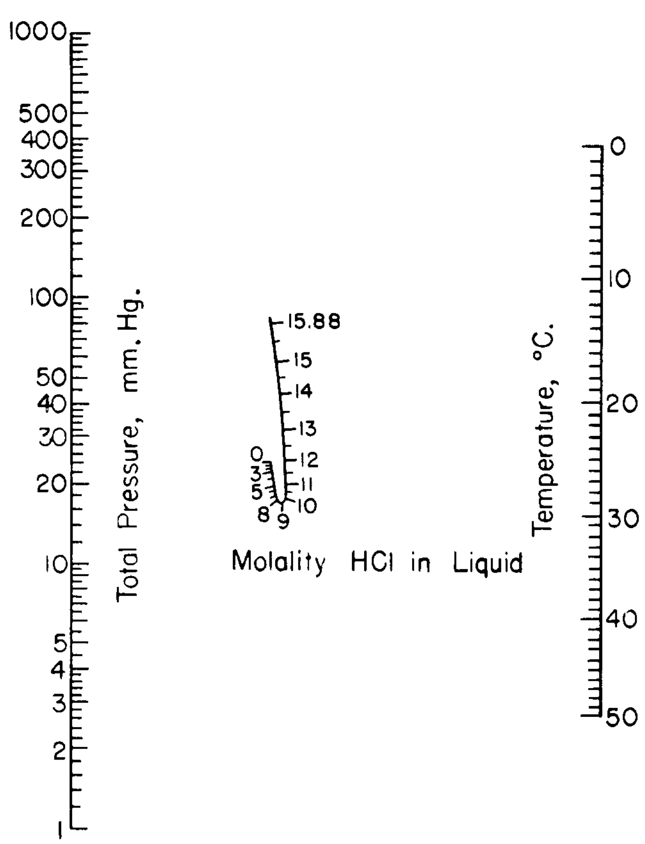

Figure 7. Nomogram of the total pressures of water and of aqueous solutions of hydrochloric acid

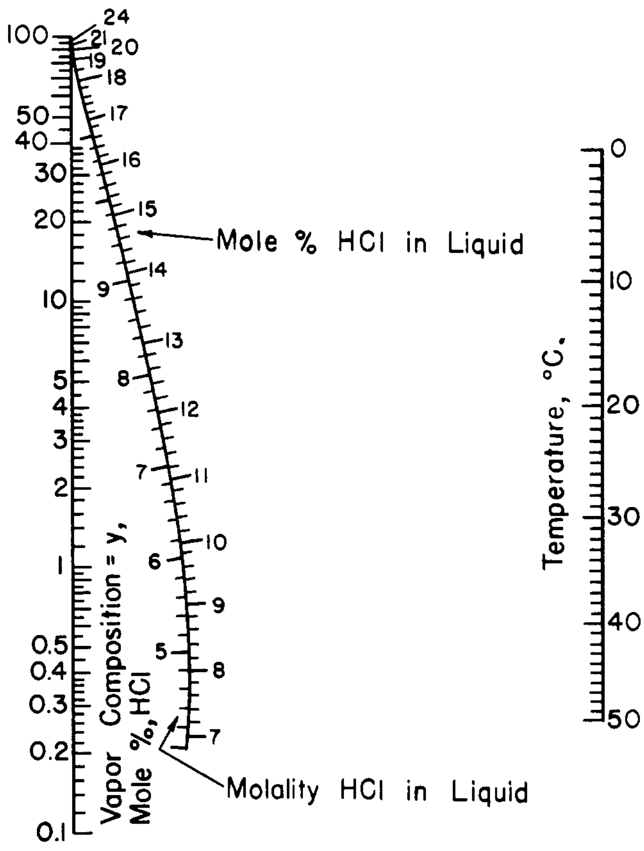

Figure 8. Nomogram of the vapor compositions (y) in mole % of hydrogen chloride out of aqueous hydrochloric acid

compositions resulted from study of the report by Fritz and Fuget (2) and its review for publication in this journal. Appreciation is expressed to Ronald C. Kowalski for drafting the figures.

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Vapor Pressure of Aqueous Hydrogen Chloride Solutions, 0° to 50° C.

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Partial and total vapor pressures of hydrogen chloride and water have been calculated from electromotive force data for the system, water-hydrogen chloride. Calculations have been made for the temperature range of 0° to 50° C. and the composition range, 0.01 to 15.88 molal. The methods used are discussed briefly. Tables of the vapor pressures as a function of molality at temperature intervals of 10° C. are given.

