

T H E S I S

BY

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THE VAPOR PRESSURE OF HYDROGEN CHLORIDE AND
HYDROGEN BROMIDE ABOVE THEIR
AQUEOUS SOLUTIONS AT 25

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INTRODUCTION.

The free energy of formation of the hydrogen halides at ordinary temperatures may be calculated most readily by the aid of electromotive force data and of vapor-pressure measurements. Thus, from the electromotive force of the cell H_2 (1 atm.), HCl (c formal), Cl_2 (1 atm.), may be calculated the free energy of $1HCl$ in a c formal solution. By adding to this the free energy increase attending the compression of $1HCl$ from the pressure at which hydrogen chloride is in equilibrium with its c formal solution to a pressure of one atmosphere, the free energy of formation of hydrogen chloride is obtained.

The necessary electromotive force data, in the case of hydrogen chloride, have been determined with a considerable degree of accuracy; but, as pointed out by Ellis¹, the existing data for the vapor-pressures 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.

A comparison of the values determined by Gahl²

1. Ellis, J. Am. Chem. Soc., 38, 737 (1916).
2. Zeit. Phys. Chem., 33, 178 (1900).

at 25° and by Dolezalek¹ at 30° for the vapor-pressures of hydrogen chloride above its aqueous solutions indicates inaccuracy in the methods of one or of both of these investigators. Thus Linhart² has calculated from Dolezalek's results that at 25° the vapor-pressure of a solution containing 6.75 mols of HCl per 1000 grams of water is 0.27 mm.; and Gahl found the vapor-pressure of a solution of this concentration to be but 0.08 mm.

Dolezalek's method consisted in passing 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. The volume of the gases 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 fifteen liters of gas were passed in from 5 to 8 hours. In this way the vapor-pressure at 30° of hydrochloric acid gas above its aqueous solutions from 5 to 10 normal was determined.

1. Zeit. Phys. Chem., 26, 334, (1898).
2. J. Am. Chem. Soc., 39, 2601 (1917).

Gahl investigated the vapor-pressures 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 solutions through saturators filled with the hydrochloric acid solutions and then through a conductivity cell containing about 1 cc. of water. The volume of gases passed was calculated from the quantity of electricity used in decomposing the potassium hydroxide solution. The gases were 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.

OUTLINE OF METHOD.

The method employed in this investigation was to determine the hydrogen chloride contained in a given quantity of air in equilibrium with a hydrochloric acid solution 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 the temperature of the experiment, the vapor-pressure of hydrogen chloride gas could then be computed. This method avoids the rather difficult determination of the volume of inert gases passed through the apparatus.

The air was first passed through a preliminary saturating apparatus which consisted of a series of three Emmerling 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, which was of the type designed by Berkeley 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 along the walls of the vessel which are being continually wet with the solution. In this way more complete saturation is obtained than in the more commonly employed air-bubbling method, and danger of carrying spray over into the absorber is greatly reduced. Indeed, as was shown in this investigation, it is made entirely negligible. The total length of path over which the air travelled in passing through the saturator 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 hydrochloric acid solution while the last limb contained only 10 cc.

1. Proc. Roy. Soc. London, *XV*, 156 (1906).
2. H. B. Gordon, Univ. of Ill., Thesis. (1912).

The hydrogen chloride was absorbed from the saturated air by then passing the latter over a dilute sodium hydroxide solution contained in a small two-limbed absorber, similar in construction to the saturator. This absorber contained about 10 cc. of the alkaline solution in each limb. The concentration of the sodium hydroxide solution varied from 0.1 to 0.5 normal - depending upon the amount of hydrogen chloride which was to be absorbed.

After the absorption of the hydrogen chloride, the air, already almost saturated with water vapor, was completely saturated by passing it through a saturator of the same type and size as that used for the hydrogen chloride gas saturation. The amount of water contained in this air was determined by absorbing it in a series of four U tubes, the first contained calcium chloride, the others broken pumice stone moistened with concentrated sulphuric acid.

The saturators and the hydrogen chloride absorber were in a thermostat mounted on a rocking device which oscillated about 30 times a minute. The U tubes for absorbing the water were outside the thermostat. To avoid possible condensation of water vapor, the tube connecting the last saturator with the U tubes was kept at a slightly higher temperature than the thermostat by passing a small electric current through a wire wound around it.

Finally, the air passed through a roughly calibrated gas meter. This served to indicate the approximate rate of flow of air through the system.

