RESULTS

Experimental results are given in Table III.

NOMENCLATURE

n_D^{30} = refractive index at 30° C. in sodium light
x = mole fraction in liquid phase
y = mole fraction in vapor phase
π = total pressure, mm. of Hg

Subscripts

c = corrected
o = observed

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Vapor-Liquid Equilibrium of Water–Hydrogen Chloride System

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An experimental method for determining the vapor-liquid equilibrium of corrosive systems under moderate pressure is a static method with internal agitation and direct vapor phase sample injection to a gas chromatography unit. Experimental data were obtained for the water–hydrogen chloride system from −10.0° to 70.0° C. with pressure up to 222 p.s.i.a. The reproducibility of the liquid phase composition data was better than 0.4%, the vapor phase composition data about 5%. The interaction second virial coefficients for water and hydrogen chloride were calculated from the data.

THE thermodynamic properties of the H_2O-HCl binary system have been studied extensively in the past hundred years. Experimental vapor-liquid equilibrium measurements are normally limited to 1 atm. or less in pressure and to 30 mole % or less HCl in concentration. The most complete compilation of low pressure data is due to Zeisberg (15), who, in 1925, consolidated all reliable sources to tabulate the partial pressure of H_2O and HCl over aqueous HCl solution from 2 to 46 weight % HCl from 0° to 110° C. His work has been the basis of most engineering calculations and is quoted in Perry's handbook (11).

Based on thermodynamic deduction, the vapor-liquid equilibrium of the H_2O-HCl system can also be calculated from the e.m.f. measurement of a Pt.H_2/HCl (Aq.)/AgCl.-Ag cell. Fritz and Fuget (3) and Othmer and Naphtali (10) carried out such calculations from the e.m.f. data of Harned and Ehlers (6) and Åkerlöf and Teare (1) from 0° to 50° C. and composition from 0.01 to 15.8 molal HCl. The calculated partial pressures of HCl between 6 and 11 molal agreed within 5% with those compiled by Zeisberg (15) from manometric and calorimetric data. At lower concentration, because of experimental difficulties associated with other methods, the e.m.f. measurements give more consistent results. However, this method is normally limited to low pressure.

In 1960, Thumm (5) measured the solubility of HCl in water at and near the phase separation between 0° and 35° C. The concentrations of HCl in the aqueous phase

with two liquid phases present agree reasonably (0.5 to 0.8% lower) with the values reported by Rupert (13).

The phase behavior of the water–hydrogen chloride system is normally classified as a type IV nonideal system, which has a maximum boiling azeotrope at low pressure and a phase separation at high pressure.

Most published vapor-liquid equilibrium data are around these two ends. There are practically no data in between for most applications. An experimental program to determine the equilibrium vapor-liquid compositions from −10° to 70° C. with pressure up to 222 p.s.i.a. was therefore initiated to fill this gap.

EXPERIMENTAL

Chemicals. Laboratory-distilled water was degassed for 10 minutes by boiling. Its purity was checked on a gas chromatograph normally used for vapor-liquid equilibrium composition analysis. No detectable organic and/or halogen compounds were found.

The HCl was purchased from the Matheson Co. Initially, technical grade was used; the impurities, mostly chlorinated hydrocarbons, interfered with the separation of water on the chromatographic column. An electronic grade with a minimum purity of 99.9% proved satisfactory.

Apparatus. The method used is generally known as the static method. The solution is charged into a closed cell, immersed in a thermostat. The contents are agitated until

equilibrium is established between the liquid and its vapor, when samples are removed from both phases for analysis.

This method was adapted because of its simplicity in both construction and operation. It is especially suitable for studying corrosive systems when the material of construction is restricted.

The schematic flow diagram is shown in Figure 1. The entire system can be grouped, according to function, into subsystems: the equilibrium cell, the gas chromatograph, the sampling system, and the auxiliary systems.

EQUILIBRIUM CELL. The equilibrium cell was a glass column with tantalum closure at both ends to form a cylindrical, closed vessel (Figure 2).

The column was a piece of heavy-walled borosilicate glass pipe with an internal volume about 100 cc. Both ends were cut square and ground to make a perfect seal against Viton-A O-rings.

