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THE VAPOR PRESSURE OF SALT - HCL - WATER SOLUTIONS BELOW 0C.(U)
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"A School of Mineral Resources"
UNIVERSITY OF NEVADA, RENO
RENO, NEVADA 89557

Department of Chemical & Metallurgical Engineering

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THE VAPOR PRESSURE OF SALT - HCl - WATER SOLUTIONS BELOW 0C

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Work Performed by: E. Miller

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Contract: Grant AFOSR - 77 - 3333

Prepared for: AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (NA)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Vapor-liquid equilibria data forhydrochloric acid solutions,composition from 7.07 to 37.24 wt pct HCl at temperatures between 0 & -40C, saturated with sodium chloride are presented. Solubility and solution densities are reported. Evidence obtained for the formation of a solid NaCl hydrate in equilibrium with the saturated solutions. Quadrupole mass filter sensitivity factors of water to HCl determined and agree with thermodynamic predictions to -4 to + 14 pct.

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ABSTRACT

Vapor-liquid equilibria data for hydrochloric acid solutions, composition from 7.07 to 37.24 wt pct HCl at temperatures between 0 and -40C, saturated with sodium chloride are presented. Solubility and solution densities have also been measured and are reported. Evidence has been obtained for the formation of a solid NaCl hydrate in equilibrium with the saturated solutions in the temperature range of -7 to -25C. Quadrupole mass filter sensitivity factors of water to HCl have been determined experimentally and agree with previous thermodynamic predictions to -4 to +14 pct.

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INTRODUCTION

The equilibrium vapor pressures of hydrochloric acid solutions are important to the modelling of secondary smoke in reduced smoke ammonium perchlorate solid propellant rocket plumes, ref 1, since the growth of the acid smoke droplets is dependent on their equilibrium pressure. In addition, the behavior of strong electrolytes in aqueous solution is of fundamental interest. No data were available for hydrochloric acid below 0C prior to the measurements made by the principal investigator at the University of Nevada, Reno under the sponsorship of AFOSR. The experimental effort during the last two years has been directed toward the measurements of the vapor pressure of hydrochloric acid solutions saturated with NaCl. The pure acid measurements were reported in ref 2.

It is known that inorganic salts dissolved in hydrochloric acid will significantly modify its equilibrium vapor pressure due to their effects of the activities of the HCl and water in the liquid phase, ref 3. The change in the vapor pressure will in turn affect the formation of the secondary smoke, refs 4, 5. The major contaminants found in manufactured ammonium perchlorate are sodium and potassium salts. Tricalcium phosphate is added to the ammonium perchlorate in propellant processing, providing a major source of soluble electrolyte. All these are present in sufficient quantity in the plume to nucleate the formation of secondary smoke, and to subsequently influence the dynamics of formation of the smoke droplets. Typically there are approximately 0.2 wt pct of tricalcium and 200 ppm of sodium cation in the ammonium perchlorate. Assuming that the average condensation nucleus radius is 0.06 micron, ref 6, the number of nuclei emitted from a typical reduced smoke rocket as $CaCl_2$ may be estimated to be 3.6×15 per sec ft^2 and 1.2×13 per sec ft^2 as NaCl. Reference 1 reports 8.4×14 per sec ft^2 measured for such a reduced smoke rocket. Although the calculation is approximate, there is clearly sufficient salt present in the rocket plume to nucleate the observed secondary smoke. Inclusion of other soluble salts by entrainment in the plume from the atmosphere are relatively small. Other sources of soluble salts found in the propellant formulation include ballistic modifiers and combustion resonance suppressors. If iron and copper modifiers are avoided, none of the others commonly used will provide salts soluble enough in hydrochloric acid to produce major effects on its vapor pressure. The choice of NaCl and $CaCl_2$ as the salts for the study were based on these practical considerations as well as for the

scientific implications.

Data are available for the activities of NaCl-HCl-water solutions for 0 to 50C, ref 3, permitting predictions of vapor pressure over this temperature range. The present grant research covers the range below 0C to -40C. Less data exist for $CaCl_2$-HCl-water but only the 0 to -40C range is being studied since this range is more important from a smoke viewpoint. Further, the experimental equipment is most suitable for this range. The $CaCl_2$ solution studies have been initiated but it is too early to report any results at this time.

EXPERIMENTAL

As shown schematically in Figure 1, a 2 liter Pyrex flask is immersed in an insulated methylene chloride bath cooled by a two-stage mechanical refrigeration system. The temperature of the bath is held within ± 0.1C, monitored by a calibrated platinum resistance thermometer. Removal of air from the system is accomplished by a mechanical vacuum pump in series with a liquid nitrogen trap. Pressures are measured with two MKS Baratron Type 220 gauges (10^{-04} to 1 torr, and 10^{-02} to 10^{2} torr) calibrated by the manufacturer by means of a transfer standard and a CEC air deadweight tester to ±0.02 pct of full range. The acid is separated from the salt by distillation in a closed glass system. Samples of the distilled acid and the salt dissolved in water are analyzed to ±2% maximum standard deviation using a Barnstead Model PM-70CB electroconductivity bridge, a Yellowstone YSI 3400 Pyrex cell, and standard solutions.

Vapor compositions are measured for samples drawn from the vapor chamber into a Varian VGA-100 quadrupole mass filter. The ratio of partial pressures of water to HCl is determined from the recorded mass spectra in the range of 14 - 20 and 34 - 40 mass numbers. The spectra are obtained at mass filter pressures of approximately 3.0 -06 torr, sampling continuously from the vapor chamber open to the solution flask, and pumping on the mass filter with a Varian 20 liter per sec Vacion pump. As described in ref 2, the relative sensitivity of the instrument to water and HCl was determined to be 3.95 from thermodynamic analysis of the data near the azeotrope. Independent sensitivity measurements described below have been made which are 4.2% lower to 13.9% higher depending on the composition of the gases.

All valves and fittings are made of AISI 304 and 315 steel. Viton O-rings and copper gaskets are used in the valves and fittings. All metal parts in continuous contact with

acid vapor are coated with Dow vacuum grease. No significant corrosion of metal parts has been experienced.

The experimental procedure followed is:

(1) The solution is cooled to the desired temperature over night or longer. The whole system is then pumped down to a pressure below the range of the Baratron gauges. The solution itself is deaerated by slowly opening the flask to the evacuated vapor chamber, allowing the system to reach equilibrium, reisolating the flask and repumping down the vapor chamber - repeating the cycle at least five times before taking any data.