Vapor pressures of electrolytes, such as hydrogen chloride, over their aqueous solutions have proved difficult to measure directly. This is especially true of dilute solutions where the vapor pressures are very small. The experimental results reported by various investigators have frequently been discordant. On the other hand, measurements of cell potentials have been made with great precision for common electrolytes. These are a measure of the vapor pressure of the solute and may permit its evaluation with greater accuracy than available direct measurements.

For hydrogen chloride, the reaction occurring in the cell

$$\mathrm{Pt, H_2 \,|\, HCl\ (solvent) \,|\, AgCl, Ag} \qquad (1)$$

may be written as

TABLE I. VAPOR PRESSURE OF HYDROGEN CHLORIDE ABOVE AQUEOUS SOLUTIONS

Molality	Wt.% HCl	Vapor Pressure of HCl, Mm. Hg					
		0° C.	10° C.	20° C.	30° C.	40° C.	50° C.
0.01	0.0364	2.10×10^{-9}	6.37×10^{-9}	1.84×10^{-8}	5.01×10^{-8}	1.32×10^{-7}	3.35×10^{-7}
0.05	0.1820	4.46×10^{-8}	1.35×10^{-7}	3.88×10^{-7}	1.06×10^{-6}	2.79×10^{-6}	7.00×10^{-6}
0.10	0.3633	1.65×10^{-7}	1.01×10^{-6}	1.43×10^{-6}	3.88×10^{-6}	1.01×10^{-5}	2.52×10^{-5}
0.20	0.724	6.16×10^{-7}	1.85×10^{-6}	5.28×10^{-6}	1.43×10^{-5}	3.72×10^{-5}	9.37×10^{-5}
0.50	1.790	3.87×10^{-6}	1.15×10^{-5}	3.26×10^{-5}	8.38×10^{-5}	2.20×10^{-4}	5.41×10^{-4}
1.0	3.513	1.81×10^{-5}	5.33×10^{-5}	1.49×10^{-4}	3.96×10^{-4}	1.01×10^{-3}	2.45×10^{-3}
2.0	6.796	1.20×10^{-4}	3.45×10^{-4}	9.44×10^{-4}	2.43×10^{-3}	6.05×10^{-3}	0.0143
3.0	9.859	4.68×10^{-4}	1.32×10^{-3}	3.51×10^{-3}	8.88×10^{-3}	0.0211	0.0497
4.0	12.73	1.59×10^{-3}	4.36×10^{-3}	0.0114	0.0279	0.0659	0.149
5.0	15.42	4.89×10^{-3}	0.0131	0.0333	0.0794	0.183	0.401
6.0	17.95	0.0141	0.0366	0.0903	0.210	0.468	1.001
7.0	20.34	0.0382	0.0964	0.231	0.521	1.132	2.354
8.0	22.58	0.0987	0.242	0.563	1.236	2.61	5.27
9.0	24.70	0.240	0.571	1.295	2.76	5.69	11.20
10.0	26.72	0.552	1.278	2.83	5.87	11.73	22.6
11.0	28.63	1.229	2.77	5.86	11.97	23.28	43.9
12.0	30.43	2.55	5.60	11.75	23.14	44.1	80.9
13.0	32.16	5.11	11.00	22.25	43.6	79.5	140
14.0	33.79	9.99	20.75	41.1	76.8	137.4	242
15.0	35.35	18.56	38.0	72.2	132.5	232	400
15.88	36.63	31.0	61.2	114.8	201.4	360	

$$\tfrac{1}{2}H_2(g) + AgCl(s) = HCl(g) + Ag(s) \qquad (2)$$

The cell potential is then given by

$$E = E_g^0 - \frac{RT}{F} \ln \frac{f_{HCl}}{(f_{H_2})^{1/2}} \qquad (3)$$

where f_{HCl} and f_{H_2} are the fugacities of the two gases, and E_g^0 is the standard potential with each as an ideal gas at 1-atm. pressure. The fugacity, and thus the vapor pressure, of hydrogen chloride may be calculated directly from cell measurements by use of Equation 3. The necessary standard potential, E_g^0, is independent of the solvent used.

Aston and Gittler (2) recently determined E_g^0 at 25° C. directly by measurements of the cell in aqueous acetic acid. They calculated E_g^0 for temperatures from 0° to 40° C. The standard potential at higher temperatures can readily be obtained by extension of the tables they compiled.

