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Reactor Experimental Engineering Division

PHYSICAL BEHAVIOR OF THE H_2-O_2-H_2O SYSTEM UNDER PRESSURE

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Date Issued

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ABSTRACT

The solubilities of H_2, O_2, and a $2H_2:1O_2$ mixture in water and salt solutions have been correlated over the range of temperature from 25 to 300° C and of pressure from atmospheric to 2,000 pounds per square inch. Discussions and correlations are presented on the water vapor concentration in the gas phases, the relative volatilities of several gases in water, and the temperature changes upon adiabatic expansion of saturated vapors of these systems.

INTRODUCTION

The solubility of gases in liquids may be correlated by Henry's Law constants for moderate pressures and temperatures at which the solvent is present in the vapor at low concentrations [4]. Whenever the vapor pressure of the solvent represents a substantial part of the total pressure, it is better to consider solubility phenomena as vapor-liquid equilibria in which each constituent is distributed between the phases. This report treats the H_2-H_2O, O_2-H_2O, and the ($2H_2 + O_2$) system on both bases at temperatures from 25 to 300° C and at pressures from atmospheric to 2000 psia. The influence of dissolved salt on the solubility of gas in water is considered. The effect of pressure on the enthalpy of H_2-O_2-H_2O vapors is included.

SOLUBILITY OF H_2 AND O_2 IN WATER

The data on H_2-H_2O systems are more extensive and they will be treated first. As a result of the commercial development of the process for producing ammonia from nitrogen, the solubilities of N_2 and H_2 and 3:1 mixtures of the two gases in water have been studied up to 1000 atmospheres pressure and from 0 to 100° C. The most precise work appears to be that of Wiebe and co-workers [20], [21], [23]. The high temperature data are much more limited; Teadoravich and Ipatieff [17] made measurements from 100 to 225° C at hydrogen partial pressures (defined as total pressure minus vapor pressure of water) up to 116 atmospheres. More recently Pray, et al [10] at Battelle Memorial Institute made a preliminary investigation of the solubility of hydrogen and of oxygen in water up to 343° C, but at a maximum gas partial pressure of but 350 psi.

Sibbitt and Suciu [15] at Purdue made measurements at total pressures of 1000 and 2000 psia from 100 to 275° C for the solubility of hydrogen and of nitrogen in water.

These experimental results are shown in Figures 1 and 2 as solubility (cc of gas at 0° C, 760 mm, S.T.P., per g. of H_2O) versus gas partial pressure, defined as total pressure minus vapor pressure of pure water. The 100° C curve is well established, although the tendency of the data of Teadoravich and Ipatieff to be low is apparent even at this temperature. At higher temperatures the solubility is less well defined, although it seems reasonable to assume that the Russian results are too low here as well. The data of Pray and Sibbitt agree reasonably well at temperatures of 200° C and above. At the lower temperatures the range of pressures investigated are so different in the two cases that direct comparison is not possible. The Pray data at 100° C are definitely too high in view of Wiebe and Gaddy and Sibbitt's results. It is clear that extrapolation of the Pray data to high pressures on the basis of Henry's Law may lead to serious errors. The solid curves drawn on Figures 1 and 2 are believed to represent the best analysis of the available data. Figure 3 is a cross-plot of these curves versus temperature. The experimental data of Wiebe and Gaddy at 50, 75, and 100° C are also shown on the graph for comparison.

O_2-H_2O System

The data for the solubility of oxygen in water are meager [3a] [4]. The work of Pray [10] apparently represents the only measurements above 100° C. The available information is shown in Figure 4. For a final working plot of the oxygen solubility, reasonable curves were drawn through the data in Figure 4 and cross-plotted versus temperature in Figure 5.

