Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Correlating Pressures and Vapor Compositions of Aqueous Hydrochloric Acid

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For calculations in design of such important industrial equipment as absorption towers for hydrogen chloride gas, graphical presentation of more accurate data than heretofore available is useful. The high-accuracy data computed by Fritz and Fuget for partial and total vapor pressures of aqueous hydrochloric acid solutions have been correlated by logarithmically plotting pressures versus pressures of a reference substance, water, at constant temperatures. Nomograms are shown from which the computations of Fritz and Fuget can be readily interpolated or extrapolated, and vapor compositions not included by these authors are calculated.

In previous papers (4, 5) it was shown that when using classic data of the literature, partial pressures, total pressures, and vapor compositions of hydrochloric acid and water solutions form straight lines when plotted on logarithmic paper against a temperature scale developed from the vapor pressures of water at a constant temperature.

The relationship of data so taken as partial pressures or total pressures by manometric or similar methods were shown to correlate with heats of solution determined calorimetrically, and also with activity data determined electrochemically by Åkerlöf and Teare (1). These fundamental interrelations were shown to be thermodynamically exact; measurements in one field were shown to be useful in computing data in the other.

Fritz and Fuget (2), in a carefully executed system of calculation, have now computed, from the activity data of Åkerlöf and Teare, partial and total pressures over hydrochloric acid solutions. Their computations are probably more nearly correct than any measurements made directly heretofore; furthermore, they are probably as nearly correct as direct vapor pressure measurements can ever be made, particularly in low vapor pressure ranges.

PRESENTATION OF DATA

Tabular values of the high-accuracy data presented by Fritz and Fuget correlate well by the previously used methods (3) of logarithmically plotting vapor pressures versus the vapor pressures of a reference substance at constant temperatures. This has been done for the partial pressures of water and hydrochloric acid, as well as for total pressure of the system in Figures 1, 2, and 3 where the lines represent constant molality hydrochloric acid. Vapor compositions, not given by Fritz and Fuget, have been calculated and are included in Table I. The corresponding vapor compositions at constant liquid compositions are plotted in Figure 4 where the lines again represent constant molality hydrochloric acid.

As would be expected from the fundamental thermodynamic derivations which are the basis of these plots,