The top and bottom closure plates were machined from a tantalum rod. A groove was cut on each plate to receive an O-ring. Two ports were drilled vertically and tapped for connection to the pressure gage and charging system, and for sampling. A short piece of Teflon tubing was inserted through the sampling port and extended into the vapor space. One port in the bottom plate was used for sampling liquid. Holes were also drilled in the closure plates to receive tie rods and guard the connection rods between the air piston and the outside magnet. The pressure on the O-ring was adjusted using the nuts on the tie rods.

The magnetic agitator consisted of the inside magnet, the outside magnet, the air piston, and the control system. The inside magnet was a football-shaped, Teflon-coated magnetic stirrer bar which could slide freely inside the cell. The outside magnet was a Teflon sleeve with magnetic stirrer bars. The sleeve was moved up and down by the air piston. The motion pattern was controlled by relays and valves. The two phases were mixed during each stroke. A portion of the liquid was carried upward and dripped down during the upward stroke and splashed into the vapor space during the downward stroke. The agitation was very effective, as indicated by the rapid decrease in the pressure
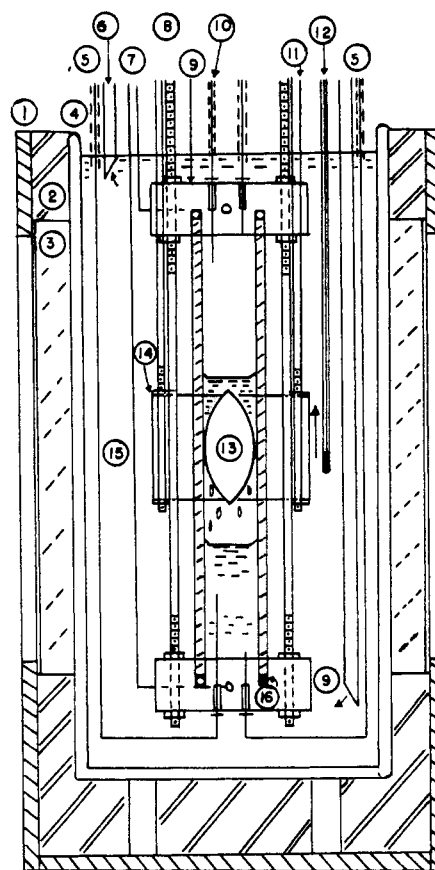

Figure 2. Equilibrium cell assembly

1.	Aluminum tank	10.	Gas sampling line
2.	Glass fiber insulation	11.	Connecting rod between
3.	Glass window		outside magnet and piston
4.	Glass jar	12.	Thermometer
5.	Liquid sampling line	13.	Inside magnet
6.	Circulating fluid outlet	14.	Outside magnet
7.	Thermocouple	15.	Silicone bath fluid
8.	Tie rod	16.	O-ring
9.	Tantalum top closure		
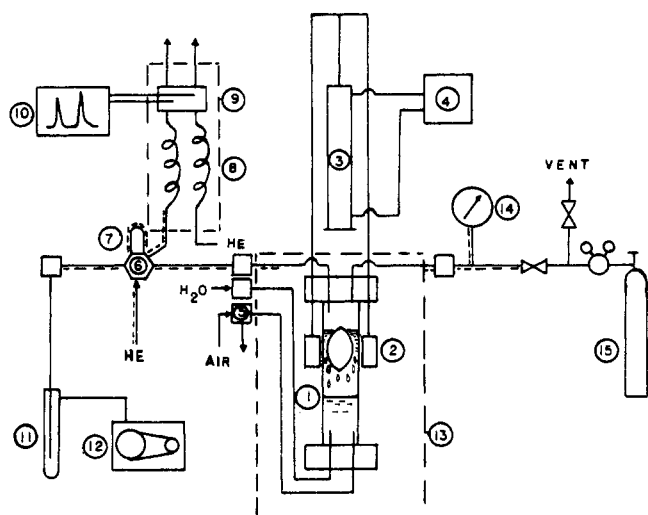
Figure 1. Schematic flow diagram of vapor-liquid equilibrium apparatus

1.	Equilibrium cell	9.	T. C. detector
2.	Magnetic agitator	10.	Recorder
3.	Air piston	11.	Cold trap
4.	Control relay assembly	12.	Vacuum pump
5.	Liquid sampling valve	13.	Thermostat
6.	Gas sampling valve	14.	Heise pressure gage
7.	Gas sample loop	15.	HCl gas cylinder
8.	Column	☐.	Teflon valve
		—.	Heated Teflon capillary tubing

during the first few strokes. The outside magnet also agitated the bath fluid.

