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THE VAPOR PRESSURES AND FREE ENERGIES OF THE HYDROGEN HALIDES IN AQUEOUS SOLUTION; THE FREE ENERGY OF FORMATION OF HYDROGEN CHLORIDE.

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1. Purpose of the Investigation.

The free energy of formation of the hydrogen halides at ordinary temperatures may be calculated 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 molal), Cl_2 (1 atm.), may be calculated the free energy of 1 HCl in c molal solution. By adding to this the free-energy increase attending the compression of 1 HCl from the pressure at which hydrogen chloride is in equilibrium with its c molal 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 Ellis,[2] the existing data for the partial 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.

In addition the vapor pressures at 25° of hydrogen bromide and of hydrogen iodide above their aqueous solutions were determined. The previous data[3] for these acids are very fragmentary; none of it is at 25°. The absence of the necessary electromotive force data makes impossible the computation of the free energies of formation of these halides by the method employed for hydrogen chloride; fortunately it has been possible to calculate these values from other data.

2. Previous Determinations.

A comparison of the values determined by Gahl[4] at 25° and by Dolezalek[5] at 30° for the partial pressures of hydrogen chloride above its

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[2] THIS JOURNAL, **38**, 737 (1916).

[3] Bodenstein and Geiger, *Z. physik. Chem.*, **49**, 70 (1904); Stegmuller, *Z. Elektrochem.*, **16**, 85 (1910).

[4] *Z. physik. Chem.*, **33**, 178 (1900).

[5] *Ibid.*, **26**, 334 (1898).

aqueous solutions indicates inaccuracy in the methods of one or of both of these investigators. Thus from Dolezalek's results Linhart[1] calculated the vapor pressure of a solution containing 6.75 mols of hydrogen chloride per 1000 g. of water to be 0.27 mm. at 25°, while Gahl determined 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, 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 hrs. In this way vapor pressures at 30° of hydrogen chloride above its aqueous solutions from 5 to 10 *N* were determined.

Gahl investigated the vapor pressures at 25° of hydrogen chloride in equilibrium with its solutions from 1 to 6 *N*. He passed a mixture of hydrogen and oxygen generated by the electrolytic decomposition of a potassium hydroxide solution through saturators filled with hydrochloric acid and then through a conductivity cell containing about one 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 one 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.

3. Description of Method and Apparatus.

The method employed in this investigation was to determine the hydrogen halide contained in a given quantity of air[2] in equilibrium with its aqueous 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 the halide may then be computed.

The air was first passed through a preliminary saturating apparatus which consisted of a series of 3 Emmerling tubes containing glass beads and partially filled with a solution of 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 Berkeley and Hartley[3] with

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[1] THIS JOURNAL, 39, 2601 (1917).

[2] Nitrogen was employed in the case of hydrogen iodide.

[3] *Proc. Roy Soc. London*, 77, 156 (1906).

the modifications made by Washburn and his associates.[1] 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 5 limbs of the saturator was about $^1/_3$ filled by placing in it 30 cc. of acid solution while the last limb contained only 10 cc.

The hydrogen halide was then absorbed from the saturated air by passing the latter over a dil. sodium hydroxide solution contained in a small two-limbed absorber. This was similar in construction to the saturator and contained about 10 cc. of the solution in each limb. The solutions employed contained no detectable trace of halides; their concentrations varied from 0.1 to 0.5 *N*, depending upon the amount of halide which was to be absorbed.

After the absorption of the hydrogen halide gas, 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 halide saturation. The amount of water contained in this air was determined by absorbing it in a series of 4 U-tubes, the first of which contained calcium chloride, the others broken pumice stone moistened with conc. sulfuric acid.

The saturators and the halide 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 the air through the system.