(2) The flask valve is opened slowly to the evacuated vapor chamber to avoid violent boiling and splattering, and the pressure measured as a function of time over at least a fifteen minute period. Measurements are repeated five or more times. Small corrections for minor leaks are made from the slope of the vapor pressure - time curve.

(3) Subsequently, mass spectrographic analyses are made by bleeding samples of gas from the vapor chamber into the gas analyzer. Measurements are made at 15 minute intervals until equilibrium is established. Small corrections are made for background water and HCl in the gas analyzer. The mass filter is pumped down below 1. -08 torr before introducing the gas samples to minimize background spectra.

(4) A sample of the liquid solution is taken after each test sequence, and the acid separated from the salt by distillation. Acid samples are subsequently diluted by 50 to 200 to 1 depending on the initial concentration. The salt recovered is dissolved in 20 ml of distilled water. The conductivity of the acid samples is compared with those of certified N/30 and N/10 standards. Salt solution conductivity is compared with standardized 0.0025, 0.005, 0.04 and 0.1N solutions made up from reagent grade sodium chloride and distilled water.

RESULTS

A. Relative Sensitivity of Water to HCl of Quadrupole Mass Filter

As described in ref 2, the relative sensitivity was determined to be 3.95 from a comparison of experimental vapor liquid equilibria data of pure hydrochloric acid solutions near the azeotrope with thermodynamic predictions using the Gibbs-Duhem equation and total pressure - liquid composition data. T he prediction was necessarily based on limited data and it was decided to modify the experimental equipment to measure the sensitivity directly. Pure HCl or water vapors were introduced directly into the mass filter and the relative

sensitivity measured over a range in instrument pressures - 0.2 -07 to 3.0 -06 torr. By comparing the spectral areas of water and HCl at the same pressure, the relative sensitivity was obtained as a function of partial pressure of HCl. The data for HCl and for water were each correlated by least square deviation to a linear correlation of area and pressure. No significant decrease in deviations resulted from using a second or third order polynomial, although a better correlation was obtained when the data below 1. -06 were correlated separately. The resulting correlations were as follows:

$P \leq 1.0\text{-}06$:

$p_{HCl} = 1.177\text{-}05\ A_{HCl} - 1.651\text{-}07,\ \sigma = 1.\text{-}07$ torr

$p_{H_2O} = 2.493\text{-}05\ A_{H_2O} - 1.325\text{-}07,\ \sigma = 6.\text{-}08$

$P \leq 3.0\text{-}06$:

$p_{HCl} = 9.758\text{-}06\ A_{HCl} - 3.258\text{-}08,\ \sigma = 2.\text{-}07$

$p_{H_2O} = 2.446\text{-}05\ A_{H_2O} - 1.171\text{-}07,\ \sigma = 3.\text{-}07$

The measurements were made for a detector sensitivity of 10^{-10} and 10^{-09} amp/div for HCl and water respectively with a three second sweep at a recorder setting of 1V full range at a chart speed of 1 in/sec.

The relative sensitivity of water to HCl, F, calculated from these correlations is shown in Figure 2 as a function of p_{HCl} in the mass filter. The factor previously derived from the Gibbs-Duhem equation is 4.2% higher to 13.9% lower than the factors in Figure 2 for the range of measurements. All vapor data obtained have now been corrected for the new sensitivity factors. They are used in a paper to be submitted for publication reporting on the results of the pure HCl solutions.

B. NaCl-HCl-Water Solutions

(1) Thermodynamic Consistency Equations

A thermodynamic consistency equation based on the Gibbs-Duhem equation has been derived for the salt-acid solutions analogous to the one previously used for the pure solutions:

$$dP'/dy' = P'(y_1' - x_1')/(y_1'(1 - y_1') - (P'x_3'/a_3)da_3/dy' \quad (1)$$

where a_3 = activity of the salt in solution

x_1' = $x_1/(x_1 + x_2)$

x_3' = $x_3/(x_1 + x_2)$

x_1, x_2, x_3 = mol fractions of HCl, water and salt in liquid phase

y_1' = mol fraction of HCl in vapor phase

P' = total equilibrium vapor pressure of salted solution

For these solutions, the composition of the vapor phase cannot be predicted solely from the total pressure and the liquid phase mol fractions, as was the case for the pure solution. However equation (1) does permit the computation of the activity of the salt in solution. Correlation of the excess free energy calculated from the activity coefficients by a polynomial expression can be thermodynamically tested for major discrepancies. Additionally, the Setschenow equation,

$$S_1 = p_1'/p_1 = y_1'P'/y_1P = \exp(k_s C_s) \qquad (2)$$

can be used to test the experimental partial pressure data of the salted solutions, p_1', compared with that of the pure solution, p_1, for the same ratio of HCl to water with increasing salt concentration, C_s. k_s is a salt coefficient and y_1 the vapor mol fraction for the pure solution.

(2) Experimental Results

a) Vapor-Liquid Equilibria

The vapor pressures for saturated solutions are given in Figures 3 through 5 for the nominal temperature range of 0 to -40C. Previous measurements for saturated concentrated hydrochloric acid (12N at room temeperature) and for the 6N solution (at room temperature) were repeated because of suspect results. The total pressure measurements repeated very satisfactorily, confirming the precision of the measurements. The partial pressures of HCl are higher (and the partial pressures of water lower) for the 6N solution than obtained originally. Also the measured composition of the liquid phase for the concentrated solution is higher. The results are now more consistent with the results for lower acid concentration.

b) Solubility of NaCl in Hydrochloric Acid

Solubility data are only available in the literature for approximately room temperature. Last year's report, ref 2, presented early data for solutions below 0C. Additional, more complete data has since been obtained. In Figure 6 are presented the experimental solubility data for NaCl in gmol per 1000 g H_2O as a function of acid composition and temperature.

c) Density of NaCl-HCl-Water Solutions

In order to express the solubility independently of temperature, as a mol fraction or molality, density values are needed. No data could be found for saturated solutions below 20 - 30C. A series of measurements was made with Gay-Lussac 2 ml and 10 ml pycnometers. Vaporization of the solutions was minimized by the use of capillary caps and by rapid weighing. The results are precise to 1 mg/ml. They are given in Figure 7 compared with the literature data for salted and pure solutions. The salt solution densities are significantly

different
/from pure HCl solutions for acid concentrations more dilute than 7M.