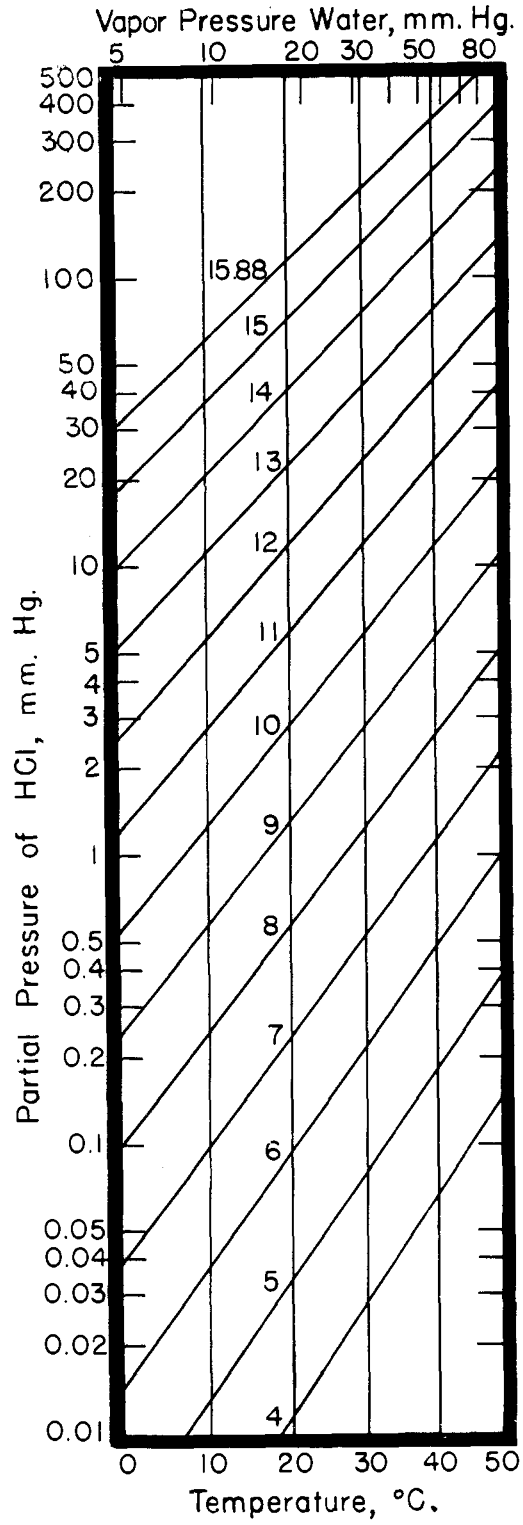

Figure 1. Logarithmic plot of partial pressures for hydrogen chloride over aqueous solutions vs. a temperature scale derived from vapor pressures of water

these data are all represented by straight lines which, because of their closeness to each other, are not plotted.

There are slight, casual deviations within the precision of the experimental electrochemical work and resulting computations. These show on large scale plots, but because of the thickness of the lines, they are too small to show in the figures shown here. There are, however, no systematic deviations; the lines may be regarded as an averaging of errors to give a more nearly precise picture of the relationship as a whole.

In Figure 3, because of the constant boiling mixture, there is a decrease in total pressures for solutions of 0 to about 9 molalities of hydrochloric acid and then from about 9 to 15.88 molalities. Hence, the lower lines cross each other at small angles; only the left half of some lines and the right half of the other lines are shown. In each case, they may be continued throughout the range, but this causes confusion in lines.

NOMOGRAMS

Standard methods allow graphical data which fall as a group of straight lines on a coordinate plot to be readily transformed into a nomogram. Thus, Figures 1, 2, 3, and 4 give Figures 5, 6, 7, and 8, respectively. Straight lines through a point of pressure or temperature on the side axis and a concentration point on the center axis give a corresponding value at their intersection with the other side axis. From these nomograms it is possible to obtain data readily and to interpolate or extrapolate that computed by Fritz and Fuget.

In Figure 5, a line drawn through any point on either of the center scales to the side scales indicates the respective partial pressure of hydrogen chloride and the corresponding temperature. If the left molality scale is used (from 9 to 15.88), the partial pressure is indicated directly; if the right molality scale is used (from 4 to 9), it is necessary to multiply the reading of the partial pressure by 0.01 in order to obtain the correct partial pressure.

In Figures 6 and 7, a line drawn through a point of liquid composition on the center molality scale gives on the side scales the partial pressure (Figure 6) and the total pressure (Figure 7) of water with the corresponding temperature.

The central liquid-composition scale is calibrated in both mole % of hydrogen chloride and molality to allow the use of either, or the conversion of one value to another. A line drawn through a point of liquid composition on the center scale gives the vapor composition in mole % of hydrogen chloride and the corresponding temperature on the side scale.

Besides the convenience of these nomograms for presentation of data, other important relationships are made evident by this type of plot. Thus, in Figure 7, if lines are drawn tangent to points of concentration on the lower hook of the middle scale, the intersections on the right and the left scales indicate the temperatures and pressures of the corresponding constant boiling mixtures of these indicated molalities.

UTILITY

This correlation is particularly good for vapor compositions, even of this nonideal system, and illustrates well the applicability of this general technique to correlating vapor-liquid equilibria. Of particular industrial interest is the graphical presentation of more accurate data than hitherto available for calculations in design of such important equipment as absorption towers for hydrogen chloride gas.

COMPARISON WITH CALORIMETRIC RESULTS

According to methods previously described (4), partial pressure data can be used to compute partial heats of solution of water in hydrochloric acid solutions. Such heats of solution may be determined from the slopes of these lines, or more readily from the slopes of lines of activities on a