From 60 to 125 liters of air were passed in each determination through the system at a rate of 7 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 an Erlenmeyer flask, and the absorber rinsed with four 10 cc. portions of distilled water, which was shown by tests to be ample to remove all chlorides. When more than 0.001 equivalent of chlorine was present in the absorber, it was determined by the standard method of Gooch. Smaller amounts were determined by the method of McLean and Van Slyke¹ modified as follows: the halide was precipitated in the presence of a known amount (about one gram) of free nitric acid with an excess of 0.025 normal silver nitrate solution. After coagulation of the colloidal precipitate had been accomplished by shaking the mixture for a few seconds with two drops of caprylic alcohol², the silver chloride was removed by filtration through a Gooch crucible. The excess silver nitrate contained in the filtrate was titrated with 0.01 normal potassium iodide which has been standardized against the silver

1. J. Amer. Chem. Soc., 37, 1128 (1916).

2. Ber. 24, 3351 (1891).

nitrate solution. Just before titration four cc. of trisodium citrate solution³ were added from a burette for each gram of free nitric acid present. Under these conditions, using starch as an indicator, two drops of the 0.01 normal potassium iodide gave a sharp color change that could be seen in 150 cc. of solution. This corresponds to about 0.02 mg. of chlorine.

The concentration of the hydrochloric acid solution whose vapor-pressure was being determined was found by taking, at the end of a run, a sample from the last two limbs of the saturator and titrating this acid against a weighed amount of sodium carbonate.

REAGENTS USED.

For concentrations below 6 normal the hydrochloric acid used was prepared by the distillation of Baker's C. P. 6 normal acid, the first and last portions of the distillate being rejected. This constant boiling mixture, which was approximately 6 normal, was diluted to the desired concentration with distilled water. For concentrations above 6 normal Eimer and Amend's C. P. 11.2 normal acid was diluted.

The silver nitrate solution, which was prepared from the pure salt, was standardized by precipitating and weighing as silver chloride, employing a Gooch crucible. The potassium iodide solution was prepared

1. McLean and Van Slyke, loc. cit.

from Baker's C. P. salt and standardized against the silver nitrate solution. The sodium carbonate was Baker's C. P. and was thoroughly dried before using. Tests showed that all of the reagents employed were free from chlorides.

PRELIMINARY EXPERIMENTS.

Preliminary experiments were made to determine the effectiveness of the saturator and of the absorber. To test the degree of saturation of the air with the hydrogen chloride, three runs were made. In each of these runs about 100 liters of air were passed through the system at rates of five, ten, and twenty liters per hour respectively. The vapor pressures thus determined agreed with one another to within 2 per cent. To further test the saturation, the preliminary saturating device was temporarily removed and a run made. The value given by this experiment was within 1 per cent of those previously found. The experiments of Gordon and of 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 conditions. Thus in one experiment air was passed at a rate of 27 liters per hour.

1. J. Am. Chem. Soc., 27, 309 (1915).

The difference between the vapor-pressures of water as given by two such saturators in series was 0.02 per cent.

The efficiency of the absorber was demonstrated by the fact that, when 60 liters of air were passed through 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. It was further tested by examining the water contained in the water saturator. If the hydrogen chloride were not completely removed from the air during its passage through the absorber containing the sodium hydroxide solution, it would be largely taken up by the following part of the system, namely, the water saturator. After two or three runs had been made without renewing the water in the saturator, it was tested and found to yield less than 0.1 milligram.

The concentrated sulphuric acid in the last U tube in the water absorbing device was frequently removed. This U tube usually increased in weight about 4 milligrams as compared with a total weight of water absorbed of approximately one and a half grams. The amount of water which escaped absorption was certainly less than 0.1 per cent. Differential manometers

placed between various parts of the system showed that any pressure differences in the system were less than 0.1 mm. of mercury. In the final experiments the manometers were not used.

METHOD OF COMPUTING THE VAPOR PRESSURES.

In computing the results from the experimental data it is assumed that the water-vapor and the hydrogen chloride gas at the low pressures involved obey the perfect-gas law. The error introduced by these assumptions is certainly much less than the errors of the experimental method.