The cell was immersed totally in a silicon oil or ethanol bath which consisted of an inner glass jar and an outside aluminum tank. The tank was a protection in the event of cell rupture. Slots were cut vertically in the front and back of the tank wall to allow for visual observation. A small lamp behind the slot window illuminated the whole cell.

The cell was designed for 500-p.s.i.a. working pressure. One cell was tested up to 1000 p.s.i.a. without leakage. It finally ruptured at 1200 p.s.i.a. Throughout this project, the cell was operated under 250 p.s.i.a., well below the bursting pressure.

The temperature of the bath was controlled by a constant temperature circulator. The sensitivity is 0.005° C. The control pattern is proportional. A heat exchanger with ice or dry ice was used for the isotherms below the room temperature.

GAS CHROMATOGRAPH. The basic gas chromatographic unit was a modified Varian Model 202-1B with dual columns, dual T. C. detectors, and regular WX filaments. Modifications included replacement of the regular metallic parts, such as columns, detector block, and outlet tubes, by Teflon parts, so that the flow system from injection

valve to outlet was in contact only with Teflon and Kel-F. Errors due to the reaction of HCl and adsorption of water by the system wall were thus minimized. Although the filaments were not Teflon-coated, they were made of rhenium-tungsten which resisted HCl attack well.

A single pen recorder equipped with a disc integrator was used for peak tracking and integration.

The columns were $\frac{1}{8}$-inch o.d., 8-foot-long Teflon tubing packed with 100- to 120-mesh Porapak R (8). It was packed with a pressure packer and tapped to provide a solid packing fill. After packing, the columns were installed and preconditioned for 2 hours at 230°C. to remove trace amounts of residue.

The Porapak R separates water and HCl well, although the latter peak is skewed and shows a tail. Increase in temperature and flow rate usually reduces the degree of skewness. The elution of HCl was very slow. A trace amount of HCl continues to be present in the carrier gas even though the recorder pen has returned to the base line. The water peak will tail badly and sometimes shift the base line if the carrier stream is not free of HCl. However, the peak height was not affected. Therefore, after the area of the water peak had been taken for the first injection, the areas of the water peak in the successive injections were obtained from the peak height. The calibration is given in Appendix A (filed with ASIS).

The adsorption problem was solved by the injection of a pure hydrogen chloride sample before injection of the sample mixture.

The optimum flow rate for the $\frac{1}{8}$-inch column was about 20 cc. per minute. The oven temperature was set at 100°C., the injector at 125°C., and the detector at 140°C. The filament current was 175 ma. The retention time was 3.5 minutes for water and 10 minutes for hydrogen chloride.

The column performed well for the gas sample with trace amount of water. For liquid samples, water was always present in excess and the separation efficiency became poor because of tailing. A more accurate titration method was therefore used to determine the liquid phase composition.

SAMPLING SYSTEM. It is believed that in most vapor-liquid equilibrium studies, errors are introduced by poor sampling techniques rather than an inaccurate analysis method. Such error sources as contamination, reaction, partial evaporation, and/or condensation are common. Emphasis is placed here on having a direct sample injection system, so that the sample is kept at the same conditions as in the equilibrium cell and is in contact only with Teflon and Kel-F.

The vapor sampling system consists of two Chromatronix type CAV valves with 0.031-inch bore and one Chromatronix sample injection valve. Teflon tubings $\frac{1}{32}$ inch in i.d. were used to connect the sampling train to the cell at one end and to the vacuum pump at the other. The sample loop is a piece of $\frac{1}{32}$-inch i.d. Teflon tubing of various lengths from 6 to 12 inches to give the necessary sensitivity. The internal volume is about 75 μl. for a loop 6 inches long. The sampling line, including the loop, was heated to 5°C. above the system temperature. The temperature was controlled by a temperature controller. The thermocouple tip was placed at the sample loop. The heating cycle was regulated by the adjustment of a Powerstat. The sampling line was not heated for isotherms below room temperature.

The sample injection valve at loading positions allows carrier gas to flow through a dummy loop, while the sample flows through the sample loop. By pushing to the injection position, the sample loop is connected in series to the carrier stream.