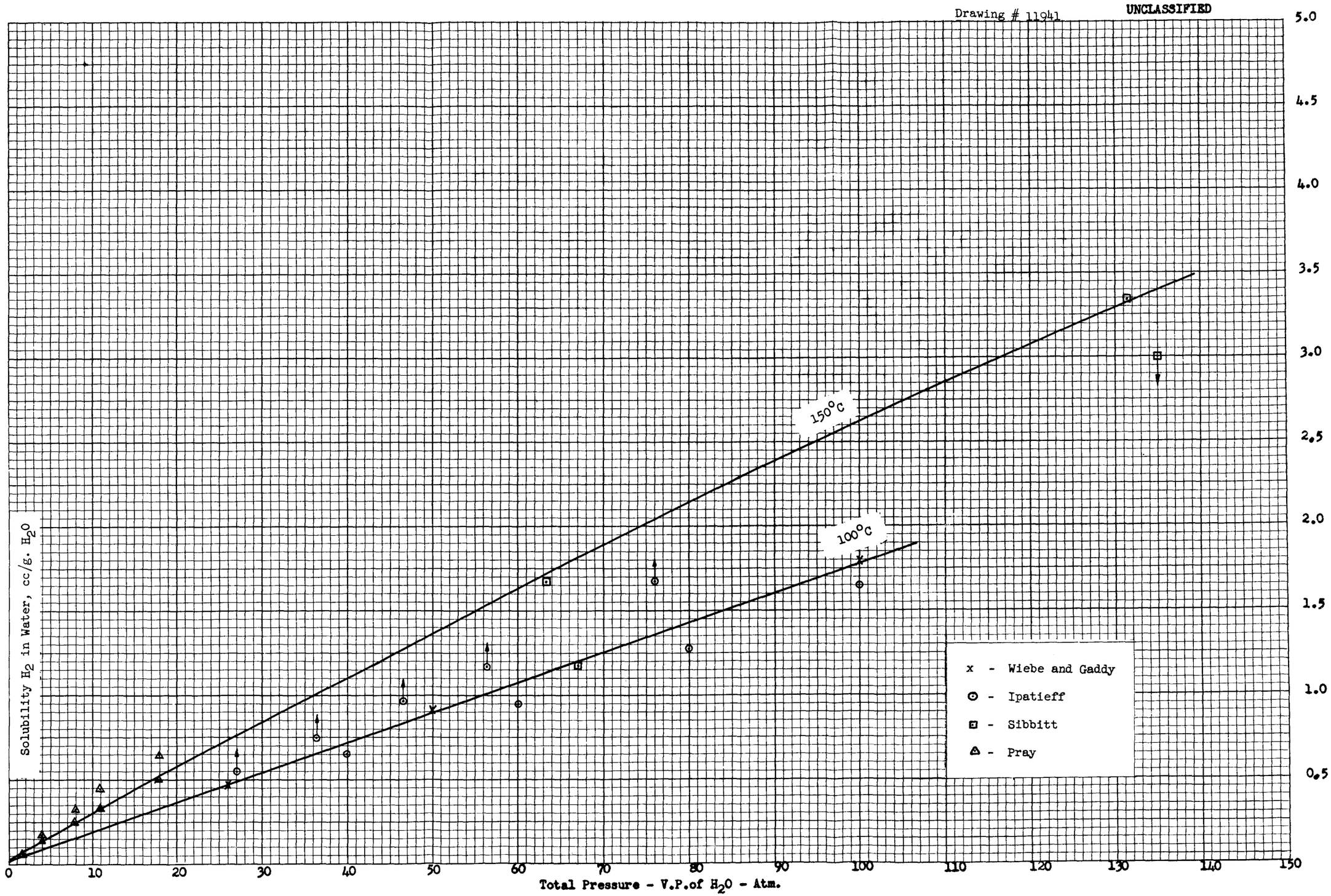

Figure 1 - Solubility of H_2 in H_2O at 100° C and 150° C

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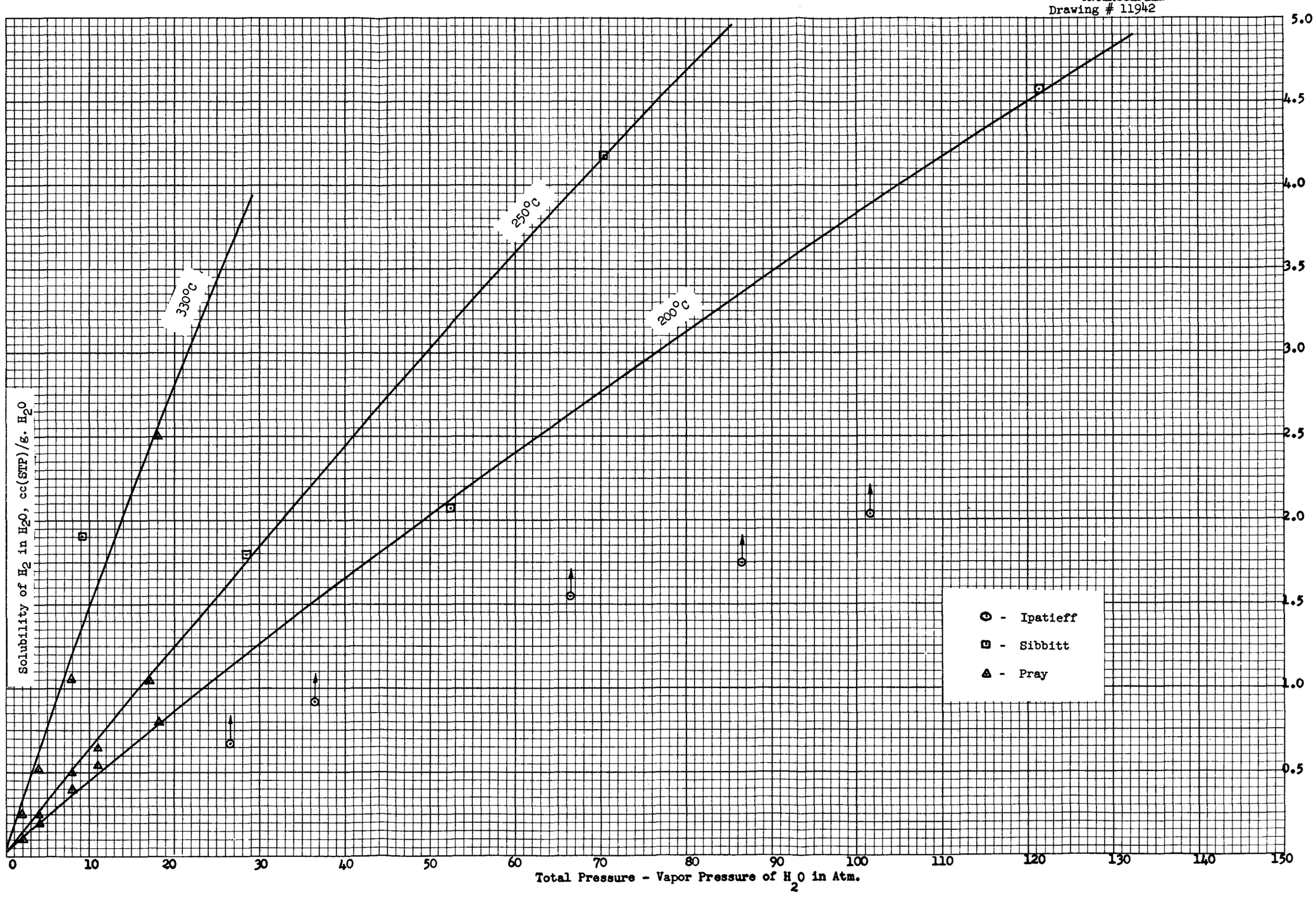

Figure 2 - Solubility of H_2 in H_2O at 200, 250, and 330° C

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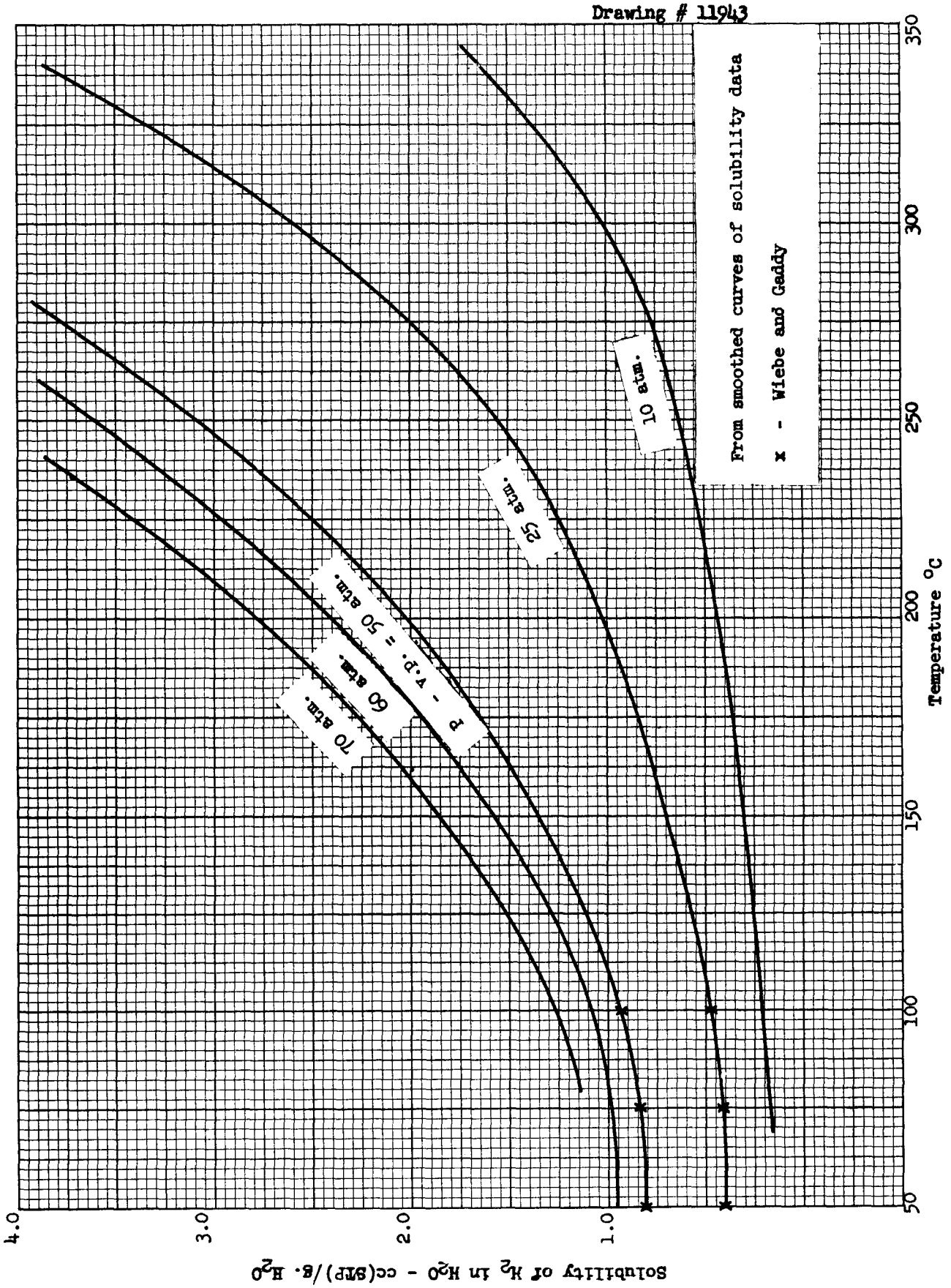