For cell data converted to 1-atm. pressure of hydrogen, the fugacity of hydrogen chloride is then given by

$$\ln f_{HCl} = \frac{F}{RT}(E_g^0 - E) \qquad (4)$$

The fugacity of the solvent is obtained by integration of the Duhem equation in the form

$$d\ln f_1 = \frac{mM_1}{1000} d\ln f_2 \qquad (5)$$

where m is the molality, M_1 the molecular weight of solvent, and and f_2 are solvent and solute activities. Using the customary approximation, the vapor pressure of solute and solvent may be substituted for their fugacities.

APPLICATION TO AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE

The only extensive compilation of partial vapor pressures for aqueous hydrogen chloride solutions, to our knowledge, is that prepared by Zeisberg (6) for International Critical Tables. Zeisberg evaluated the data then available and used it to compile a table of partial vapor pressures of hydrogen chloride for concentrations from 2 to 46 weight % of hydrogen chloride at temperatures from 0° to 110° C. He claimed an accuracy of about 2% in the most favorable regions of concentration and temperature, and 5 to 15% in the less favorable regions. The 2% accuracy was the best claimed for any measurements used in preparation of the table; it appears now that Zeisberg's estimates of accuracy were somewhat optimistic. Preliminary tests of I. C. T. data made several years ago by one of us indicated that they were not consistent with more recent data on the electromotive force of cells containing aqueous hydrogen chloride.

Using the procedure outlined here, the vapor pressures of hydrogen chloride and water above aqueous hydrogen chloride have been calculated from the electromotive force data of Harned and Ehlers (3, 4) and Akerlof and Teare (1). The calculations were carried from 0° C. to the temperature limit (50° C.) of the cell measurements at the higher concentrations. The original data of Akerlof and Teare (1) had been corrected to 1-atm. pressure of hydrogen by using the vapor pressure data of Zeisberg (6). At the higher concentrations it was necessary to recalculate these corrections (by successive approximations) in order to make them consistent with vapor pressures obtained from cell data.

The values of E_g^0 from 0° to 30° C. were taken from Aston and Gittler (2). The values used at 40° and 50° C., calculated from their data, were -0.1402 and -0.1332 absolute volts, respectively.

RESULTS

Table I gives partial pressures of hydrogen chloride above its aqueous solutions at concentrations from 0.01 to 15.88 molal and at temperatures from 0° to 50° C. For convenience, the compositions are given both in molality

TABLE II. VAPOR PRESSURE OF WATER ABOVE HCl SOLUTIONS

Molality	Vapor Pressure of Water, Mm. Hg					
	0° C.	10° C.	20° C.	30° C.	40° C.	50° C.
0.0	4.579	9.209	17.535	31.824	55.324	92.51
0.05	4.575	9.19	17.51	31.78	55.23	92.44
0.10	4.57	9.18	17.47	31.71	55.13	92.18
0.20	4.56	9.15	17.42	31.62	54.94	91.88
0.50	4.51	9.05	17.22	31.32	54.35	90.94
1.0	4.42	8.87	16.78	30.70	53.27	89.18
2.0	4.22	8.44	16.08	29.96	50.8	87.63
3.0	3.99	7.95	15.17	27.63	48.8	80.60
4.0	3.69	7.38	14.09	25.70	45.2	75.3
5.0	3.37	6.75	12.91	23.6	41.7	69.5
6.0	3.03	6.09	11.71	21.5	38.0	63.5
7.0	2.70	5.45	10.49	19.3	34.3	57.5
8.0	2.48	4.81	9.35	17.2	30.6	51.5
9.0	2.13	4.21	8.26	15.6	27.2	45.6
10.0	1.80	3.69	7.22	13.4	24.0	40.6
11.0	1.59	3.17	6.28	11.7	21.0	35.5
12.0	1.34	2.75	5.45	10.2	18.4	31.6
13.0	1.11	2.36	4.72	8.86	16.2	27.8
14.0	0.98	2.02	4.05	7.73	14.1	24.4
15.0	0.83	1.73	3.49	6.71	12.9	21.4
15.88	0.72	1.51	3.07	6.00	11.4	