A Chromatronix three-way valve was used as a sampling valve to obtain a liquid sample for titration. One inlet of the valve was connected to the equilibrium cell and the other to the compressed air source. The outlet was

a piece of $\frac{1}{32}$-inch i.d. Teflon tubing about 6 inches long. At the closing portion, air flowed from the inlet to the outlet. At the loading position, the sample flowed from the other inlet to the outlet. The remaining sample in the outlet line was blown out when the valve was returned to the closing position.

AUXILIARY EQUIPMENT. A Heise pressure gage of 250 p.s.i. was connected to the equilibrium cell for measuring pressure. The pressure is readable to 0.25 p.s.i. The Bourdon tube was filled with mercury to prevent corrosion by hydrochloric acid. A mercury reservoir was used with the gage to damp out pressure surges.

Five thermometers, $-30°$ to $30°$, $-5°$ to $25°$, $30°$ to $50°$, $45°$ to $75°$, and $70°$ to $100°$C., were used to measure the temperature. The thermometer was immersed half way in the bath and about 1 inch from the cell. The lowest and highest temperature thermometers were checked in an ice bath and in boiling water, respectively. The others were checked against these two over the range that overlapped.

A vacuum pump with a liquid nitrogen trap was connected to the sampling and charging system.

Operational Procedures. The equilibrium cell was cleaned, dried, assembled, and pressure-tested to 250 p.s.i.a. The constant temperature bath was then raised and set at the desired temperature. The system was evacuated overnight and flushed several times with the gas to be tested. About 20 cc. of water were charged through the liquid sampling line. The gas was then charged through the gas charging line. The magnetic agitator was started. The pressure dropped until the equilibrium value was reached. Both pressure and temperature were recorded. The agitator was stopped and the system was ready for sampling and analysis, which were repeated until reproducible results were obtained. If the results showed a continuous decreasing or increasing trend, the system was approaching equilibrium, and further agitation was needed. After the results became reproducible, the liquid sample was taken as follows.

About 20 cc. of distilled water were charged into a 25-ml. glass volumetric flask. The total weight of the flask and water was determined on a four-place microbalance. The outlet of the three-way sampling valve was then placed below the water level. The valve was pushed slowly to the charging position. A liquid sample was pushed out by the system pressure and dissolved immediately in the water. After collecting about 2 or 3 cc. of sample, the valve was pushed back. Air from another inlet now forced the acid droplets into the collecting flask, which was weighed again. The amount of HCl was titrated with 0.1N standardized sodium hydroxide solution with phenolthalein as an indicator.

Precision and Accuracy. The accuracy and control sensitivity of the constant temperature circulator were $\pm0.004°$ and $\pm0.002°$C., respectively. The actual bath temperature was controlled within $\pm0.02°$C. of the desired value. The thermometers, both mercury in glass and platinum resistance, are readable to $\pm0.02°$C. and calibrated to the ice point and boiling point of water. The uncertainty in calibration was about $\pm0.02°$C. The measured temperature is believed to be within $\pm0.04°$C. of the stated value. The temperature gradient along the cell was checked. No detectable temperature difference was found.

The Heise pressure gage was originally calibrated by the manufacturer against a dead weight gage calibrated to the NBS standard. The pressure gage is graduated at 0.25 p.s.i.a., readable to 0.15 p.s.i.a.

In summary, the relative precision and accuracy for composition analysis by gas chromatograph are of the following order: water, $\pm0.5\%$; and HCl, $\pm2\%$. There is no simple way to estimate the magnitude of errors other than those due to analysis, such as those due to nonequilibrium state, poor sampling, etc. The reproducibility, however, approached the relative error stated above. The precision

of the data should be based on thermodynamic considerations.

For aqueous hydrochloric acid, titration gives much more reliable results than the gas chromatographic method. The error of the former method is less than ±0.2% and the reproducibility was better than ±0.4%. The reproducibility of the latter method was about 15%. All liquid phase compositions were determined by the titration method.

RESULTS AND DISCUSSION

The experimental vapor-liquid equilibrium compositions were measured at −10.0°, 10.0°, 30.0°, 50.0°, and 70.0° C. with pressures up to 222 p.s.i.a. (Table I).

The typical bubble point-dew point of this system is shown in Figure 3 for the 50.0° C. isotherm by combining with published data (3, 5, 10, 13, 15).