On account of the oxidizing action of air upon hydriodic acid, nitrogen was employed as the inert gas in the experiments upon this halide. An apparatus similar to that described by Hulett[2] was employed to reduce to a negligible amount the small percentage of oxygen which the commercial nitrogen contained. Before starting a run the air was swept out of the preliminary saturating apparatus and the connecting tube by means of hydrogen, and a current of this gas was passed through the saturator

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[1] This Journal, **37**, 309 (1915).

[2] *Ibid.*, **27**, 1415 (1905).

while the hydriodic acid was being transferred to it. In spite of these precautions the more concentrated solutions became slightly brown before the run was started. During the run the oxidation did not increase to a noticeable extent. In order to determine the maximum effect of oxidation a modified run on 9.3 molal acid was made. In this run the precautions observed in filling the apparatus were not taken and the small amount of oxygen contained in the nitrogen was not removed. The gases from the saturator were passed over carbon tetrachloride contained in the absorbing device. The iodine taken up by the carbon tetrachloride amounted to less than 2% of the total iodide found in the absorber at the end of a regular experiment in which acid of the same concentration was employed. In the latter run the amount of oxidation, as indicated by the color of the solution in the saturator was very much less; the resulting error was certainly less than 0.5%.

In each of the determinations from 50 to 200 liters of air or nitrogen was passed through the system at rates 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 the hydrogen halide was poured into an Erlenmeyer flask, and the absorber rinsed with four 10 cc. portions of distilled water; this was shown by tests to be ample to remove all halides. When more than about 0.001 equivalent of halide 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 Slyke,[1] 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 *N* 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 alcohol, the silver halide was removed by filtration through a Gooch crucible. The excess silver nitrate contained in the filtrate was titrated with 0.01 *N* potassium iodide which had been standardized against the silver nitrate solution. Just before titration 4 cc. of trisodium citrate solution[2] was added for each gram of free nitric acid present. Under these conditions, using starch as an indicator, 0.05 cc. of 0.01 *N* potassium iodide gave distinct color change in 150 cc. of solution.

The concentrations of the hydrochloric and hydrobromic acid solutions whose vapor pressures were determined were found by titration against sodium carbonate. In the case of the hydriodic acid, the concentrations were determined by diluting a weighed amount of acid and titrating the resulting solution against 0.05 *N* silver nitrate solution, by the

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[1] THIS JOURNAL, 37, 1128 (1915).

[2] McLean and Van Slyke, *Loc. cit.*

method of McLean and Van Slyke. The acid solutions employed were obtained by redistilling Baker's C. P. acids, the first and last portions of the distillates being rejected.

4. 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 halide, three runs were made employing the same solution of hydrochloric acid. In each of these runs about 100 liters of air was passed through the system at rates of 5, 10 and 20 liters per hour, respectively. The vapor pressures thus determined agreed with one another to within 2%. 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% of those previously found. The experiments of Washburn and Heuse[1] 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. The difference between the vapor pressures of water as given by two such saturators in series was 0.02 %.

The efficiency of the absorber was demonstrated by the fact that, when 60 liters of air was passed through the apparatus at a rate twice as great as that 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 halide 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 3 runs had been made without renewing the water in the saturator, it was tested and found to yield less than 0.002 milli-equivalent of halide.

In order to make certain that none of the acid solution was being carried from the saturator to the absorber in the form of spray, a run was made in which the saturator contained 4 molal potassium chloride. Although the air was passed through the system at a rate greater than that employed in the final experiments, no trace of halide was found in the absorber at the end of the run.

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.

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[1] THIS JOURNAL, 37, 309 (1915).