Figure 3 - Solubility of H_2 in Water as a Function of Temperature

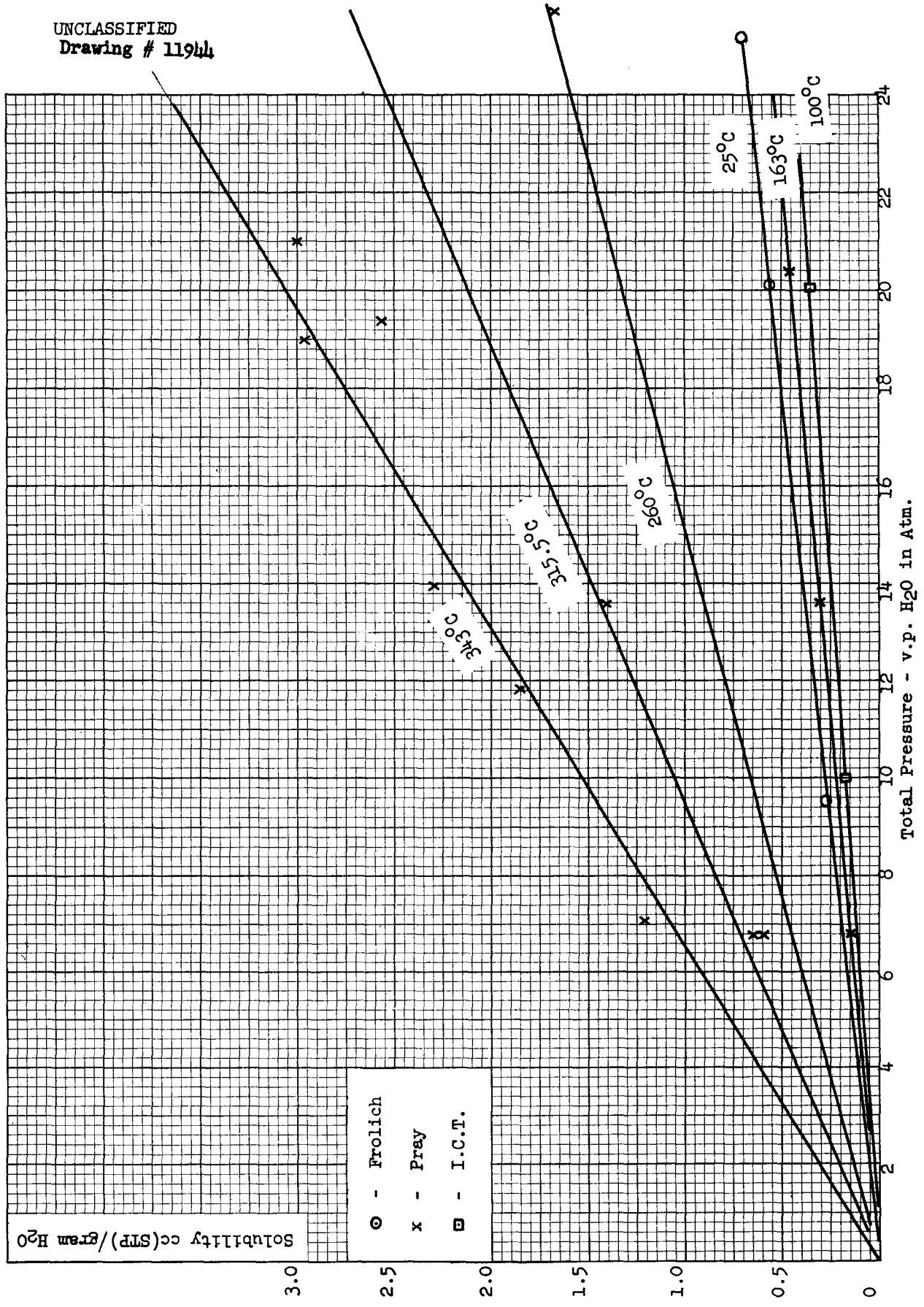

Figure 4 - Solubility of O_2 in Water Versus Pressure

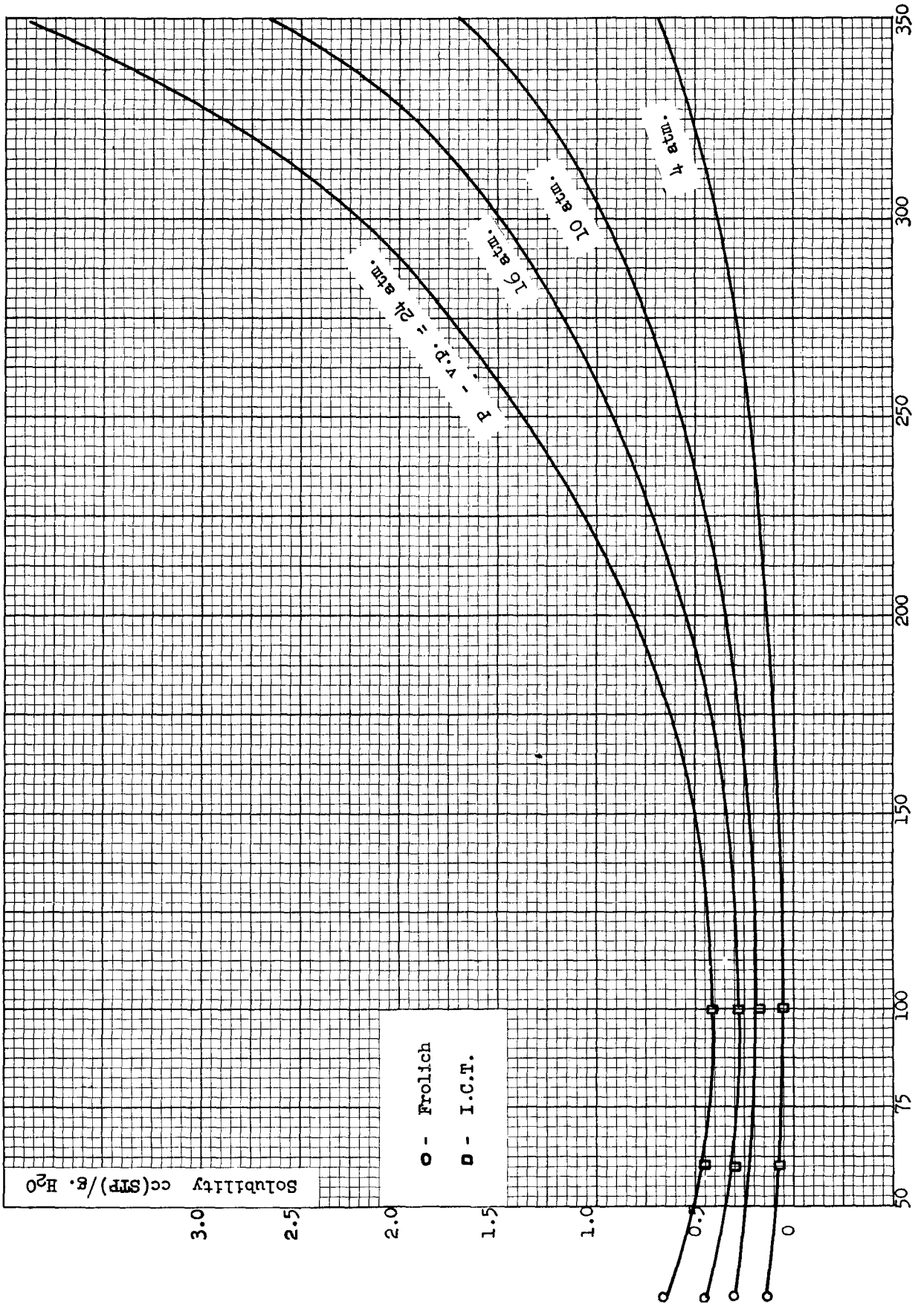

Figure 5 - Solubility of O_2 in Water as a Function of Temperature

SOLUBILITY OF $2H_2:1O_2$ IN WATER

Although no data are available on the solubility of H_2 and O_2 mixtures in water, it is possible to compute the solubility by assuming that one constituent has no effect on the other. Wiebe and Gaddy [23] measured the solubility of 76.4 mol% H_2 and 23.6% N_2 in water at 25° C from 50 to 1000 atmospheres. They computed the solubility of the gas from the mixture by taking for H_2 76.4% of the solubility of pure H_2 at the same temperature and total pressure and 23.6% of the N_2 solubility. Table I shows that the solubility so computed checks the experimental values within 3%.

