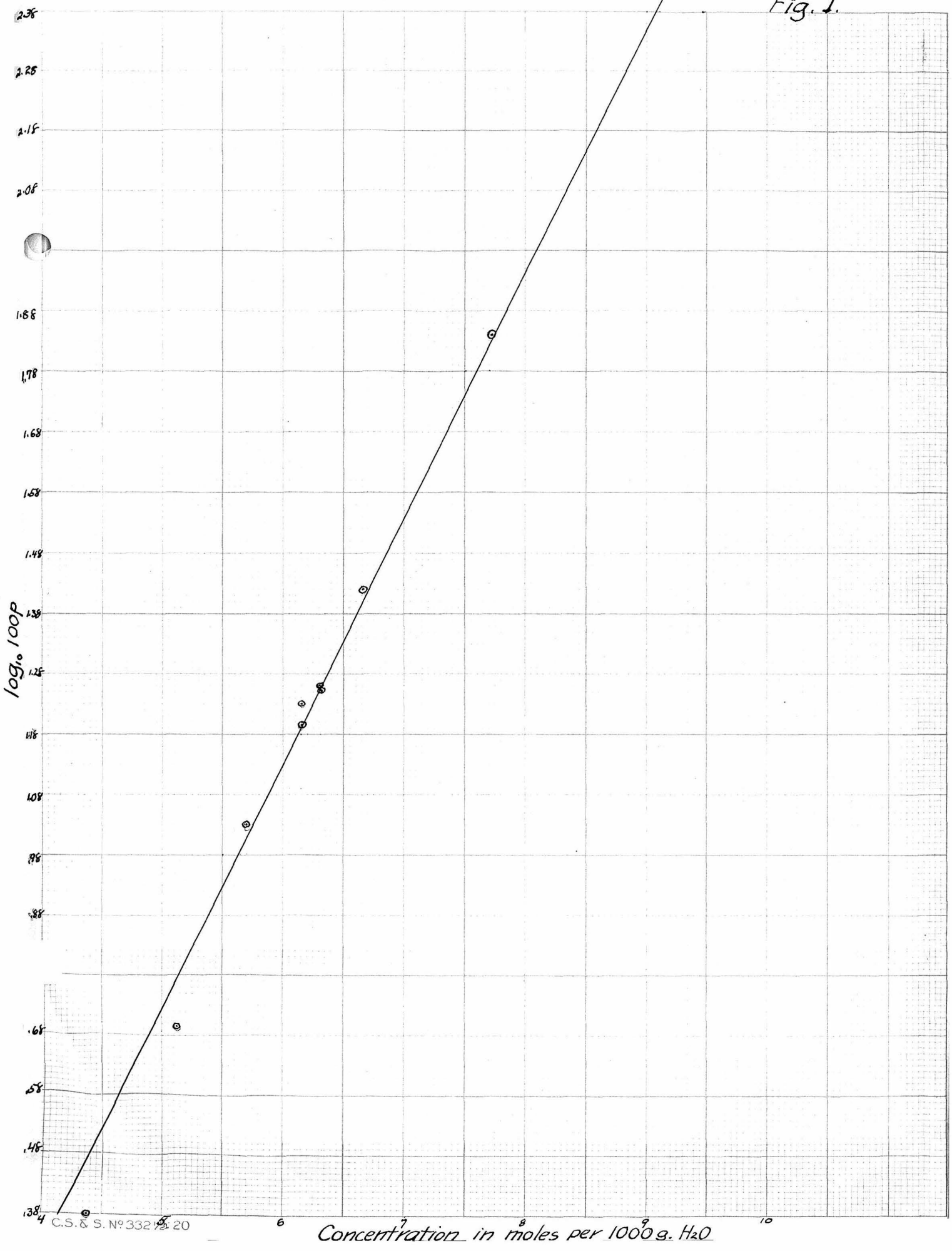
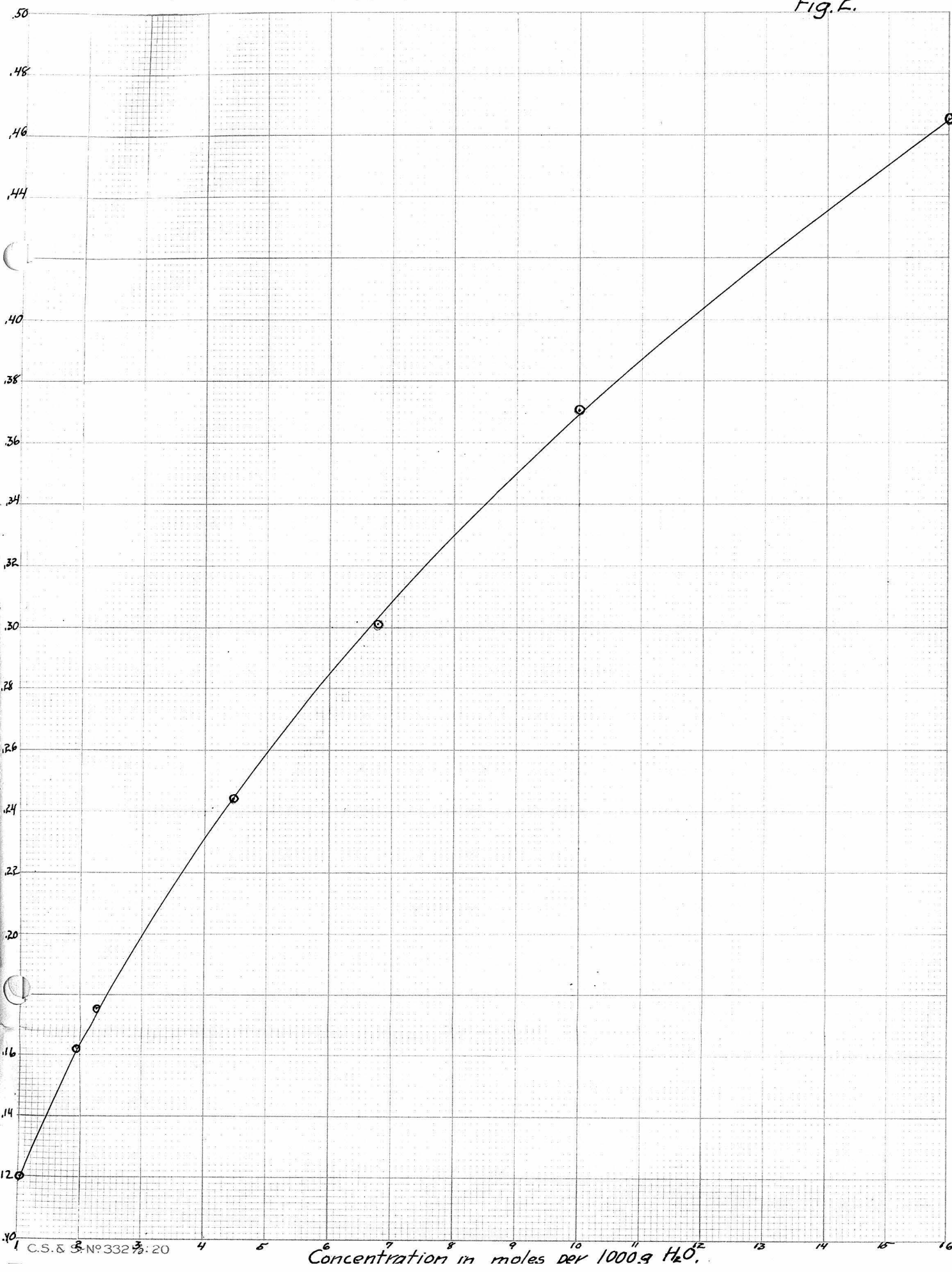