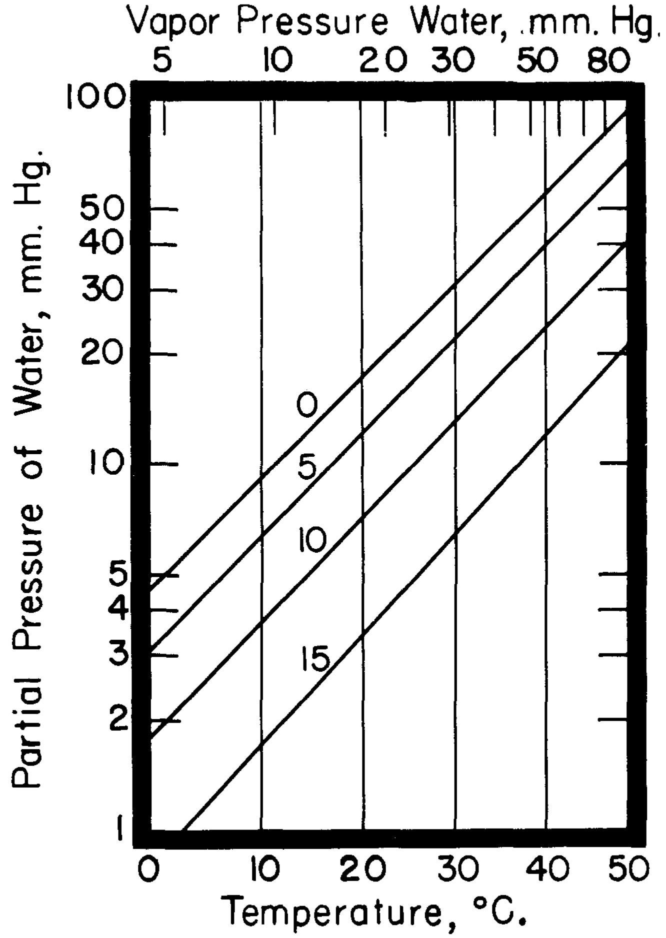

Figure 2. Logarithmic plot of partial pressures of water over aqueous hydrochloric acid vs. a temperature scale derived from vapor pressures of water

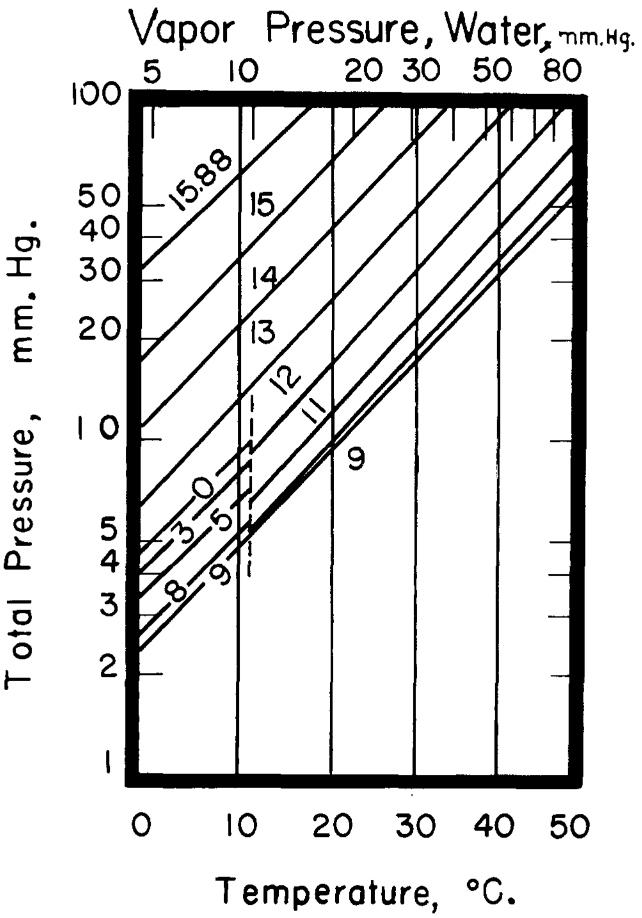

Figure 3. Logarithmic plot of total pressures over aqueous hydrochloric acid vs. a temperature scale derived from vapor pressures of water

similar plot, and may be compared with data determined calorimetrically. However, partial pressure data which are correlated in this report, are derived from activity data obtained from e.m.f. measurements. These activity data have been used (4) to obtain directly the partial heats of solution which check with the precise calorimetric data, fortunately available for this particular system (6,7), more closely than did those determined from the best experimental partial pressure data. Consequently, the partial pressure data calculated by Fritz and Fuget (2), also from the same activity data, check the calorimetric data more closely than do the partial pressure data experimentally determined. Thus, by extending the previous thermodynamic reasoning (4), the conclusion given here was reached that these calculated data are probably closer to actual values than any which have been determined experimentally. The