Table I

Comparison of Measured and Calculated Solubilities of Gas Mixtures at 25° C [23]

Press. Atm.	Calculated Solubility from Data on Pure Gases cc gas S.T.P./ gm H_2O	Measured Solubility cc gas S.T.P./ gm H_2O
50	0.822	0.8349
100	1.619	1.643
200	3.123	3.209
400	5.914	6.068
1000	13.302	13.724

Using the solubility results for pure H_2 and O_2 described above, the solubilities in water of a mixture composed of two mols of H_2 to one mol of O_2 ($2H_2:O_2$) have been computed.

Figures 6 and 7 show the separate solubilities of H_2 and O_2 in a $2H_2:O_2$ mixture in equilibrium with water. Figures 8 and 9 present the combined solubility of hydrogen plus oxygen. In preparing these curves it was assumed that the partial pressure of each gas was equal to the total pressure

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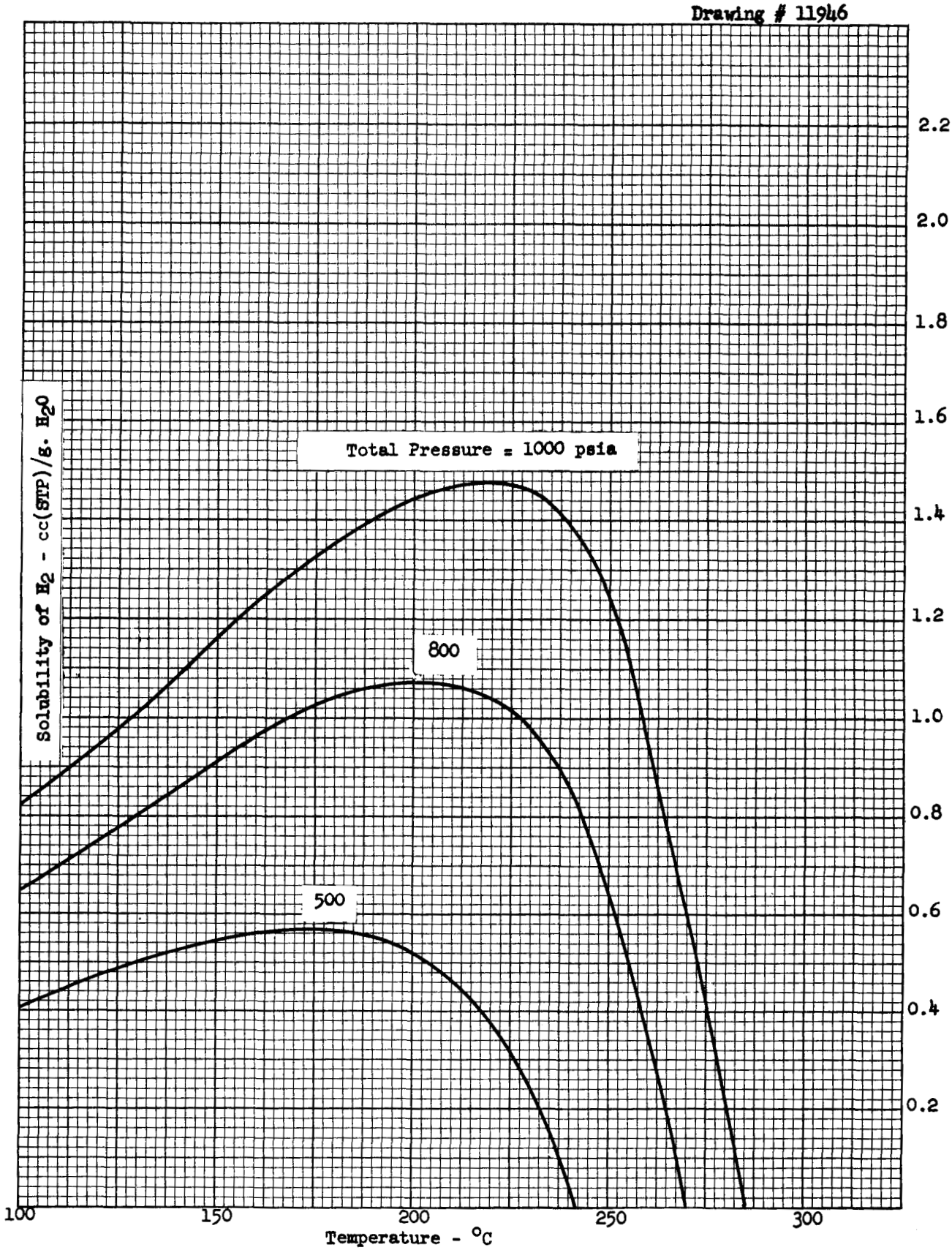

Figure 6 - Solubility of H_2 in $2H_2:O_2$-H_2O System as a Function of Temperature

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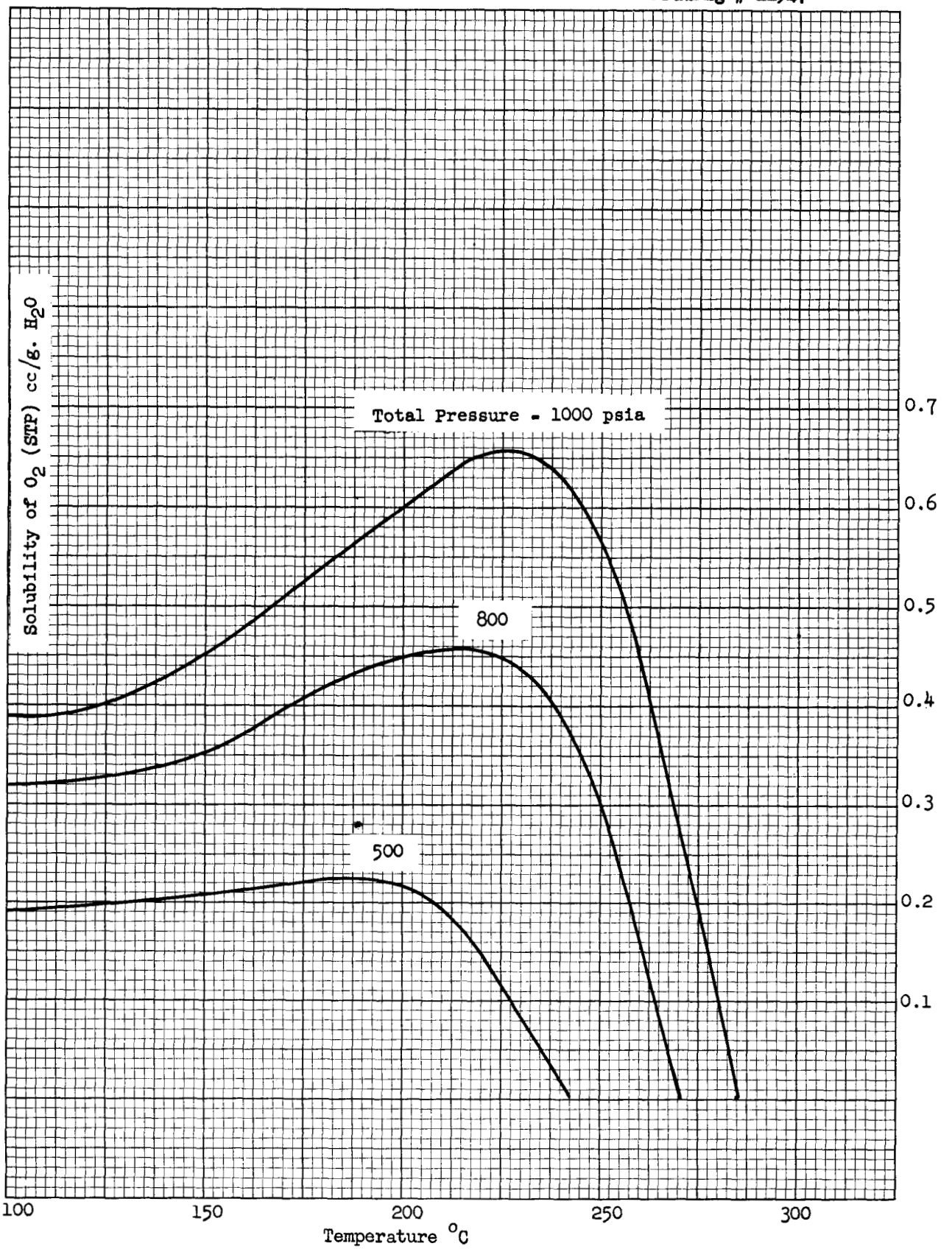