DISCUSSION

A. Vapor-Liquid Equilibria

In all solutions, the salt increases the equilibrium partial pressure of HCl and decreases the partial pressure of water. The effect of the NaCl is greater in less concentrated acid since the amount of salt dissolved is one to two orders of magnitude larger than for the more concentrated solutions. It is interesting to note that in a salted solution, the liquid composition at which the minimum total pressure occurs does not necessarily correspond to equal vapor and liquid composition, as it does for pure solutions. An examination of equation (1) indicates why this is so, i.e. the activity of the salt in solution is a significant factor in the change of total pressure with composition. Experimentally, Figures 4 and 4a show partial pressures of HCl at x_{HCl} of 0.1101 to be higher than for x_{HCl} of 0.1475 for example. For pure acid solutions, the partial pressure of HCl decreases regularly with a decrease in liquid acid mol fraction.

B. Solubility of NaCl in Hydrochloric Acid

The general decrease in solubility of NaCl with increasing acidity as shown in Figure 6 is expected. The change in the solubility characteristic at lower temperatures for a fixed acid composition, i.e. the appearance of a maximum in solubility was surprising. It suggests the formation of $NaCl \cdot nH_2O$ with n most likely to be 1 or 2 as is known for equilibrium salt-water solutions below 0C. The temperature at which the salt hydrate forms varies with the acid concentration. The data suggest that the lowest temperature for formation of the salt hydrate occurs near the minimum pressure composition.

The formation of the salt hydrate had no significant effect on the partial pressures of HCl and water. However, in secondary smoke formation, the hydrate will be another sink for water condensation in the plume, partially compensated by a temperature rise of the droplet due to the heat of hydration.

FUTURE PLANS

(1) Complete the measurement of the equilibrium vapor pressures of the NaCl-HCl-water solutions for NaCl concentrations between zero molality and saturation for nominal acid compositions of 7 - 37 wt pct at temperatures between

0 and -40C.

(2) Conduct vapor-liquid equilibria measurements for hydrochloric acid solutions containing dissolved calcium chloride.

(3) Perform thermodynamic consistency tests on the salt-acid solution data. Repeat measurements as required. Extrapolate data thermodynamically to compositions which are beyond the capability of the experimental equipment.

(4) Submit a manuscript for publication in an archive journal for the NaCl-HCl-water solution vapor-liquid equilibria.

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(5) Miller, E., J.W. Connaughton & L.B. Thorn, "Measured and Predicted Laser Attenuation Through a Solid Rocket Plume." JANNAF Propulsion Meeting (1980)

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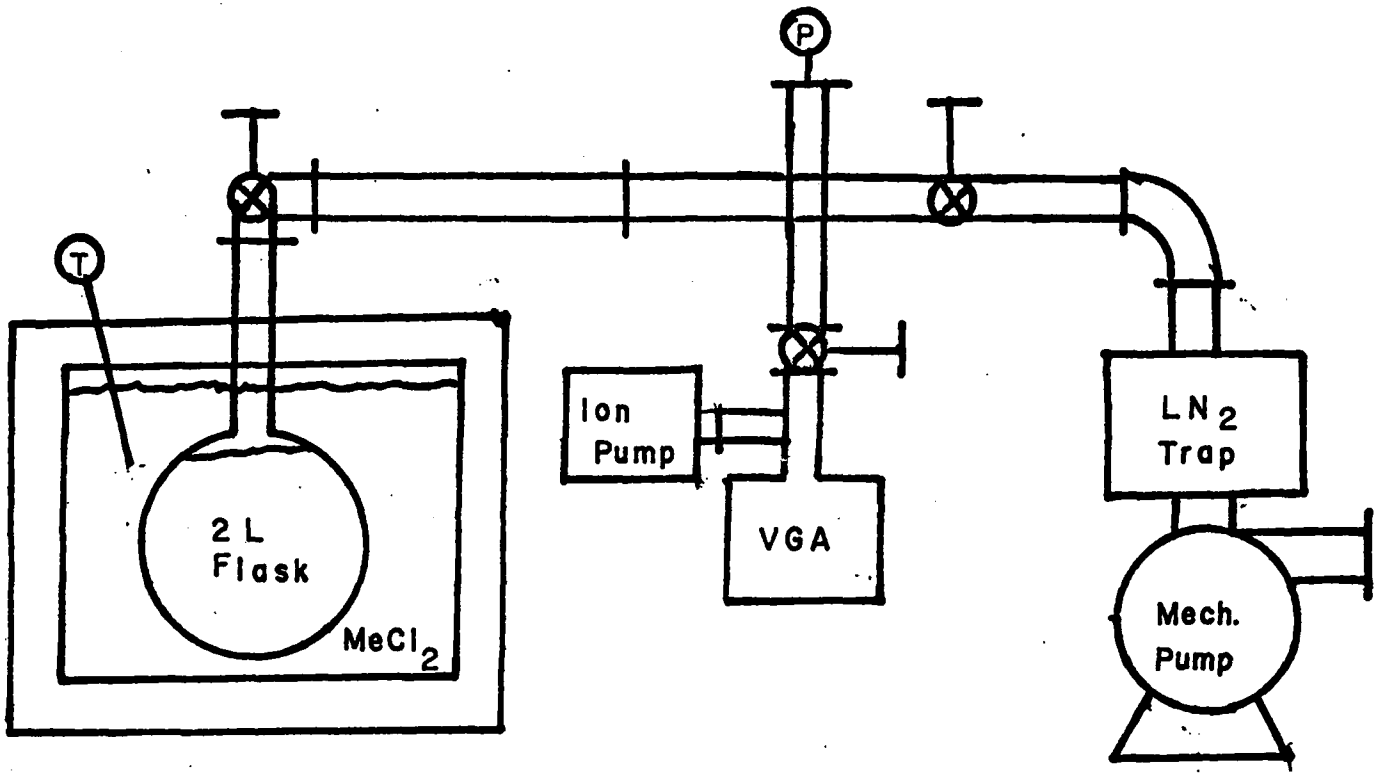

FIGURE I.