TABLE III. TOTAL VAPOR PRESSURE OF HCl SOLUTIONS

Molality	Total Pressure, Mm. Hg					
	0° C.	10° C.	20° C.	30° C.	40° C.	50° C.
0.0	4.58	9.21	17.54	31.82	55.32	92.51
0.05	. .	9.19	17.51	31.78	55.23	92.44
0.10	4.57	9.18	17.47	31.71	55.13	92.18
0.20	4.56	9.15	17.42	31.62	54.94	91.88
0.50	4.51	9.05	17.22	31.32	54.35	90.94
1.0	4.42	8.87	16.78	30.70	53.27	89.18
2.0	4.22	8.44	16.08	29.96	50.8	87.64
3.0	3.99	7.95	15.17	27.64	48.8	80.65
4.0	3.69	7.38	14.10	25.73	45.3	75.4
5.0	3.37	6.76	12.94	23.7	41.9	69.9
6.0	3.04	6.13	11.80	21.7	38.5	64.5
7.0	2.74	5.55	10.72	19.8	35.4	59.9
8.0	2.58	5.05	9.91	18.4	33.2	56.8
9.0	2.37	4.78	9.56	18.4	32.9	56.8
10.0	2.35	4.97	10.05	19.3	35.7	63.2
11.0	2.82	5.94	12.14	23.7	44.3	79.4
12.0	3.89	8.35	17.20	33.3	62.5	112.5
13.0	6.22	13.36	27.0	52.5	95.7	168
14.0	10.97	22.8	45.2	84.5	152	266
15.0	19.39	39.7	75.7	139	245	421
15.88	31.7	62.7	118	207	371	

and in weight per cent. The uncertainties in the pressures, estimated to be 1% at 30° C., increase to 2% at the two extreme temperatures. For approximate interpolation, log P may be plotted against the molality or weight per cent. A more accurate interpolation is obtained if log P is expressed as a linear function over a limited range of concentration, with a deviation plot in addition.

Table II gives the vapor pressure of water from solutions in the same temperature and concentration range used in Table I. The accuracy is estimated to be 2% in $\log P/P_0$, where P_0 is the vapor pressure of pure water at this temperature. This is approximately 0.1% of the vapor pressure at 2 molal, 1.5% at 9 molal, and 3.5% at 15 molal concentration. For most data in the table, linear interpolation is possible.

Table III lists the total vapor pressures of the same solutions. It will be observed that the pressure goes to a minimum at about 9 molal.

DISCUSSION OF ERRORS AND COMPARISON WITH RESULTS

Aston and Gittler (2) assigned an uncertainty of ± 0.2 mv. to their value of E_g^0 at 298° K. In addition, uncertainties in the temperature correction are about 0.1 mv. at 0° and 50° C. The precision in the cell measurements is better than 0.1 mv., but differences in results obtained by various investigators have been as large as 0.1 mv. On these bases we believe the maximum uncertainty in $E - E_g^0$ to be 0.3 mv. at 25° and 0.4 mv. at 0° and 50°. The corresponding uncertainty in the fugacity of HCl, according to Equation 4, is then about 1% at 25° and possibly 2% at 0° and 50° C. The error made in using fugacities for vapor pressures can not be properly estimated. However, the agreement of Aston and Gittler's results on E_g^0 with the value deduced by Randall and Young (5) for the aqueous cell, and the internal consistency of Aston and Gittler's results in acetic acid and in absolute ethanol, indicate this error to be probably less than the others.

A point-by-point comparison of the partial pressures of HCl with values interpolated from the I.C.T. was made at 0°, 30°, 50° C., and at all temperatures above 12 molal concentration. Between 6 and 11 molal, the two sets agreed within 5%, with the I.C.T. values lower at 0° and higher at the other two temperatures. Above 11 molal, the I.C.T. values are 5 to 10% high at the higher temperatures, and 10 to 20% high below 30° C. Below 5 molal, the I.C.T. values range from 10% high at 4 molal to as much as 100% high at 0.5 molal, averaging about 20% high.

The partial vapor pressures of water given in the I.C.T. are uniformly low, and do not extrapolate to the presently accepted values for the vapor pressure of pure water. In general, the tabular values are 3 to 5% lower than those listed above.

It should be remembered in this connection that at the time of Zeisberg's work (6) there was but one reliable set of measurements for partial vapor pressures of hydrogen chloride, and that is for temperatures at 25° and 30° C. only. (The situation with regard to direct measurements of the vapor pressure has not improved materially since.) Other measurements at 25° C. then available were as much as 100% high. In view of this, it is remarkable that the I.C.T. data were as little in error as our comparison indicates.

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