Figure 7 - Solubility of O_2 in $2H_2$:O_2-H_2O System as a Function of Temperature

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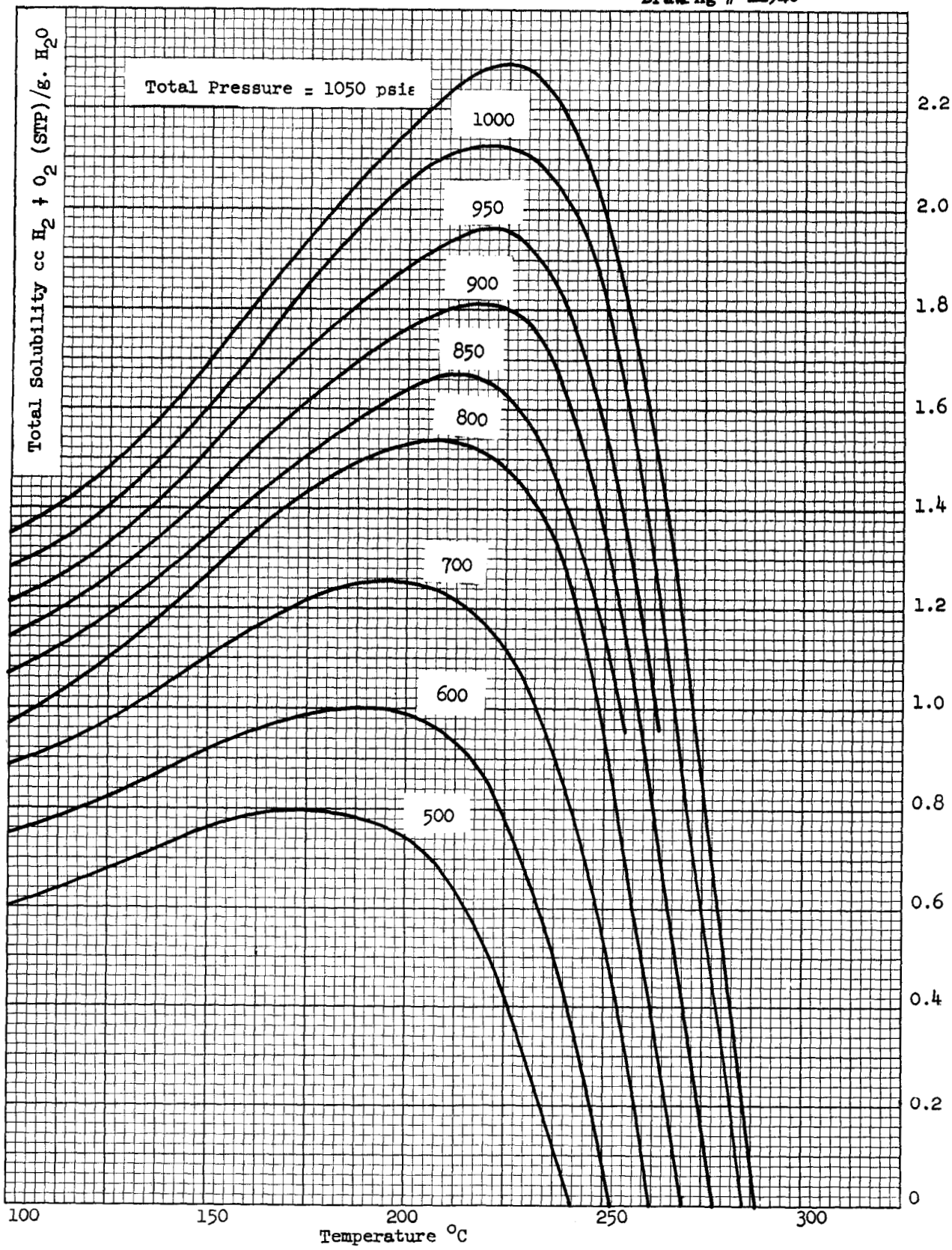

Figure 8 - Solubility of $2H_2:O_2$ in Water as a Function of Temperature

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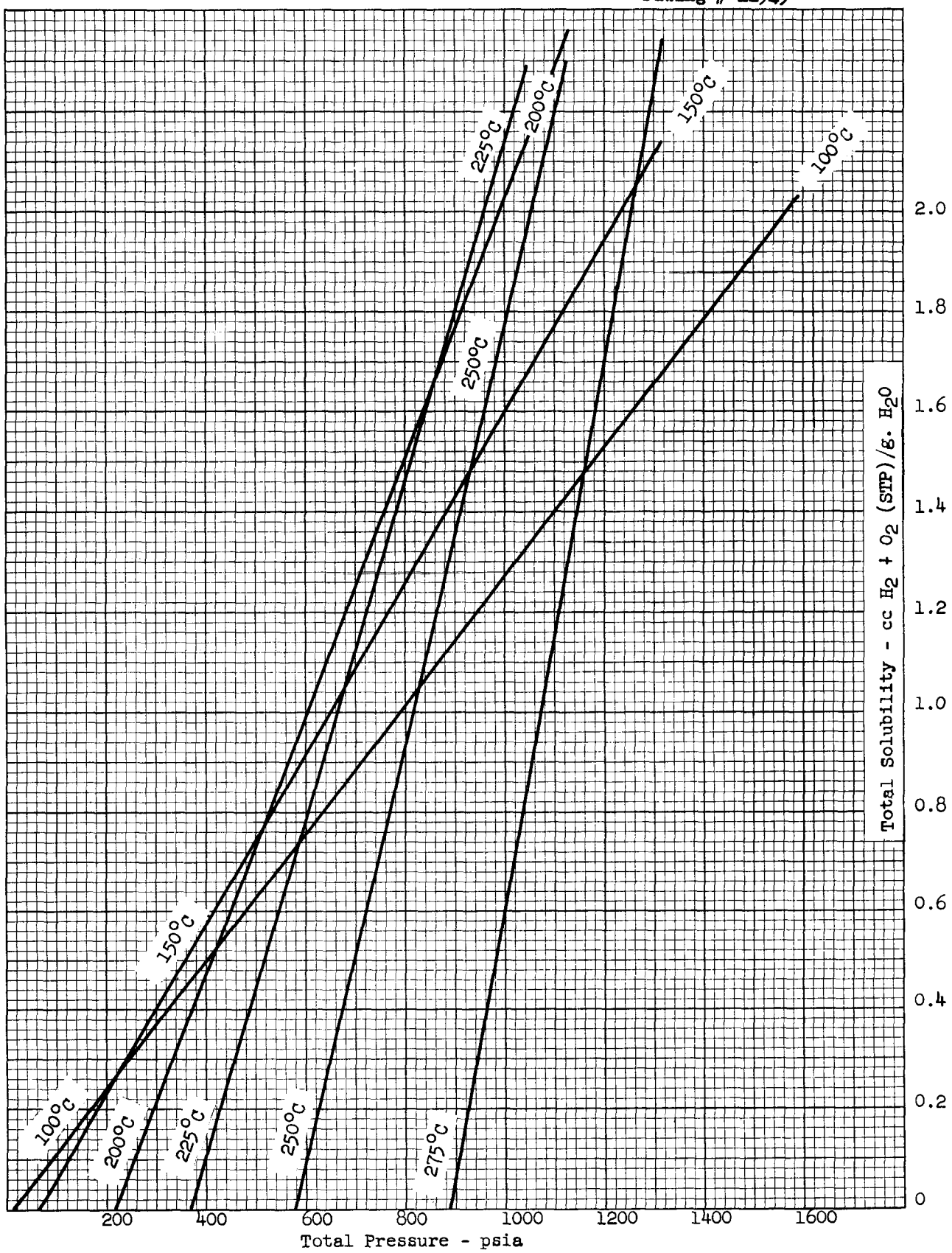