The liquid phase composition at 30.0° C. is plotted against pressure in Figure 4 for comparison. The results of this study can be extrapolated smoothly to the low pressure data of Fritz and Fuget (3) and Zeisberg (15) and the high pressure data of Rupert (13). The agreement between this study and Thumm's work (5) is fair—for example, at 30° C., 190 p.s.i.a., his results are about 2.5 mole % HCl lower. A similar discrepancy (5% lower) was found for the 10.0° C. isotherm. No such comparison can be made for −10.0°, 50.0°, and 70.0° C. isotherms. However, the results of this investigation can be extrapolated very well to Zeisberg's (15) low pressure compilation and Rupert's (13) phase separation data.

The volatility of water over hydrochloric acid decreases with increasing pressure and/or decreasing temperature. The vapor phase is essentially pure hydrogen chloride. There are no published vapor phase data for comparison over the temperature and pressure range studied. However, this result can again be extrapolated very well to the low pressure vapor phase composition of Zeisberg (15) and Fritz and Fuget (3). A typical plot is shown in Figure 5 for the 50.0° C. isotherm.
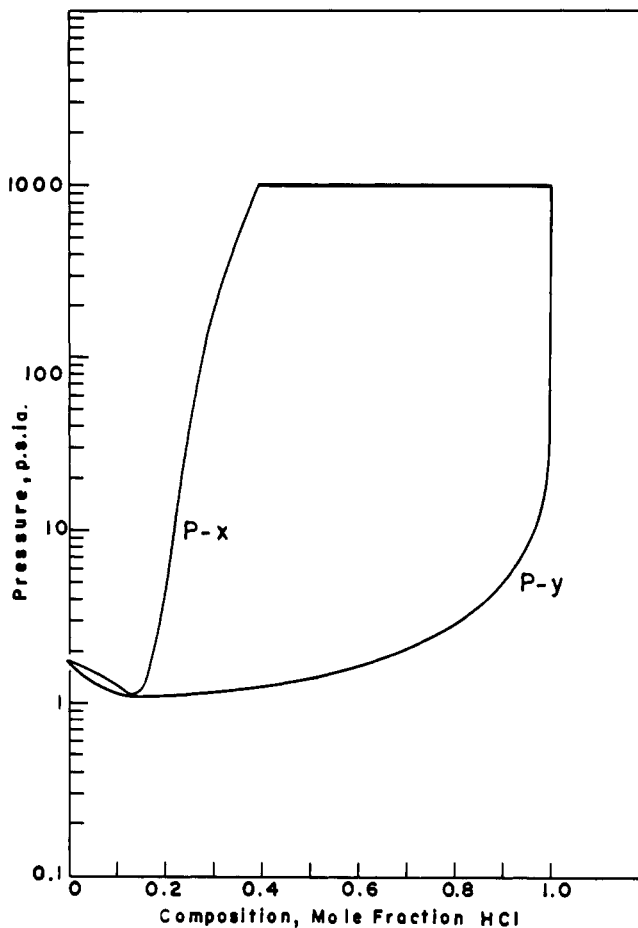

Figure 3. Vapor-liquid equilibrium of H_2O-HCl at 50.0° C.

The idealized vapor phase composition can be calculated with the Gibbs-Duhem equation from the liquid phase composition (Figure 5). The calculated values are lower than the experimental values, as expected. The detailed calculation is given in Appendix B.

Interaction Second Virial Coefficients. It is desirable to make a thermodynamic consistency check of the experimental vapor-liquid equilibrium data. However, such a check is not possible because of lack of precise P-V-T data for the system. If a virial equation of state up to the second term is used, the second virial coefficient of the mixture has to be known (12). There is a reasonable amount of data on the second virial coefficient of pure water (4, 7, 9) and pure hydrogen chloride (2, 7, 14), but the interaction second virial coefficient (B_{12}) for these two substances has not been determined. Instead, the B_{12} value can be calculated if we assume that the data are consistent. This actually provides an easy method to determine the interaction second virial coefficients for this and other similar systems.

For a binary mixture at constant temperature, the Gibbs-Duhem equation is written

$$x_1 d \ln f_1 + x_2 d \ln f_2 = \frac{V^L dP}{RT} \qquad (1)$$

where index 1 stands for water and 2 for hydrogen chloride.