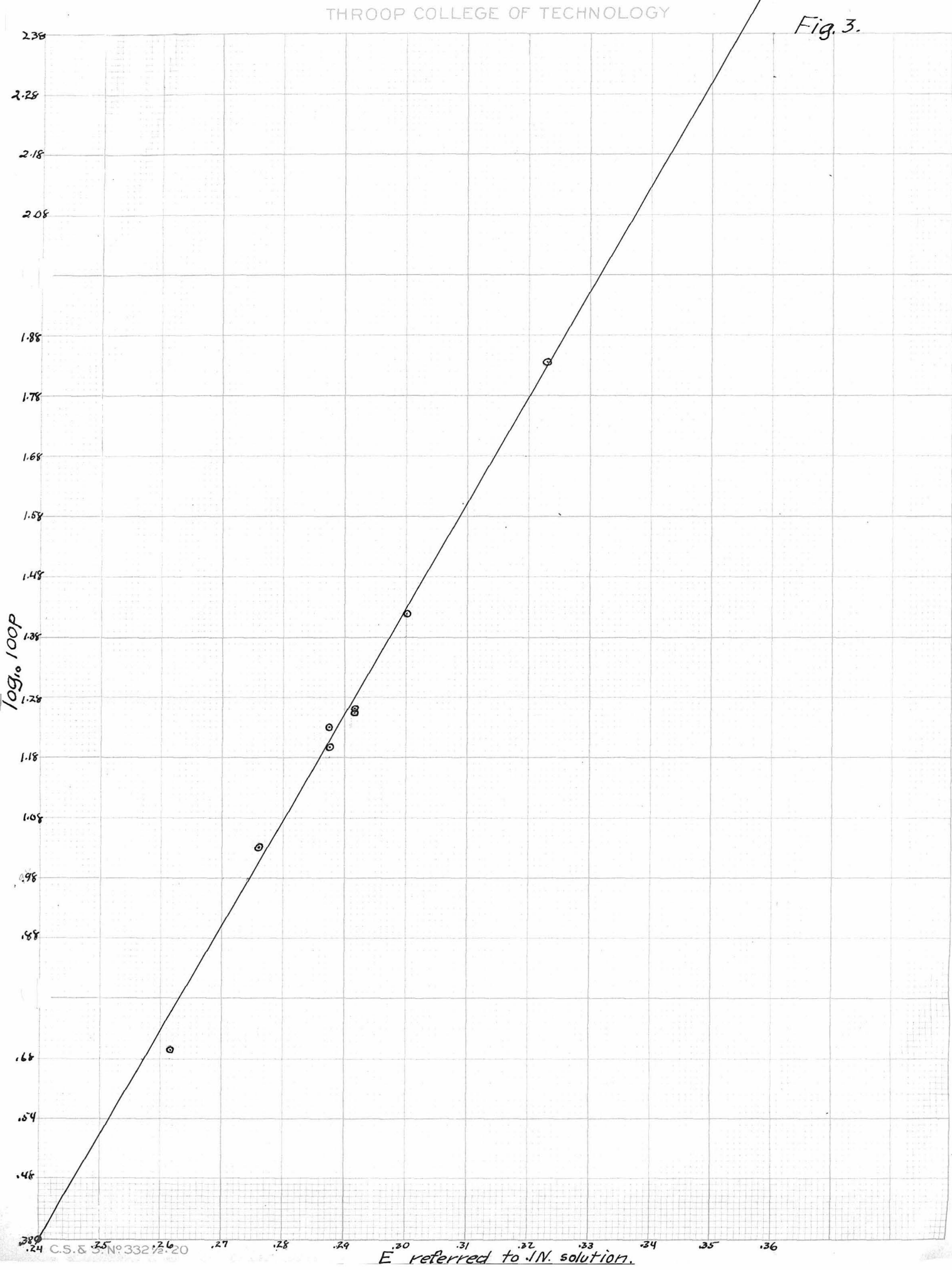
Fig. 2.



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Concentration in moles per 1000 g H₂O.

Fig. 3.



E referred to N . solution.