5. Method of Computing the Results.

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

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

$$p_1v_1 = N_1RT. \qquad (1)$$

Here N_1 is the number of mols of hydrogen halide contained at the temperature T in the volume of air v_1 which passed through the hydrogen halide saturator. For the water vapor we have the similar expression

$$p_2v_2 = N_2RT. \qquad (2)$$

Here v_2 is the volume of the air as it passes through the saturator for water vapor. The volumes v_1 and v_2 differ slightly, 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 halide 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, *i. e.*,

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

By combining Equations 1, 2 and 3, the following expression for p_1 results:

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

For p_2, the vapor pressure of pure water, the values 23.76 mm. and 31.85 mm. were employed at 25° and 30°, respectively. The vapor pressure of water in equilibrium with the acid solution p_s, was in the case of hydrogen chloride, interpolated from the values given by Linhart.[1] For solutions of hydrobromic acid and of hydriodic acid it was assumed, because of lack of the desired data, that the values of p_s are the same as those for hydrochloric acid of the same concentrations. It was determined from the freezing-point curves for solutions of these 3 halides and also from a comparison of the vapor pressure results obtained in this investigation, that the maximum error in the values thus chosen for p_s is 20%. Such an error would cause an error of less than 0.3% in the values calculated for the partial pressures.

6. Experimental Data and Computed Vapor Pressures.

The experimental data and the calculated vapor pressures are given in Table I. In this table M is the concentration of the acid solution

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[1] THIS JOURNAL, 39, 2607 (1917).

TABLE I.—EXPERIMENTAL DATA ON THE VAPOR PRESSURE OF THE HYDROGEN HALIDES ABOVE THEIR AQUEOUS SOLUTIONS.

M.	*C.*	$E \times 10^3$.	*W.*	$p_{mm.}$	$D_{mm.}$	*D%.*
Hydrochloric Acid at 25°.						
3.240	3.021	0.0521	2.870	0.00780	0.00002	+0.3
3.952	3.656	0.0982	2.453	0.01724	0.00006	−0.3
5.041	4.570	0.3118	2.416	0.0557	0.0003	+0.5
5.364	4.834	0.3259	1.781	0.0791	0.0027	+3.5
6.018	5.359	0.7085	2.063	0.1487	0.0066	+4.6
6.270	5.559	0.7552	1.895	0.1727	0.0067	−3.7
6.457	5.706	0.983	2.073	0.206	0.007	−3.3
7.148	6.238	1.069	1.206	0.385	0.013	−3.3
8.157	6.980	3.685	1.602	0.999	0.035	+3.6
8.950	7.546	4.920	1.175	1.819	0.031	−1.6
9.960[a]	8.248	9.643	1.043	4.012	0.071	−1.7
9.971[a]	8.256	9.116	0.961	4.117	0.007	+0.2
9.990	8.270	19.483	1.985	4.260	0.079	+1.9
			Average percentage deviation =			2.8
Hydrochloric Acid at 30°.						
5.569	4.990	0.4137	1.620	0.148	...	...
7.329	6.364	1.095	0.895	0.712	...	...
8.726	7.364	6.768	1.510	2.61	...	...
9.286	7.764	6.789	1.139	3.47	...	...
Hydrobromic Acid at 25°.						
5.851	5.076	0.0130	3.695	0.00153	0.00024	+16
6.394	5.482	0.0165	2.250	(0.0032)	...	(+35)
7.632	6.374	0.0333	2.497	0.0058	0.0006	−10
8.315	6.845	0.0617	2.338	0.0115	0.0003	−3
8.325	6.850	0.0866	2.811	0.0134	0.0016	+12
9.143	7.393	0.118	2.217	0.0232	0.0023	−10
9.655	7.730	0.249	2.337	0.0466	0.0037	+8
10.440	8.221	0.460	2.261	0.0888	0.0009	+1
10.950	8.546	0.705	2.155	0.143	0.001	−1
			Average percentage deviation =			7
Hydriodic Acid at 25°.						
5.971	...	0.0041	3.529	0.00051	0.00008	−16
6.038	...	0.0033	2.696	0.00053	0.00007	−13
6.171	...	0.0064	2.974	0.00093	0.00022	+23
7.586	...	0.0195	2.388	0.00355	0.00025	−7
8.697	...	0.1187	2.692	0.0192	0.0010	+5
9.251	...	0.167	2.687	(0.0271)	...	(−98)
9.332	...	0.335	2.729	0.0536	0.0046	+8
9.776	...	0.586	2.728	0.0937	0.0018	−2
			Average percentage deviation =			10

[a] Solutions saturated with calomel.

expressed in mols per 1000 g. of water, *C* the concentration in mols per liter, *E* the equivalents of halide found in the absorber, *W* the weight in g. of water absorbed by the U-tubes, *p* the computed partial pressure of the hydrogen halide in millimeters of mercury, D_{mm} and D % the deviations, in mm. and in percentages, of the individual values from the smooth curve obtained by plotting the experimentally determined values of log p against those of M.