For the moderate pressure covered in this study, the pressure effect on the liquid phase is negligible. Equation 1 reduces to

$$x_1 d \ln f_1 + x_2 d \ln f_2 \cong 0 \qquad (2)$$

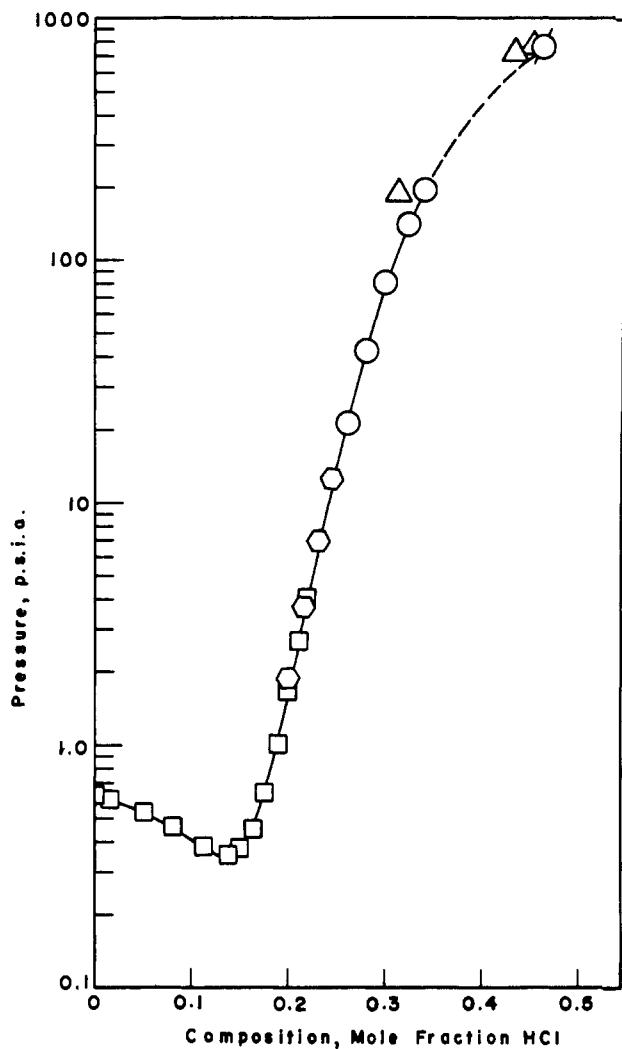On substituting $1 - x_2$ for x_1, rearranging, and integrating, Equation 2 becomes

Table I. Vapor-Liquid Equilibrium of H_2O-HCl System

Temp., ° C.	Pressure, P.S.I.A.	Liquid Composition, Mole Fraction HCl	Vapor Composition, Mole Fraction H_2O
−10.0	19.0	0.318	5.01×10^{-5}
	34.0	0.338	2.75×10^{-5}
	78.0	0.375	1.45×10^{-5}
	145.0	0.417	1.08×10^{-5}
	208.0	0.450	1.00×10^{-5}
10.0	15.5	0.279	8.70×10^{-4}
	29.0	0.299	4.30×10^{-4}
	55.0	0.322	2.38×10^{-4}
	95.0	0.346	1.52×10^{-4}
	200.0	0.386	9.40×10^{-5}
30.0	21.0	0.261	3.25×10^{-3}
	42.0	0.280	1.40×10^{-3}
	80.0	0.300	7.60×10^{-4}
	140.0	0.325	5.15×10^{-4}
	195.0	0.342	4.40×10^{-4}
50.0	22.0	0.238	1.41×10^{-2}
	41.0	0.250	6.80×10^{-3}
	83.0	0.271	3.40×10^{-3}
	141.0	0.290	2.20×10^{-3}
	222.0	0.310	1.61×10^{-3}
70.0	22.0	0.214	5.05×10^{-2}
	41.5	0.231	2.25×10^{-2}
	83.0	0.252	1.05×10^{-2}
	141.0	0.269	6.30×10^{-3}
	222.0	0.284	4.15×10^{-3}

Figure 4. Liquid composition of H_2O-HCl system at 30.0° C.