TABLE I. VAPOR COMPOSITION OF HCl-H_2O SYSTEMS

Liquid			Vapor, Mole % HCl					
Molality	Weight %	Mole %	0° C.	10° C.	20° C.	30° C.	40° C.	50° C.
1.0	3.51	1.77	4.09×10^{-4}	6.01×10^{-4}	8.88×10^{-4}	12.9×10^{-4}	19.0×10^{-4}	27.5×10^{-4}
2.0	6.80	3.48	2.84×10^{-3}	4.09×10^{-3}	5.87×10^{-3}	8.11×10^{-3}	11.9×10^{-3}	16.3×10^{-3}
3.0	9.86	5.14	11.72×10^{-3}	16.51×10^{-3}	23.12×10^{-3}	32.1×10^{-3}	4.32×10^{-2}	.0616
4.0	12.73	6.72	.04	.0592	.0808	.109	.145	.198
5.0	15.42	8.26	.15	.194	.257	.335	.437	.574
6.0	17.95	9.75	.464	.597	.767	.968	1.215	1.552
7.0	20.34	11.19	1.394	1.735	2.152	2.631	3.198	3.931
8.0	22.58	12.59	3.822	4.79	5.68	6.72	7.86	9.29
9.0	24.70	13.94	10.12	11.94	13.55	15.00	17.29	19.72
10.0	26.72	15.27	23.49	25.70	28.15	30.41	32.85	35.75
11.0	28.63	16.54	43.6	46.62	48.29	50.5	52.55	55.3
12.0	30.43	17.77	65.6	67.05	68.35	69.55	70.6	71.9
13.0	32.16	18.97	82.2	82.4	82.4	83.0	83.4	83.4
14.0	33.79	20.12	91.0	91.03	90.9	90.4	91.0	91.0
15.0	35.35	21.28	95.4	95.7	95.4	95.4	94.9	95.1
15.88	36.63	24.11	97.8	97.6	97.3	97.4	97.1	--

logarithmic plots made by the methods herein described then smooth out or average any casual errors of experiment and calculation.

ACKNOWLEDGMENT

The above graphical presentation and correlation of pressures and the calculation and presentation of vapor