Schematic of Experimental Apparatus

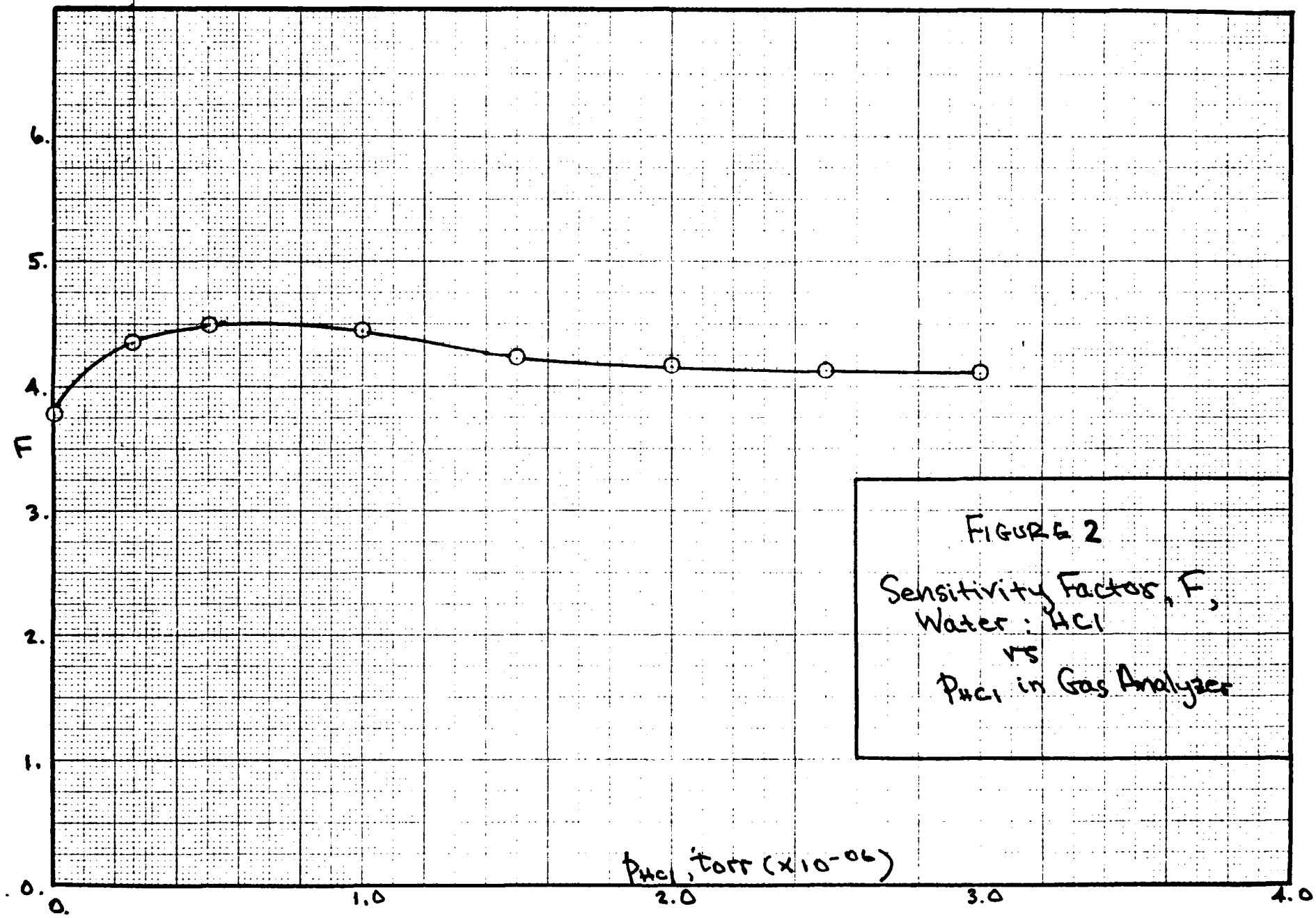

FIGURE 2

Sensitivity Factor, F,
Water : HCl
vs
p_{HCl} in Gas Analyzer

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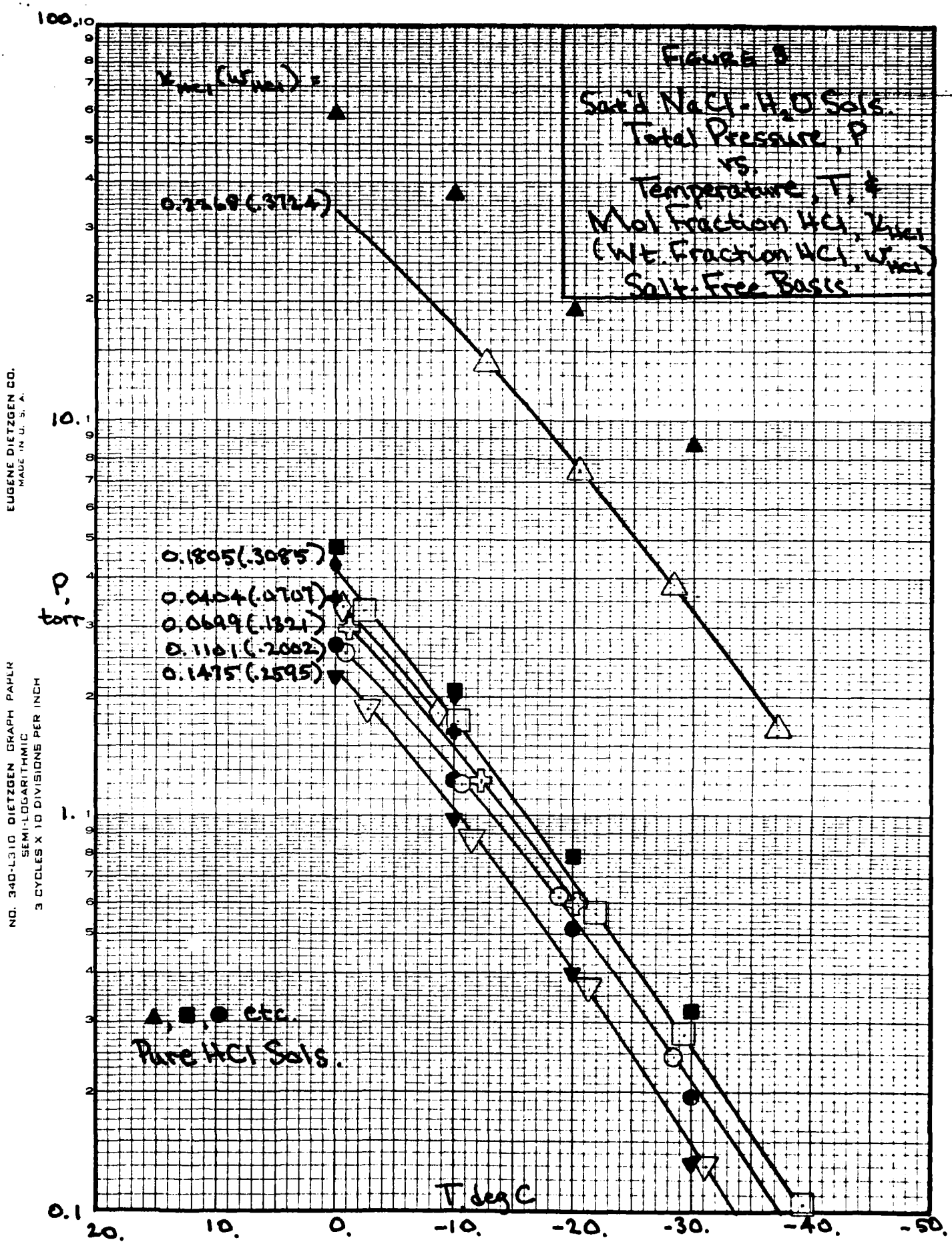
Figure 8
Sat'd NaCl-H2O Sols.
Total Pressure, P
vs.
Temperature, T, &
Mol Fraction HCl, xHCl
(Wt. Fraction HCl, wHCl)
Salt-Free Basis
xHCl (wHCl) =
0.2268 (.3724)
0.1805 (.3085)
0.0404 (.0707)
0.0699 (.1321)