The vapor-pressure p_1 of hydrogen chloride in its solution, which is equal to the partial pressure of hydrogen chloride in the air in equilibrium with it, is given by the familiar expression:

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

Here N_1 is the number of moles of hydrogen chloride contained at the temperature T in the volume of air v_1 which passes through the hydrogen chloride saturator. For the water-vapor we have the similar expression:

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

Here v_2 is the volume of air as it passes through the saturator for water-vapor. The volumes v_1 and v_2 are not exactly the same; for, though 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, p_a being the barometric pressure and p_s the vapor-pressure of water above the acid solution. Since the quantity of the air is the same in the two cases, its pressure-volume product must be the same; that is:

$$(p_a - p_s - p_1) v_1 = (p_a - p_2) v_2 \quad (3)$$

By combining equations (1), (2), and (3), the following expression for p_1 results:

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

At 25° the vapor-pressure of water vapor above the acid solution, p_s was interpolated from the values given by Linhart¹; for p_2 the value 23.76 mm. was employed, N_1 and N_2 are the moles of hydrogen chloride and of water respectively found in the absorbers. In calculating the vapor-pressure at 30°, it was assumed that the small correction factor $p_a - p_s - p_1$ had the same value, at the same concentration as at 25°. For p_2 at 30° the value 31.85 mm. was employed.

1. J. Am. Chem. Soc., 39, 2607 (1917).

EXPERIMENTAL DATA AND COMPUTED VAPOR-PRESSURES FOR
HYDROCHLORIC ACID.

The experimental data and the calculated vapor-pressures are given in Table 1. In this table c is the concentration in moles per liter of the acid solution. M is the concentration expressed in moles per 1000 grams of water¹, E is the equivalents of chlorine found in the absorber, W is the weight in grams of the water absorbed by the U tubes, p is the pressure in millimeters of mercury of hydrogen chloride above its solutions and under D mm. and $D\%$ are given the deviations, in millimeters and in percentages, of the individual values from the smooth curve obtained by plotting the experimental values of $\log_{10} p$ against those of c . (Fig. 1)

1. In order to convert concentrations in moles per litre of solution into moles per 1000 grams of water a graph was employed. The values of M were calculated from the density data in Landolt-Börnstein Tabellen, 1912, p 262, after correcting to 25°, and were plotted against corresponding values of c . A few experimental determinations made in the course of this investigation, as well as those given by Ellis and Linhart, check very closely the values obtained by these calculations.

Table 1.

t	c	M	E x 10 ³	W	P	D mm.	D%
25°	3.021	3.240	0.0521	2.8697	0.0078	0.000	0.0
	3.656	3.952	0.0982	2.4536	0.0172	0.000	-1.2
	4.570	5.041	0.3118	2.4159	0.0557	0.000	-0.5
	4.834	5.364	0.3259	1.7809	0.0791	0.002	+2.5
	5.359	6.018	0.7085	2.0632	0.149	0.006	+4.1
	5.559	6.270	0.7552	1.8951	0.173	0.006	-3.6
	5.706	6.457	0.9836	2.0729	0.206	0.006	-2.9
	6.238	7.148	1.0692	1.2060	0.385	0.012	-3.0
	6.980	8.157	3.6856	1.6026	0.999	0.052	+5.3
	7.546	8.950	4.9205	1.1756	1.819	0.004	+0.2
	8.270	9.990	19.483	1.9856	4.26	0.051	+1.2
	#8.248	9.960	9.6428	1.0436	4.01	0.096	-2.4
	#8.256	9.971	9.1160	0.9612	4.12	0.033	-0.8
						Mean = 2.1%	
30°	4.990	5.569	0.4137	1.6198	0.148		
	6.364	7.329	1.0953	0.8957	0.712		
	7.364	8.726	6.7685	1.5098	2.61		
	7.764	9.286	6.7888	1.1395	3.47		

Solutions saturated with calomel.

By the aid of the curve in Fig. 1 values of the vapor-pressures were interpolated to round concentrations. The results for 25° and 30° corresponding to both mols per 1000 grams of water and to mols per liter of solution are given in table 2.

Table 2.

t	M	p	c	p	t	M	p	c
25°	4.0	0.0186	4.0	0.0276	30°	5.0	-----	5.0 0.148
	5.0	0.0537	5.0	0.0938		6.0	0.220	6.0 0.470
	6.0	0.140	6.0	0.297		7.0	0.541	7.0 1.472
	7.0	0.345	7.0	0.973		8.0	1.254	8.0 4.75
	8.0	0.830	8.0	3.08		9.0	2.89	
	9.0	1.89						
	10.0	4.26						

The vapor-pressures at 25° given in Table 2 are two or three times as great as those interpolated at corresponding concentrations from Gahl's data. It is impossible to point out specific causes of error in Gahl's method because he apparently did not test the efficiency of his saturators and because he gives no data showing the concordance of his results, nor details such as the rate of flow of gases through his apparatus, the volume of gases passed, etc. As already stated, Ellis pointed out that Gahl's results were not consistent with the electromotive force data.