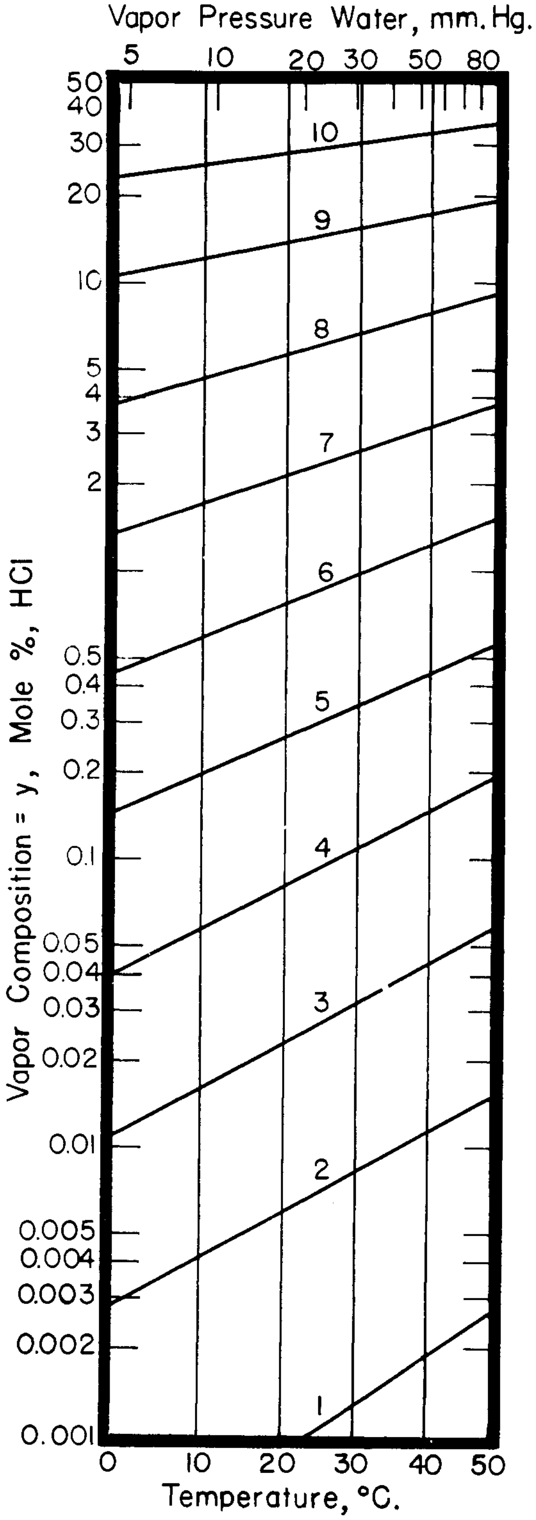

Figure 4. Logarithmic plot of vapor compositions over aqueous hydrochloric acid solutions vs. a temperature scale derived from vapor pressures of water

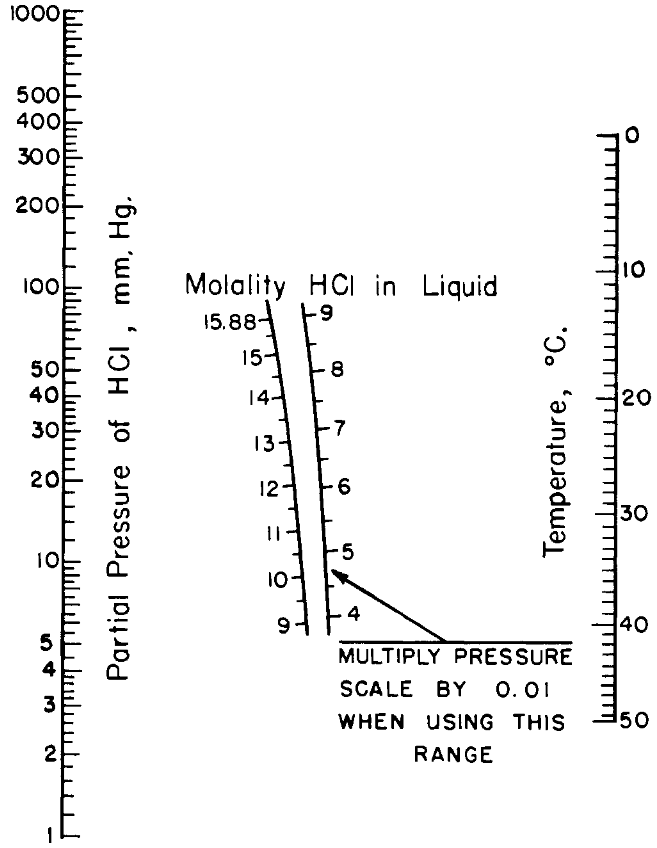

Figure 5. Nomogram of the partial pressures of hydrogen chloride out of aqueous solutions

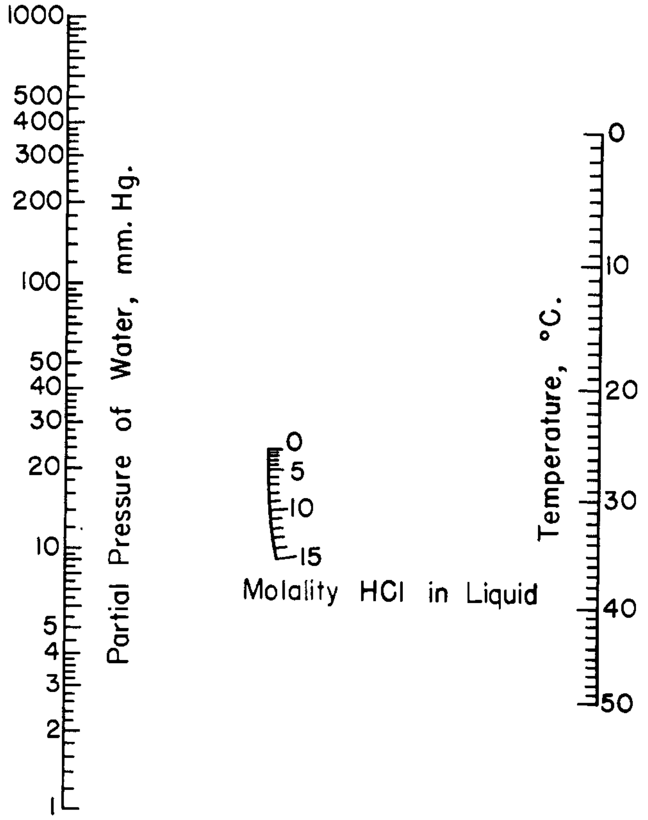

Figure 6. Nomogram of the partial pressures of water out of aqueous solutions of hydrochloric acid