0.1101 (.2002)
0.1475 (.2595)
▲, ■, ● etc.
Pure HCl Sols.
P, torr
T, deg C
100.
10.
1.
0.1
20.
10.
0.
-10.
-20.
-30.
-40.
-50.
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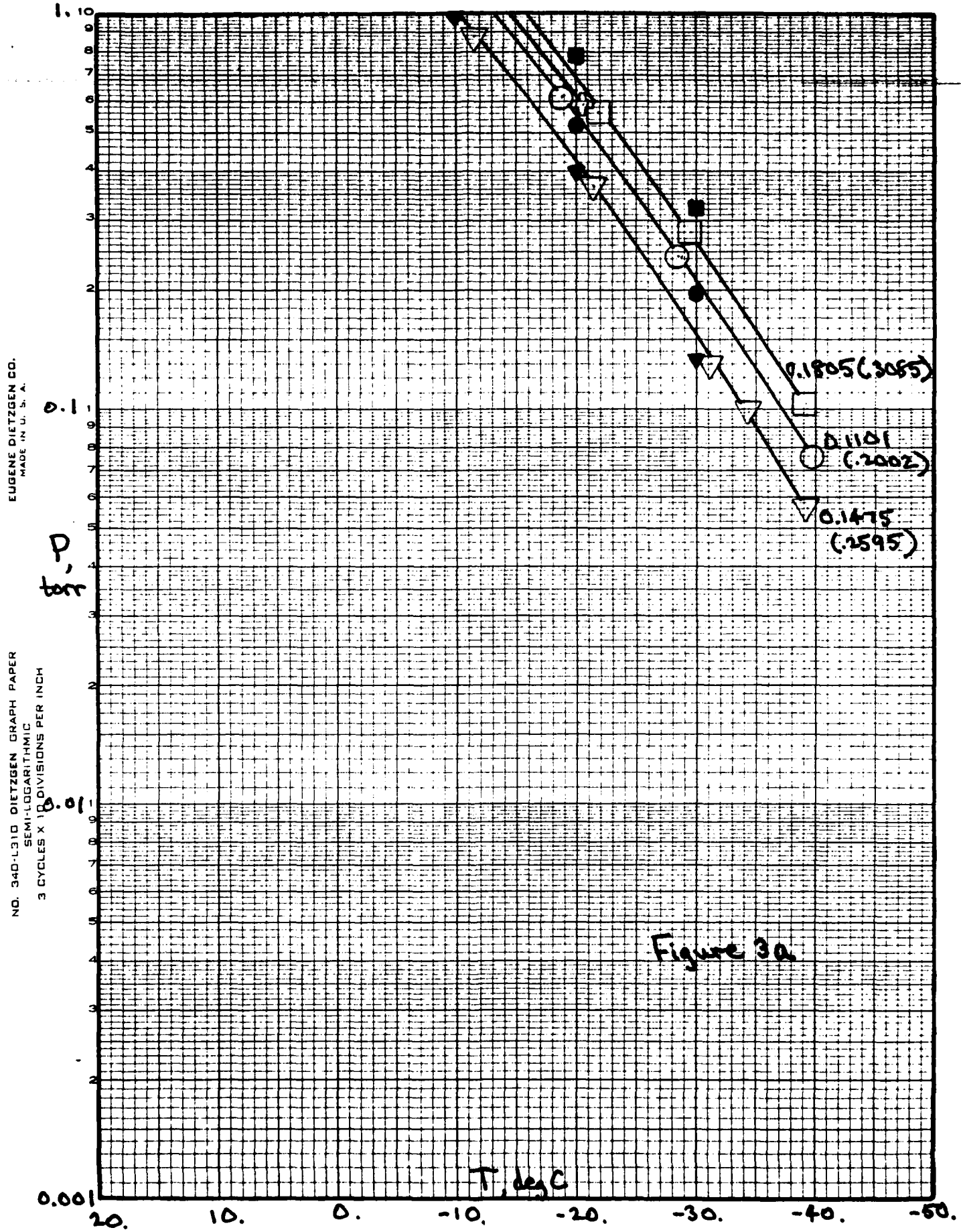
1.
0.1
0.01
0.001
P, torr
T, deg C
20.
10.
0.
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-50.
0.1805 (.3085)
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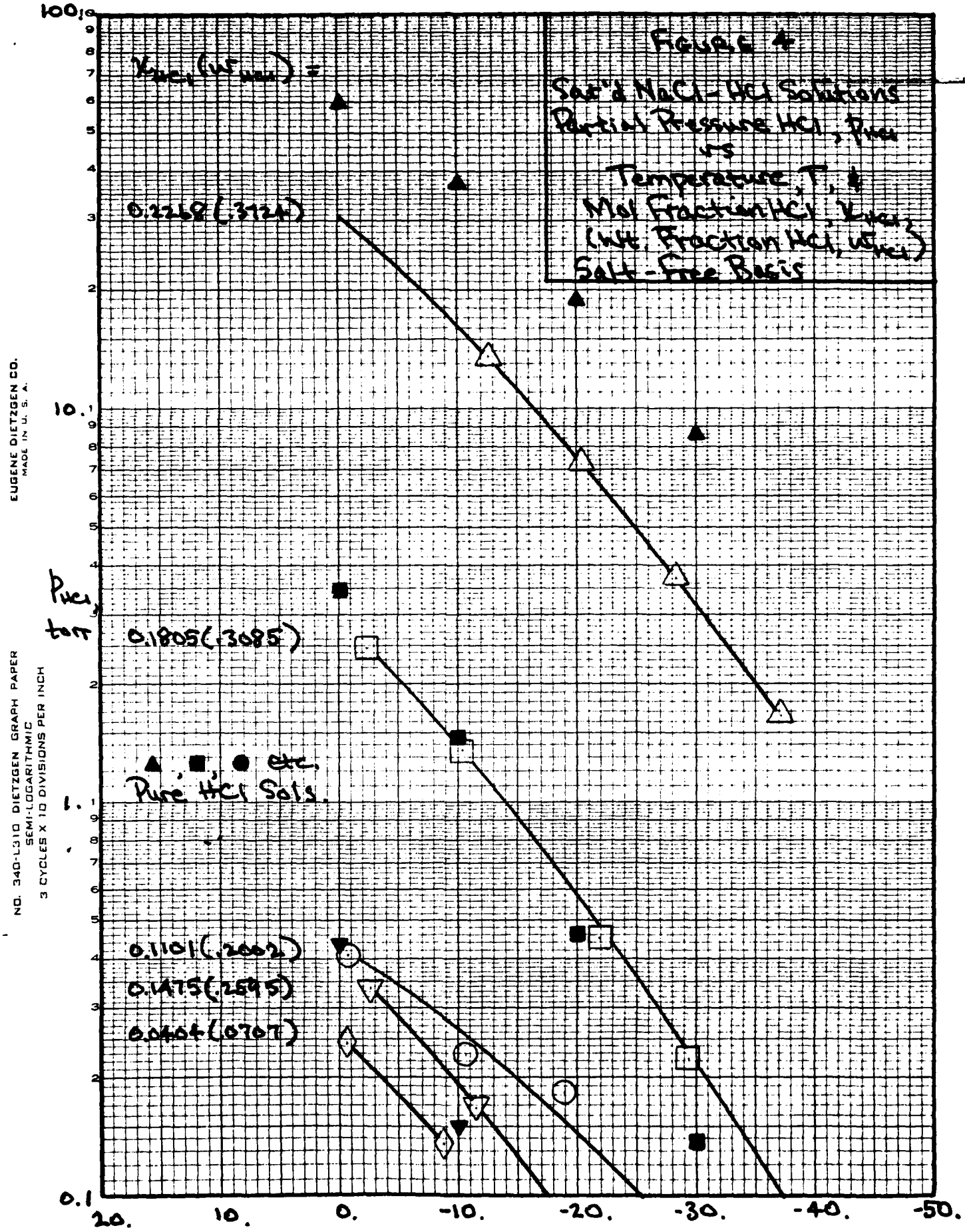
Figure 3a