The irregularities in the above results arise to a large extent from the analytical methods employed. Thus, the percentage error in the determination of the concentration of the acid employed, is increased 6 to 10 fold when expressed as a deviation of the vapor pressure results. At the lower concentrations, particularly in the case of hydrogen bromide and iodide, the minute amounts of halide present in the absorber could be determined with an accuracy of about 10% only.

The vapor pressures for hydrogen chloride at 25° given in Table I 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 4 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 above vapor pressures at 30° were compared with those at 25° by the aid of the van't Hoff equation. The average differences between the 4 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.

Table II.—Vapor Pressures of the Hydrogen Halides at 25° at Round Concentrations.

Mols per 1000 g. H_2O.	Vapor pressure in mm.		
	HCl.	HBr.	HI.
4.0	0.0182	.....	.....
5.0	0.0530	.....	.....
6.0	0.140	0.00151	0.00057
7.0	0.348	0.00370	0.00182
8.0	0.844	0.0089	0.0065
9.0	1.93	0.0226	0.0295
10.0	4.20	0.059	0.132
11.0	....	0.151	.....

The vapor-pressure data at 25° were interpolated to round concentrations by means of the curves employed for determining the deviations. The interpolated results are given in Table II.

7. Comparison with Electromotive-Force Data.

The vapor-pressure data for hydrogen chloride may be compared with the electromotive-force measurements of hydrochloric[1] acid concentration cells in the following manner. The free-energy decrease attending the transfer of 1 HCl from a solution c molal to a solution 0.1 molal[2] is given by the expression

$$-\Delta F = EF \tag{4}$$

where E is the electromotive force of a cell in which the above change in state takes place and F the value of the faraday. The same free-energy decrease may be expressed also by means of the equation

$$-\Delta F = RT \log_e p/p_{0.1} \tag{5}$$

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

$$EF = RT \log_e p/p_{0.1}$$

follows. Hence

$$\log_{10} p = \log_{10} p_{0.1} + \frac{EF}{2.303RT} \tag{6}$$

Therefore the graph obtained by plotting values of $\log_{10} p$ against corresponding values of E should be a straight line having the slope

$$F/2.303\,RT.$$

The desired values of E may be readily calculated from the results of Ellis[3] and of Linhart.[3] Both of these investigators determined the electromotive force at 25° of cells of the type

$$H_2(1\text{ atm.}),\ HCl\ (c\text{ molal}),\ Hg_2Cl_2 + Hg$$

over a considerable concentration range. By subtracting the electromotive force of the cell in which the concentration is c molal, from that of the similar cell in which the concentration is 0.1 molal, 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 g. of water. The results of Ellis and of Linhart are in good agreement with each other. From this graph values of E corresponding to

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[1] There are no corresponding data for hydrobromic acid or hydriodic 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 which follow.

[3] *Loc. cit.*

the concentrations at which the vapor pressures were experimentally determined were read off and plotted against values of $\log_{10}p$.

At concentrations below about 7.15 molal the agreement is entirely satisfactory, the points 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 straight line. This deviation can be accounted for only by assuming an error in either the electromotive force or the vapor-pressure data or in both.[1] This portion of the curve is founded upon 2 electromotive-force measurements and 5 vapor-pressure determinations. Of the latter 3 at 10 molal have an average deviation of 1.3%. An error of 10% in the vapor-pressure data, of 3 millivolts in the electromotive-force data or of 1% in the concentration of the acid would explain the discrepancy.