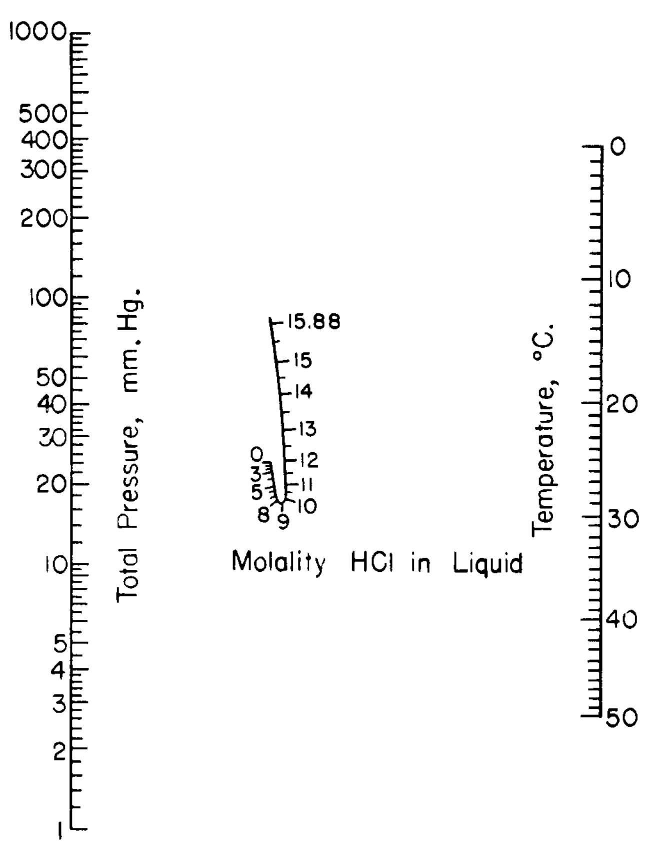

Figure 7. Nomogram of the total pressures of water and of aqueous solutions of hydrochloric acid

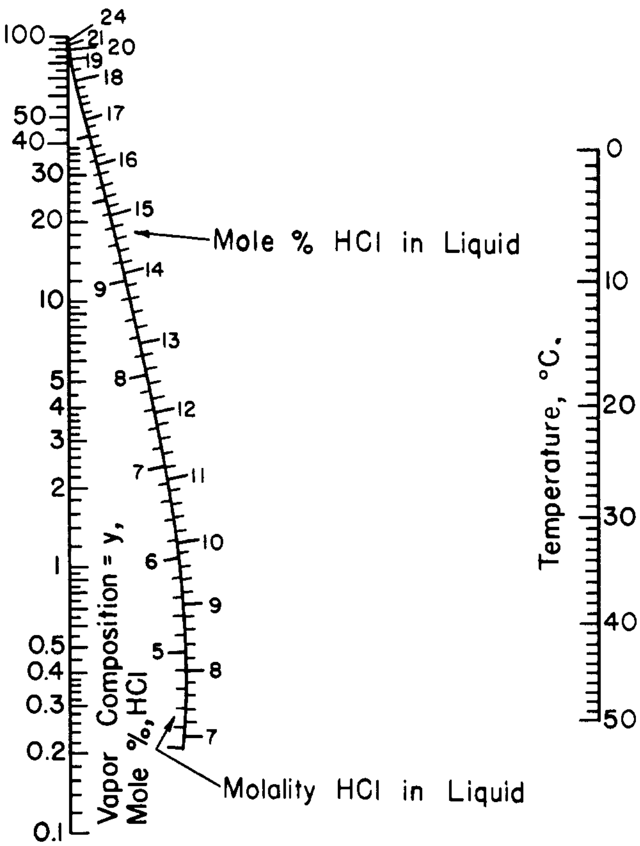

Figure 8. Nomogram of the vapor compositions (y) in mole % of hydrogen chloride out of aqueous hydrochloric acid

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

$$\text{Pt, } H_2 \mid \text{HCl (solvent)} \mid \text{AgCl, Ag} \qquad (1)$$

may be written as