Sat'd NaCl-HCl Solutions
Partial Pressure HCl, P_{HCl}
vs
Temperature, T, °F
Mol Fraction HCl, X_{HCl}
(Wt. Fraction HCl, W_{HCl})
Salt-Free Basis
X_{HCl} (W_{HCl}) =
0.2268 (.3724)
0.1805 (.3085)
0.1101 (.2002)
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0.0404 (.0707)
P_{HCl}, torr
▲, ■, ● etc.
Pure HCl Sols.
100.
10.
1.
0.1
20.
10.
0.
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FIGURE 4

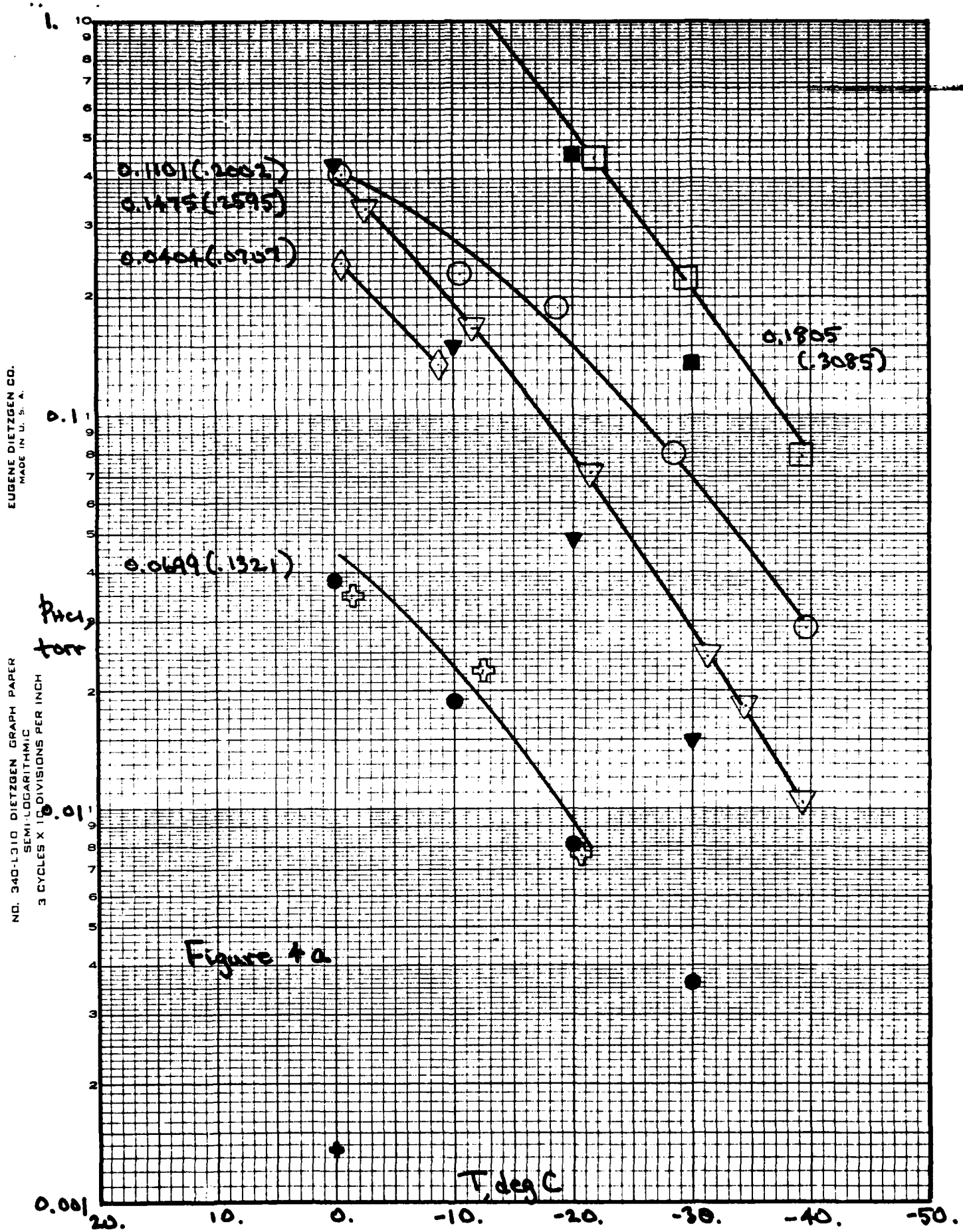
0.1101 (.2002)
0.1475 (.2595)
0.0404 (.0707)
0.1805 (.3085)
0.0699 (.1321)
P_{HCl}, torr
T, deg C
1.
0.1
0.01
0.001
20.
10.
0.
-10.
-20.
-30.
-40.
-50.
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Figure 4a