In order to test the accuracy of the values found by Dolezalek, the four determinations at 30° were made. The results obtained are more consistent with each other than are Dolezalek's, and on the average differ from the values interpolated from the data of that investigator by about 40%; in fact, at certain concentrations the values given by Dolezalek for 30° are approximately equal to those interpolated for 25°, from the results of this investigation. The vapor-pressures at 30° were compared with those at 25° by the aid of the van't Hoff equation. The average differences between the four experimental values obtained at 30° and the corresponding results calculated from the experiments at 25°, is 8%. This is not large considering the character of the data, particularly the uncertainty of the thermochemical values involved.

EXPERIMENTAL DATA AND COMPUTED VAPOR-PRESSURES FOR HYDROBROMIC ACID.

The vapor-pressures of hydrogen bromide above its aqueous solutions at 25° were determined between the concentrations 5.8 to 11.0 mols per 1000 grams of water. The experimental data and calculated results are given in table 3. In calculating the results it was assumed, because of lack of available data, that the vapor-pressures of water above the hydrobromic acid solutions are the

same as those above the hydrochloric acid solutions of the same concentrations. The error thus introduced is very small since these values appear in the correction factor.

Table 3.

5.076	5.851	0.0130	3.695	0.00153	0.0	0.0
5.482	6.394	0.0165	2.250	0.0032	---	(32.5)
6.374	7.632	0.0333	2.497	0.00577	0.001	-15.4
6.845	8.315	0.0617	2.338	0.0115	0.001	-6.5
6.850	8.325	0.0866	2.811	0.0134	0.001	-7.2
7.393	9.143	0.118	2.217	0.0232	0.002	-9.4
7.730	9.655	0.249	2.337	0.0466	0.007	-13.9
8.221	10.440	0.460	2.261	0.0888	0.001	-1.5
8.546	10.950	0.705	2.155	0.143	0.000	-0.0
					Mean	$\frac{-0.0}{6.7\%}$

The deviations were obtained from the curve obtained by plotting values of $\log_{10} p$ against values of c . (fig. 1.). Although the mean percentage error is much greater in the case of hydrogen bromide, it will be noted that the deviations expressed as mm. of mercury are smaller. The vapor-pressures of hydrogen bromide are about eighty times smaller than those of hydrogen chloride at corresponding concentrations; this is of course related to the fact that the constant boiling mixture of hydrobromic acid boils at 126° , while that

of the hydrochloric acid boils at 110°.

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 liter of solution and as mols per 1000 grams of water are given in table 4.

Table 4.

M.	p	c	p
6.0	0.00174	5.0	0.00243
7.0	0.00396	6.0	0.00435
8.0	0.00947	7.0	0.0146
9.0	0.0226	8.0	0.0622
10.0	0.0573		
11.0	0.151		

COMPARISON WITH ELECTROMOTIVE FORCE DATA.

The vapor-pressure data for hydrogen chloride may be compared with the electromotive force measurements of Ellis and of Linhart in the following manner.¹ The free-energy decrease attending the transfer of HCl from a solution c molal to a solution 0.1 molal² is given by the expression:

1. There is no corresponding electromotive force data for hydrobromic acid concentration cells.
2. The results could be referred to a solution of any other concentration within the range of the E.M.F. data; the concentration 0.1 molal offers particular advantages for the free energy calculations.

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

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 expressed also by means of the equation:

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

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

From equations (4) and (5) the relation

$$E N F = R T \log_e \frac{p}{p_{0.1}}$$

follows. Hence

$$\log_{10} p = \log_{10} p_{0.1} + \frac{E N F}{2.303 R T} \quad (6)$$

Therefore the graph obtained by plotting values of $\log_{10} p$ against corresponding values of E, should be a straight line having the slope $N F / 2.303 R T$.

The desired values of 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. By subtracting the electromotive force of the cell in which the concentration is a formal, from that of the

similar cell in which the concentration is 0.1 formal, the quantity E which is to be substituted in equation (6) is obtained. These values were calculated and plotted against concentrations expressed as mols per 1000 grams of water. The results of Ellis and of Linhart are in good agreement 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. 2.)