Figure 9 - Solubility of $2H_2:O_2$ in Water as a Function of Pressure

minus the vapor pressure of water; i.e., the partial pressure of hydrogen was

$$PP_{H_2} = (P - p_s)\ 0.667$$

and

$$PP_{O_2} = (P - p_s)\ 0.333$$

When Henry's Law applies, this is the same procedure as tested by Wiebe and Gaddy in Table I.

METHOD OF CORRELATING SOLUBILITY DATA

Although the data show that Henry's Law does not hold at pressurs above about 500 to 1000 psia, the constants are plotted as a function of temperature in Figure 10. Henry's Law constants are defined by equation (1).

$$K = \frac{p_H}{N_2} = \frac{\text{total pressure - vapor pressure pure } H_2O\text{, psia}}{\text{mol fraction of gas in liquid}} \qquad (1)$$

The solubility of the gas expressed as $\frac{\text{cc of gas @ } 0^\circ \text{ C, 760 mm}}{\text{gm } H_2O}$ may be computed from Henry's Law constants, total pressure and the vapor pressure of pure water as follows:

$$\frac{\text{Solubility as cc gas at S.T.P}}{\text{gm } H_2O} = 1244\ \frac{p_H}{K}$$

A method of correlating solubility data which does not include the assumption of Henry's Law has been developed by Krichevsky and Kasarnovsky [7]. When precise solubility data are available this method of correlation gives the most accurate extrapolation of low pressure measurements to high pressures. The precision of the available solubility data for hydrogen and oxygen, with the exception of that of Wiebe and Gaddy is not sufficient to justify application

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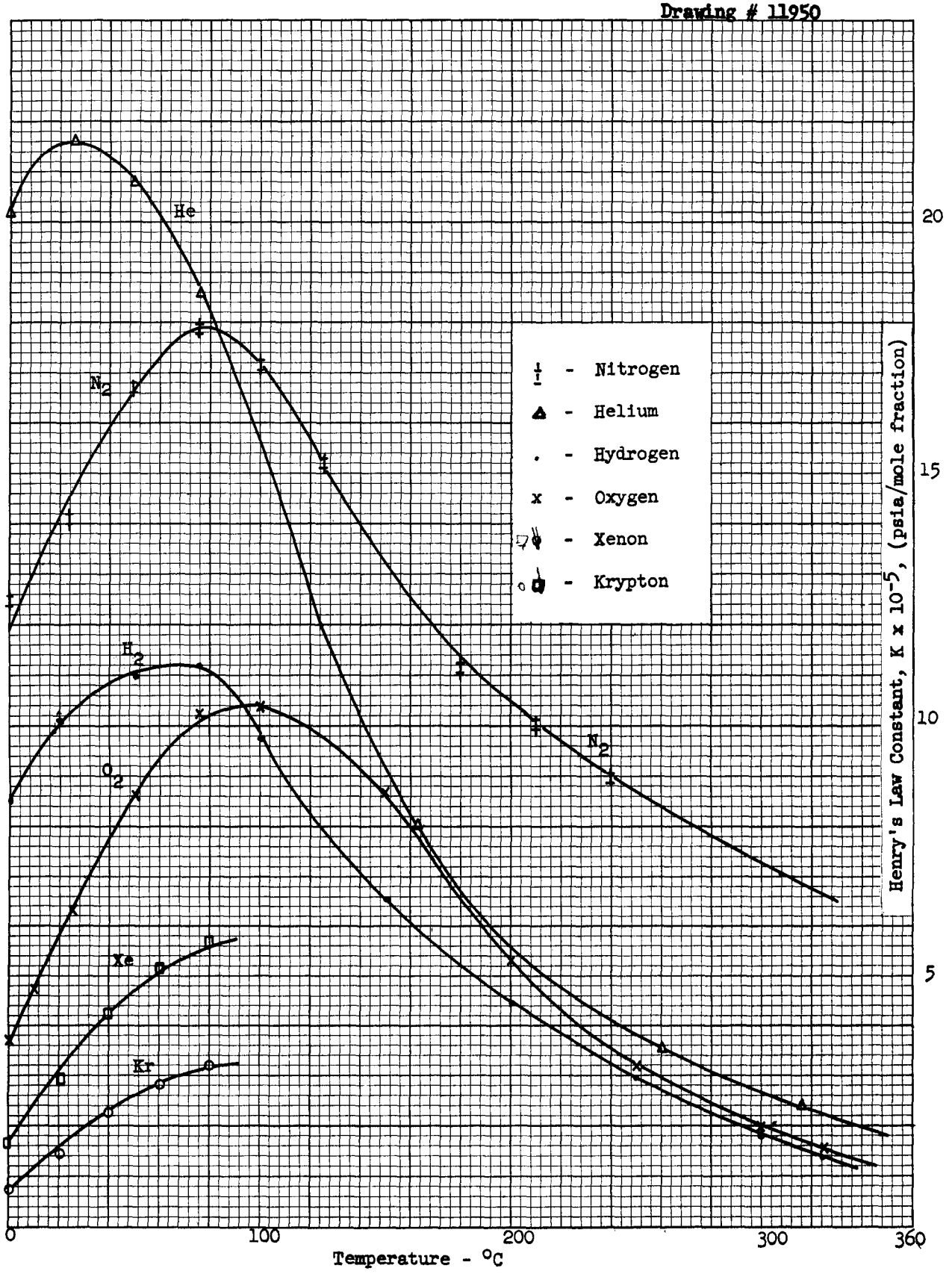

Figure 10 - Henry's Law Constants for Various Gases in Water

of the correlation procedure in this case. The method of approach is described in Appendix I of this report.

EFFECT OF DISSOLVED SALTS ON GAS SOLUBILITY

The solubility of a gas in an aqueous salt solution is less than in pure water when no chemical reactions are involved. Michels, Gerver, and Biji [8], as well as Prutton and Savage [11], give data on gas solubility in salt solutions over a range of salt concentrations, pressures, and temperatures. Figure 11 presents the data of Michels for the solubility of methane in NaCl solutions at 25° C and at 150° C.