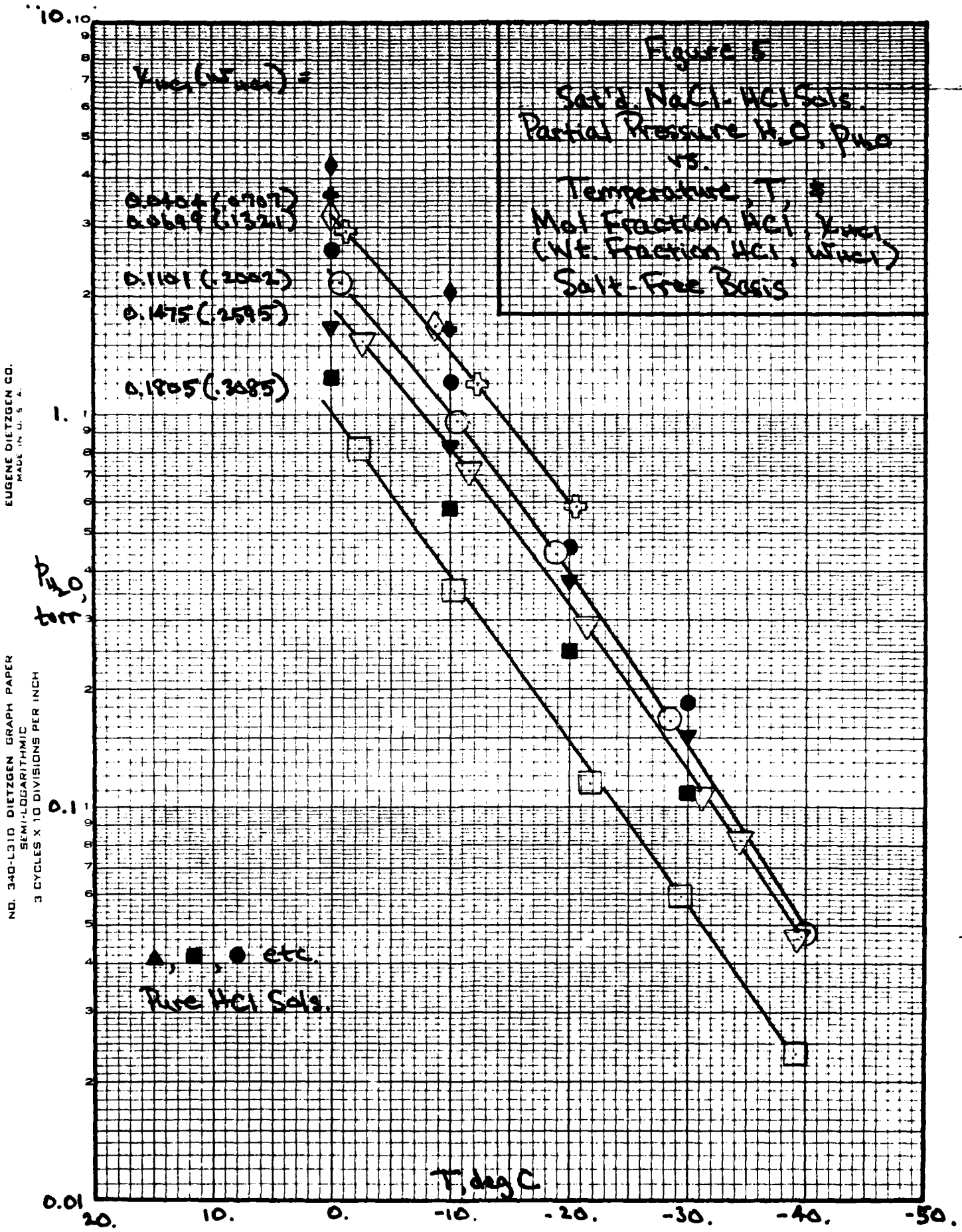
Figure 5
Sat'd. NaCl-HCl Sols.
Partial Pressure H2O, pH2O
vs.
Temperature, T, °
Mol Fraction HCl, xHCl
(Wt. Fraction HCl, wHCl)
Salt-Free Basis
xHCl (wHCl) =
0.0404 (.0707)
0.0699 (.1321)
0.1101 (.2002)
0.1475 (.2595)
0.1805 (.3085)
▲, ■, ● etc.
Pure HCl Sols.
pH2O, torr
T, deg C
10.
1.