O This work   ⌀ Rupert (13)
□ Fritz and Fuget (3)   △ Thumm (5)
O Zeisberg (15)

Table II. Interacting Second Virial Coefficients of
HCl-H_2O System from V-L Equilibrium Data

Temp., °C.	Pressure, P.S.I.A.	B_{12}, Cc./Mole	$\overline{B}_{12}$, Cc./Mole
−10.0	60.0	−1530 ⎫	
	100.0	−1840 ⎬	−1643
	200.0	−1570 ⎭	
10.0	60.0	−1345 ⎫	
	100.0	−1318 ⎬	−1317
	200.0	−1286 ⎭	
30.0	60.0	−850 ⎫	
	100.0	−1075 ⎬	−1002
	200.0	−1080 ⎭	
50.0	60.0	−714 ⎫	
	100.0	−844 ⎬	−771
	200.0	−755 ⎭	
70.0	60.0	−468 ⎫	
	100.0	−572 ⎬	−524
	200.0	−532 ⎭	

$$\int d \ln f_1 = - \int \frac{x_2}{1 - x_2} d \ln f_2 \qquad (3)$$

The condition of consistency requires that the integral on the left-hand side be equal to that on the right-hand side when both are evaluated from the vapor-liquid equilibrium data. By definition, the fugacity is related to the vapor phase composition and pressure as follows:

$$f_i \equiv \phi_i y_i P \qquad (4)$$

where ϕ_i is the fugacity coefficient, defined as

$$RT \ln \phi_i \equiv \int_0^P \left(\overline{V}_i - \frac{RT}{P} \right) dP \qquad (5)$$

If a virial equation of state up to the second term is used, the compressibility is

$$Z = \frac{PV}{RT} \cong 1 + \frac{B}{V} \qquad (6)$$

where

$$B = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22} \qquad (7)$$

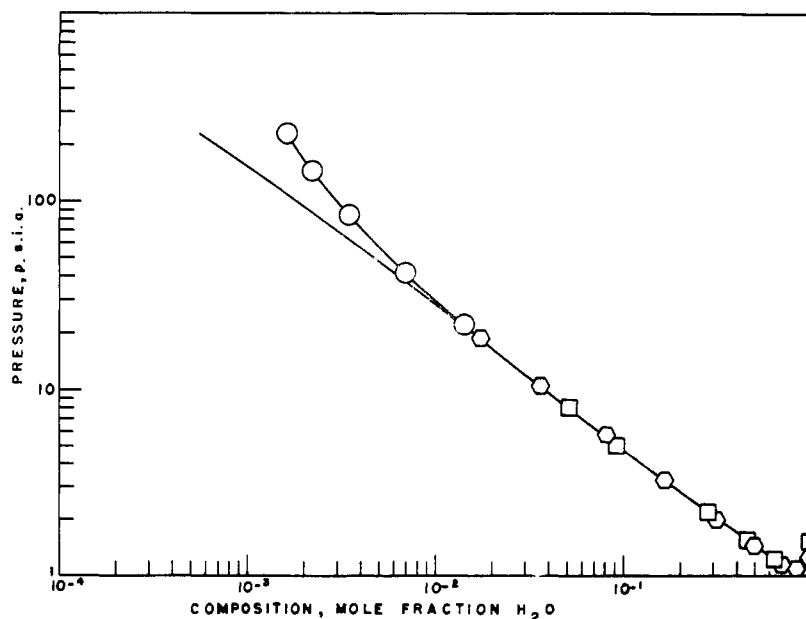To integrate Equation 5, a volume-explicit equation of

Figure 5. Vapor composition of H_2O-HCl system at 50.0° C.