A theory for the effect of salt concentration on the solubility of gases in aqueous solutions has been developed by extending the thermodynamic treatment of Krichevsky and Kasarnovsky [7] for the solubility in pure water. The development is described in Appendix III where a reasonably rigorous method of correlating solubility data is presented. It is also shown that the following simple expression represents a good approximate solution:

$$\ln \frac{N_2'}{N_2} = f \text{ (nature and concentration of salt)} \qquad (3)$$

This equation states that the ratio of the solubility (mole fraction N_2') of the gas in the salt solution to the solubility in pure water (N_2) at the same pressure and temperature is independent of pressure and temperature and a function only of the nature and concentration of the salt solution. If concentration is considered on a normality basis the effect of nature of the salt is minimized, so that curves of solubility ratio versus normality should not deviate too widely from each other.

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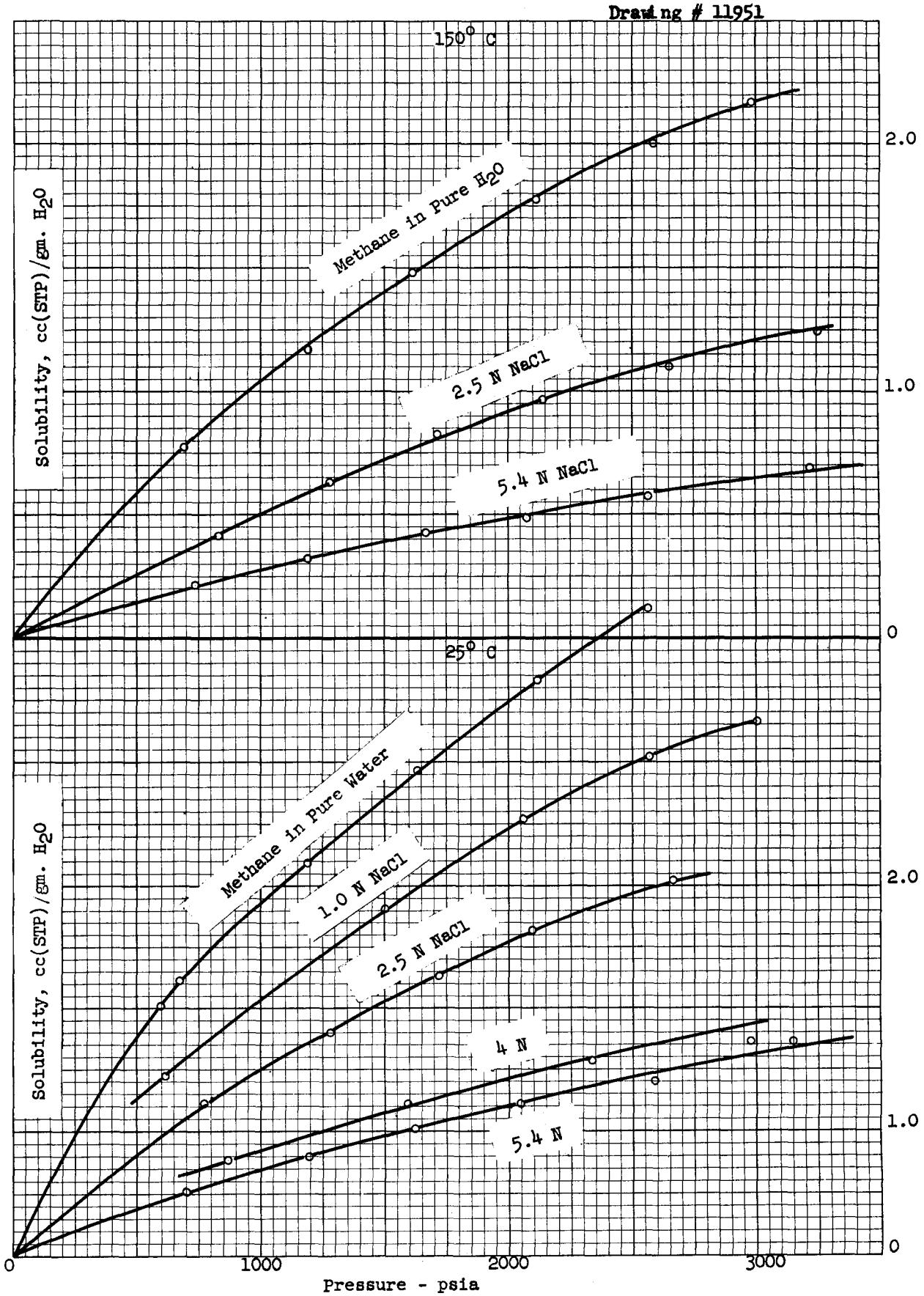

Figure 11 - Effect of Dissolved NaCl on Solubility of CH_4 in H_2O

A normal solution contains one gram equivalent of salt dissolved in a liter of solution. The effect of dissolved salts on the solubility of gases at atmospheric pressure is given by Seidell [14] and by Kobe and Markham [6]. Typical data for hydrogen in various salt solutions including known sulphates were examined and found to correlate as ratio of the solubility in salt solutions to the solubility in water at the same temperature and pressure as a function of solution normality as suggested by equation (3). The data are plotted in Figures 12A and 12B.

The data at high pressures and temperatures were computed as a ratio of the solubility in the solution to the solubility in water at the same temperature and total pressure and found to plot in the same general region on Figure 12A as the atmospheric solubility data. It should be noted that the curves of Figures 12A and 12B include not only the effect of the dissolved salt on the liquid phase but also on any change in the concentration of the gas phase at constant temperature and total pressure.

The spread of the data on the charts is probably due to the fact that the signle variable, normality, does not take into account the characteristic behavior of different salts. Although all gases and salt solutions are not likely to agree exactly with the curves in Figures 12A and 12B, they may be used as first approximations of the solubility of H_2 and O_2 in salt solutions.

WATER CONTENT OF GAS IN H_2-O_2-H_2O SYSTEMS

In general, it would be expected that the mole fraction water in the gas phase in equilibrium with the liquid in systems of water, H_2, and O_2 would depend upon the temperature, total pressure, and physical properties of the