At concentrations below about 7.15 molal the points were found to lie on a straight line having the slope required by equation (6). Above this concentration they continue to lie on a smooth curve but not upon the required straight line. This deviation can be accounted for only by assuming an error in either the electromotive force or the vapor-pressure data.¹

1. In the electromotive force determinations the hydrochloric acid solutions which were in contact with the calomel electrodes were saturated with calomel. Experiments showed that the effect of dissolved calomel upon the vapor-pressure of a 10.0 molal hydrochloric acid was negligible. See table 1.

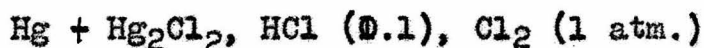
Since five concordant determinations of vapor-pressure were made between 7.15 and 10.0 molal, while but one electromotive force result is available within this range, it seems more probable that the later is incorrect. An error of 3 millivolts in the electromotive force data at 10.0 molal, or of 1 percent in the concentration of the acid employed would account for this deviation; an error of 10 percent in the vapor pressure measurements would also account for it, but at 10.0 molal three determinations were made and the mean of the corresponding values has a probable error of but 0.8 percent.

Because of this uncertainty in the data for the solutions more concentrated than 7.15 molal, only those results obtained within the range in which the electromotive force and vapor-pressure data show good agreement were employed to calculate $p_{0.1}$, the vapor-pressure of hydrogen chloride above its 0.1 molal solution; this value is employed in the free energy calculations which follow. From the experimental result at each of the 8 concentrations below 7.15 molal, the vapor-pressure of 0.1 molal HCl was calculated by means of equation (6). The mean of these values is 2.23×10^{-6} mm., the average deviation from the mean is 3.4 percent and the probable error 1.2 percent.

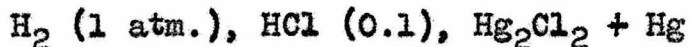
Since careful electromotive force data are available down to concentrations as low as 0.01 molal, the vapor-pressures of hydrogen chloride above its solutions of any concentration between 0.01 and 10.0 molal may be determined within a few percent by the aid of equation (6) or by interpolation from the direct vapor-pressure measurements.

FREE ENERGY OF FORMATION OF HYDROGEN CHLORIDE.

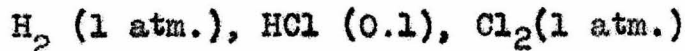
The electromotive force at 25° of the cell



has been determined to be 1.0896 volts¹ and that of the cell



to be 0.39904 volt². Hence the electromotive force of the cell



is 1.4886 volts; the probable error of this value is about 0.5 millivolt³. The relation $-4F = E N F$ then gives $-34,330 \pm 10$ calories as the free energy of one HCl in 0.1 molal solution.

1. Lewis and Rupert J. Amer. Chem. Soc. 33, 299, (1911)
2. Ellis. Ibid. 38, 754, (1916).
3. See Noyes and Ellis. Ibid. 39, 2540, (1917).

The free energy of formation of hydrogen chloride is obtained by adding to the above 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 free energy increase is given by the relation $-\Delta F = R T \log_e \frac{760}{p_{0.1}}$ (7)

This equation is based upon the assumption that the gas obeys the perfect gas law at pressures less than one atmosphere. At this pressure the deviation of hydrogen chloride is 0.74 percent at 0°; it is less at 25°. The uncertainty thus introduced into the result given by equation (7) together with that involved in the value 2.23×10^{-6} which is substituted for $p_{0.1}$ is thus about 0.6 percent. Equation (7) then gives $11,630 \pm 70$ calories as the free energy increase.

The free energy of formation of hydrogen chloride at 25° is hence $-22,700 \pm 70$ calories.

SUMMARY.

1. Determinations of the vapor-pressure of hydrogen chloride above its aqueous solutions at 25° have been made between 3.2 and 10.0 molal. The results have a probable error of 0.6 percent; they are two or three times as great as the previous data of Gahl. Four determinations carried out at 30° are concordant but give results differing greatly from those of Dolezalek.
2. Determinations of the vapor-pressure of hydrogen bromide above its aqueous solutions at 25° have been made between 5.8 molal and 11.0 molal. The results have a probable error of 2.4 percent.
3. The vapor-pressure measurements for hydrochloric acid solutions between 3.2 molal and 7.15 molal are in good agreement with the electromotive force of hydrochloric acid concentration cells. By the aid of such electromotive force data the vapor-pressure of hydrogen chloride above its aqueous solutions at concentrations as low as 0.01 molal may be calculated.
4. The free energy of hydrogen chloride at 25° is -22,700 \pm 70 calories.

Figure 1