0.1
0.01
20.
10.
0.
-10.
-20.
-30.
-40.
-50.
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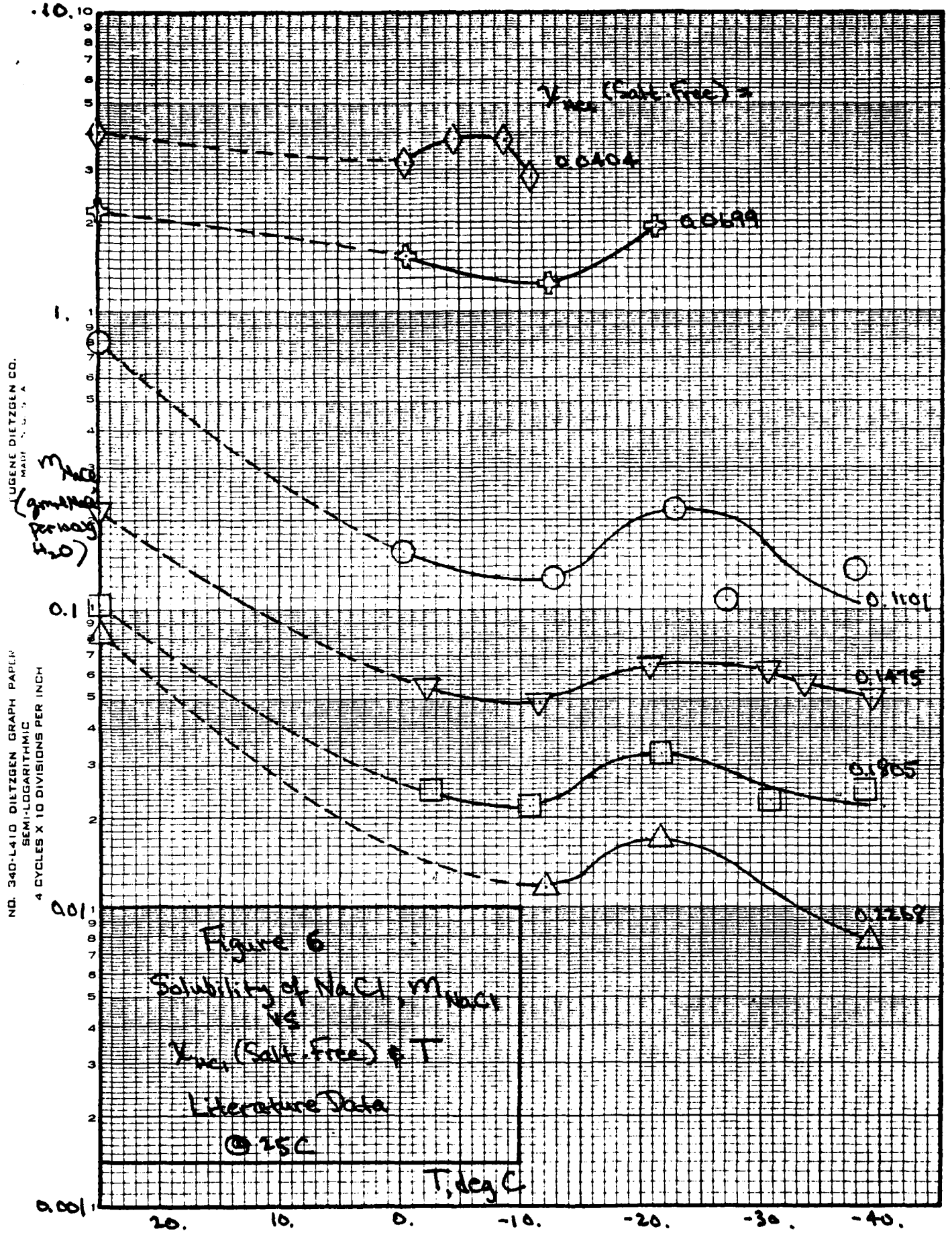
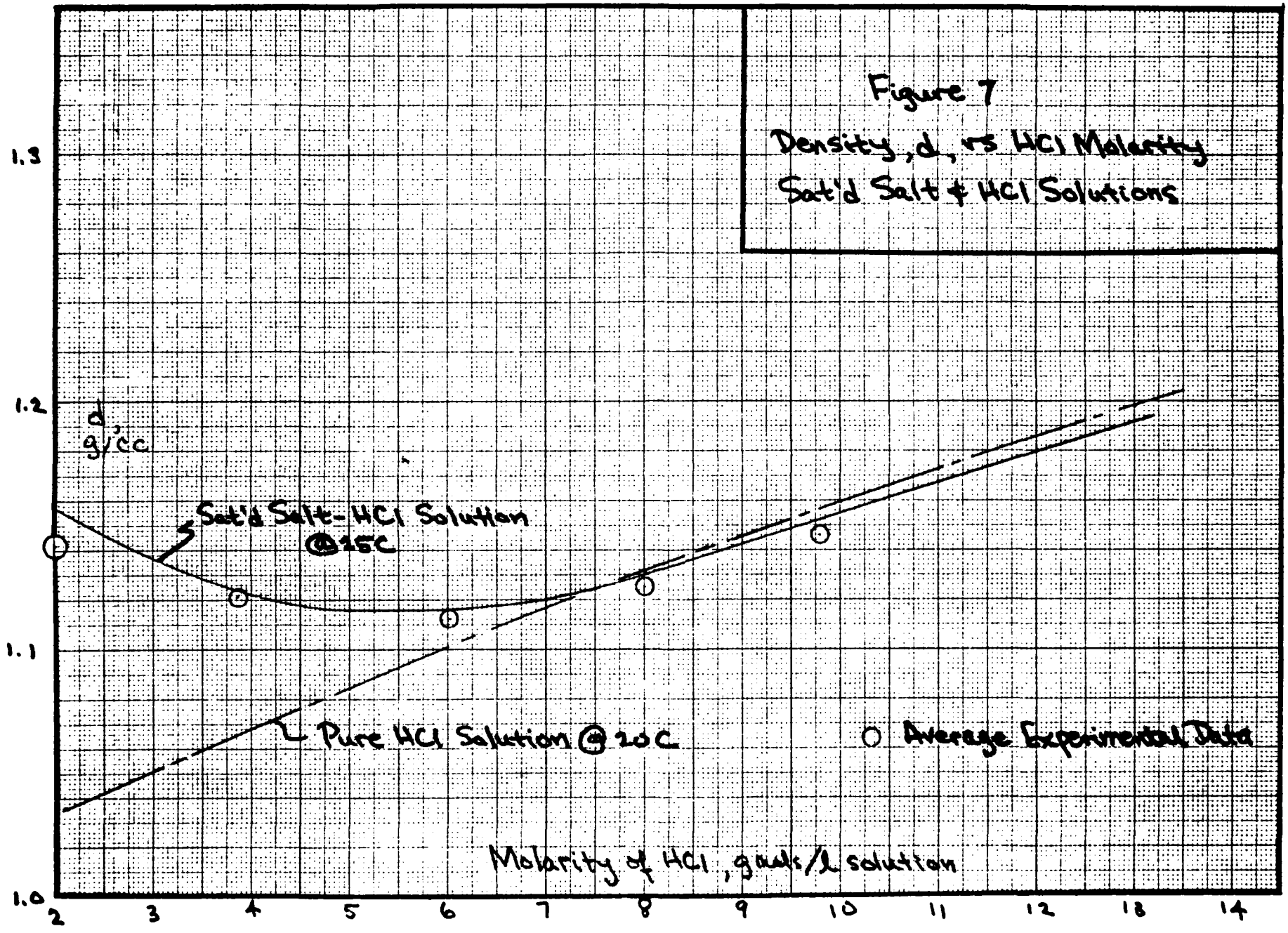


Figure 6

Solubility of NaCl, m_{NaCl} vs x_{NaCl} (Salt-Free) & T

Literature Data

@ 25C



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