O This work   □ Fritz and Fuget (3)
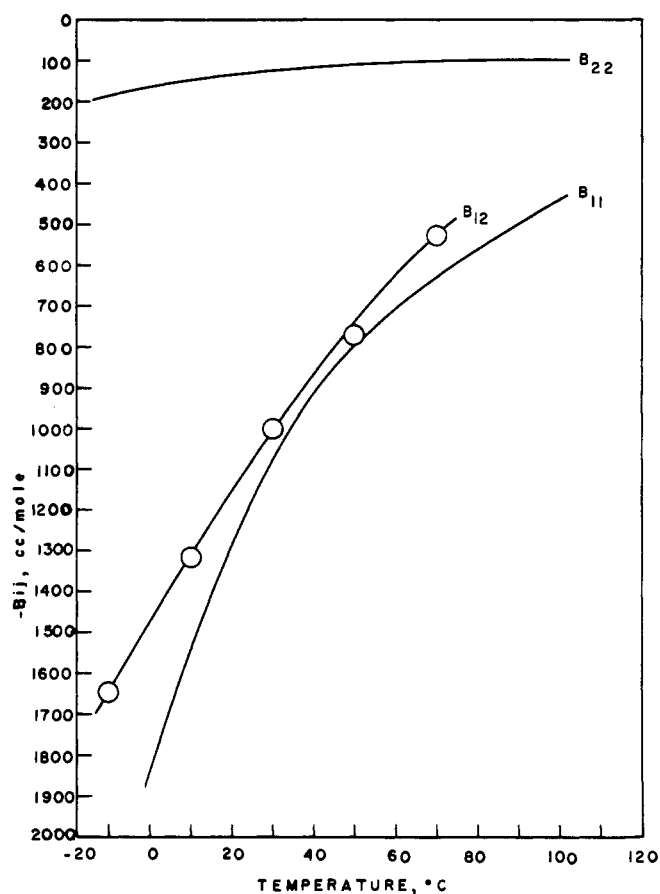O Zeisberg (15)   ▬ Calculated from Gibbs-Duhem equation with ϕ H_2O = 1

Figure 6. Second virial coefficients of system HCl-H₂O

    ○ This work
    — B_{11} (4, 9)
    — B_{22} (2, 14)

P-V-T data of pure hydrogen chloride (2, 14). If the data are assumed to be consistent, the fugacity of water can be calculated from Equation 3 with the liquid phase data given in Table I. From Equation 11, B_{12} is readily evaluated. Such calculations have been carried out for all isotherms and are illustrated in Appendix B for the 50.0° C. isotherm. The calculated B_{12} values are plotted in Figure 6 together with the second virial coefficients of water and hydrogen chloride (2, 4, 7, 9, 14).

From Equation 11 B_{12} is equal to a logarithmic function of the term $\phi_i Z$, which is related to the experimental composition. When the $\phi_i Z$ value is close to but less than unity, any error in composition is magnified in the B_{12} value—for example, 5% error in the vapor composition at 50.0° C., 60 p.s.i.a., results in a 24% error in the calculated B_{12} value (cf. Appendix). Nevertheless, a comparison of B_{12} value with both B_{11} and B_{22} is generally in favor of the consistency of the data as shown in Figure 6.

NOMENCLATURE

B_{ii} = second virial coefficient of pure component, cc./mole
B_{ij} = interaction second virial coefficient between species i and j, cc./mole
f_i = fugacity of species i, p.s.i.a.
i = index
j = index
n = number of moles
P = pressure, p.s.i.a.
ϕ = vapor phase fugacity coefficient
R = gas constant
T = temperature, ° K.
V^L = liquid molal volume, cc./mole
V = vapor molal volume, cc./mole
$\bar{V}_i$ = partial molal volume of component i, cc./mole
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = compressibility of gas

state is required. Since Equation 6 is pressure-explicit, it is necessary to change the independent variable. The equivalent expression for Equation 5 in terms of V (12) is

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial p}{\partial n_i} \right)_{T, V, n} - \frac{RT}{V} \right] dV - \ln Z \quad (8)$$

or

$$\ln \phi_i Z = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial p}{\partial n_i} \right)_{T, V, n} - \frac{RT}{V} \right] dV \quad (8a)$$

Substituting Equations 6 and 7 into 8a and carrying out the integration, we have

$$\ln \phi_i Z = 2/V \, (y_1 B_{i1} + y_2 B_{i2}) \qquad i = 1 \text{ and } 2 \quad (9)$$

Experimental values of Z should be used in Equation 9 if they are available. Otherwise, Z can be estimated from the second virial coefficients as follows:

$$Z \cong \frac{1}{2} + \left(\frac{1}{4} + \frac{BP}{RT} \right)^{1/2} \quad (10)$$

Equation 10 is obtained by solving a quadratic equation in Z resulting from substituting $V = ZRT/P$ into Equation 6.

For the water–hydrogen chloride system under the conditions studied, $y_1 \ll y_2 \cong 1$, Equation 9 can be approximated as

$$\ln \phi_1 Z \cong 2B_{12}/V \quad (11)$$

and

$$\ln \phi_2 Z \cong 2B_{22}/V \quad (12)$$

Since the vapor phase is essentially hydrogen chloride, its fugacity in the mixture can be calculated from the

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