Because of the uncertainty of the data for the solutions more concentrated than 7.15 molal, only the 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 hydrogen chloride 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%, the probable error 1.2%.

8. The Free Energy of Formation of Hydrogen Chloride and of the Hydrogen Halides in Solution.

The free energy of formation of hydrogen chloride may now be obtained by adding to the free energy of 1 HCl in 0.1 molal solution, which has been computed by Ellis[2] to be —34, 330 calories, the free energy increase which results when the pressure is increased from that which the hydrogen chloride has above its 0.1 molal solution to a pressure of one atmosphere. This free energy increase is found by the equation $\Delta F = RT \log (760/2.23 \times 10^{-6})$ to be 11,630 calories. Hence the free energy of formation at 25° of hydrogen chloride is —22, 700 calories.

The free energies of the hydrogen halides in solutions of various concentrations at 25° are given in Table III. The values for hydrogen chloride up to and including 4 molal[3] were interpolated from the results of Ellis.

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[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 10.0 molal hydrochloric acid was negligible. See Table I.

[2] *Loc. cit.* Table X.

[3] Free energies for solutions more dilute than 0.1 molal may be computed from the electromotive-force measurements of Noyes and Ellis (THIS JOURNAL, 39, 2532 (1917); and of Linhart (*Ibid.*, 41, 1175 (1919)).

TABLE III.—FREE ENERGIES OF HYDROGEN HALIDES IN SOLUTION AT VARIOUS CONCENTRATIONS AT 25°.

Mols per 1000 g. H_2O.	Free energy in calories.		
	HCl.	HBr.	HI.
0.1	—34330	—27550	—15260
0.5	—32500	.....	.....
1.0	—31590	.....	.....
2.0	—30510	.....	.....
3.0	—29690	.....	.....
4.0	—29100	.....	.....
5.0	—28365	.....	.....
6.0	—27790	—20365	—8035
7.0	—27250	—19830	—7360
8.0	—26725	—19300	—6600
9.0	—26235	—18760	—5700
10.0	—25775	—18190	—4815
11.0	.....	—17635	.....
Free energy of formation of gaseous halide	—22700	—12592	+310

At the higher concentrations the free energies were computed by adding to the free energy of 1 HCl(*g*), the free energy of expansion from a pressure of one atmosphere to a pressure equal to its partial pressure in the solution in question. The free energies of hydrogen bromide and of hydrogen iodide were calculated in a similar manner; the free energies of formation of 1 HBr(*g*) and of 1 HI(*g*) were taken as —12592 and +310 calories, respectively.[1] The free energy of hydrogen bromide in 0.1 molal solution was computed from the results of Lewis and Storch,[2] that of hydrogen iodide from the free energy of the iodide ion.[3]

9. Summary.

1. Determinations have been made of the vapor pressures of hydrogen chloride, of hydrogen bromide and of hydrogen iodide above their aqueous solutions between the concentrations 3.2 and 10.0 molal, 5.8 and 11.0 molal, and 6.0 and 9.7 molal, respectively, at 25° and of hydrogen chloride between 5.5 and 9.2 molal at 30°.

2. By the method employed partial pressures as small as 0.001 mm. were determined with an accuracy of a few per cent.

3. The vapor-pressure measurements of hydrochloric acid solutions between 3.2 and 7.15 molal are in good agreement with the electromotive-force data for hydrochloric acid concentration cells.

4. The free energy of formation at 25° of hydrogen chloride is —22,700 calories.

5. The free energies at 25° of the halide acids in aqueous solutions of various concentrations are given.

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[1] Lewis and Randall, THIS JOURNAL, **36**, 2259 (1914); *Ibid.*, **38**, 2348 (1916).

[2] THIS JOURNAL, **39**, 2544 (1917).

[3] Lewis and Randall, THIS JOURNAL, **36**, 2259 (1914).