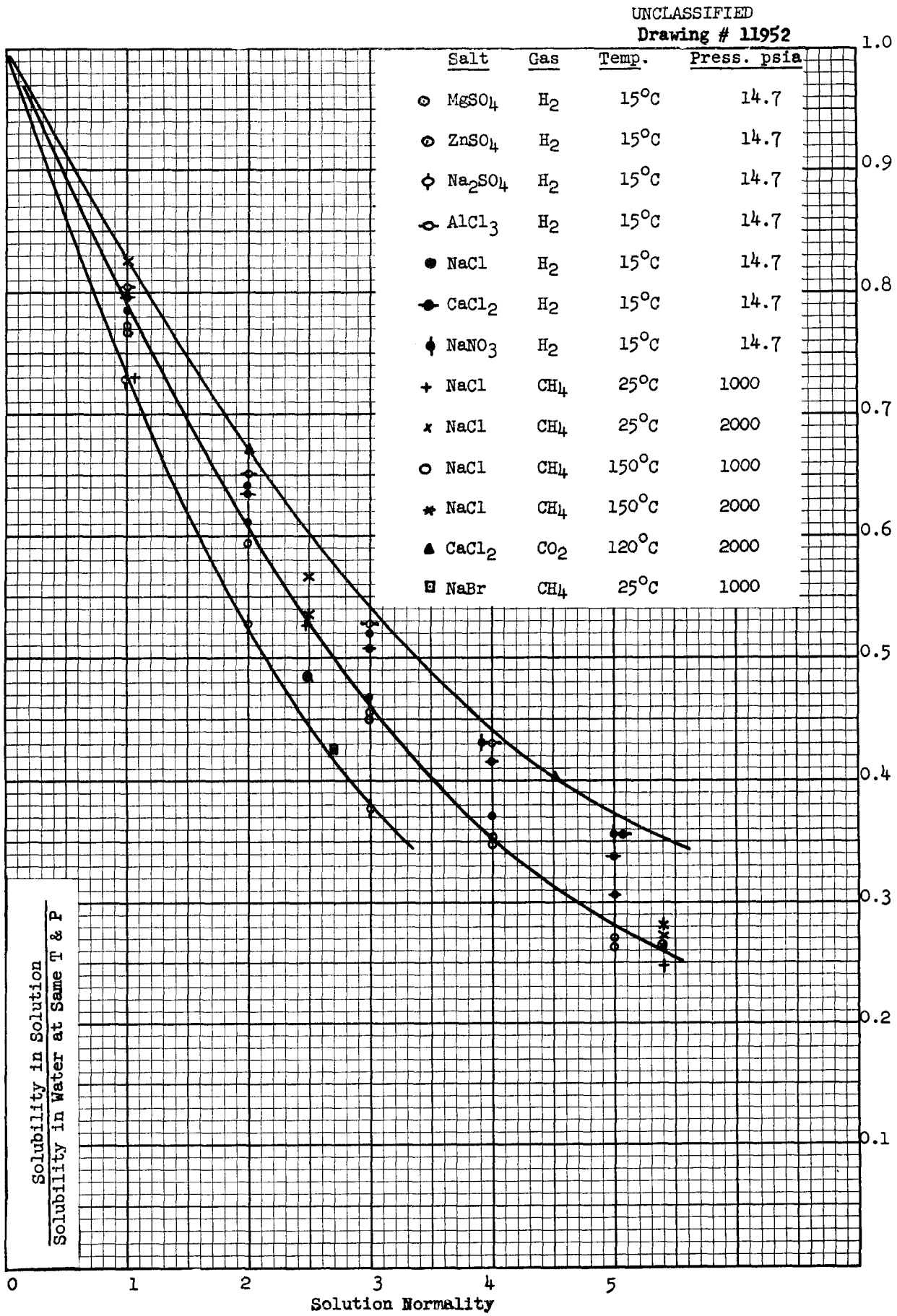

Figure 12A - Ratio of Solubility of Gases in Salt Solutions and in Water as a Function of Salt Normality

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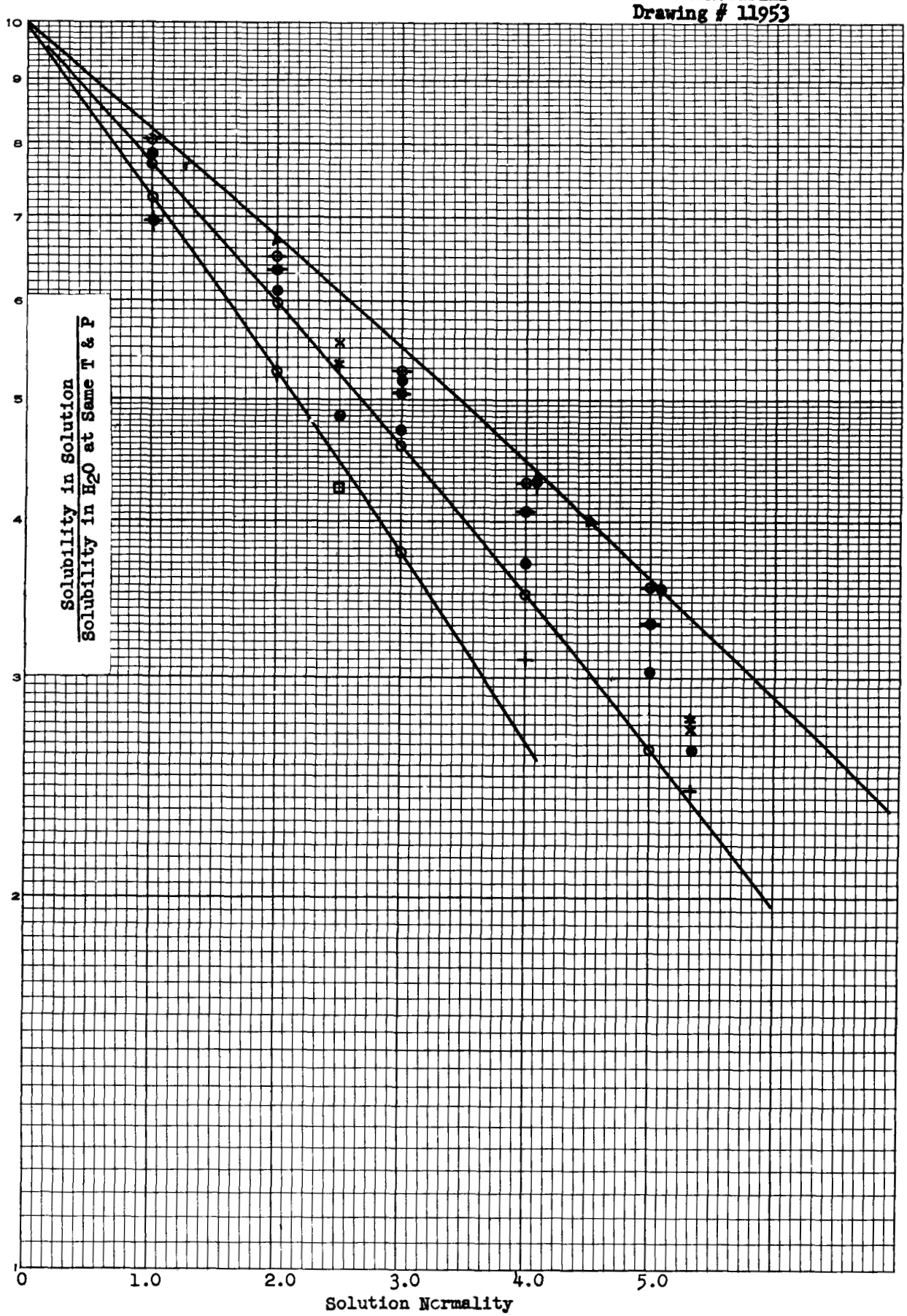

Figure 12B - Logarithmic Plot of Solubility Ratio vs. Salt Normality

hydrogen and oxygen gases. If the liquid phase (predominantly water) could be assumed to behave as an ideal solution and the gas phase as a perfect gas mixture, the properties of the H_2 and O_2 would not be involved; i.e., the water vapor mole fraction, y_w, would be given by the expression:

$$y_w = \frac{P_s x_w}{P} \tag{4}$$

P_s = vapor pressure of pure water

P = total pressure on the system

At elevated pressures the assumption of perfect gas behavior is in error; but y_w could still be computed without this assumption by substituting fugacities for pressures in equation (4):

$$y_w = \frac{f_L^o \, x_w}{f_V^o} \tag{5}$$

f_L^o = fugacity of liquid water at T and P

f_V^o = fugacity of pure water vapor at T and P

At temperatures and pressures where two phases are present in systems involving water and slightly soluble gases such as H_2 and O_2, f_V^o is a hypothetical quantity because pure water vapor cannot exist at the total pressure, P.

To avoid this difficulty, Sage and Lacey [9] [12] in their treatment of methane-water and ethane-water systems have replaced f_V^o with a proportionality factor β which can now also absorb the errors inherent in the assumption of an ideal liquid solution. Equation (5) then becomes,

$$y_w = \frac{f_L^o \, x_w}{\beta} \tag{6}$$

For gases such as H_2, O_2, CH_4, C_2H_6, which are but slightly soluble in the liquid phase, x_w can be taken as unity without appreciable error so that equation (6) becomes,

$$y_w = \frac{f_L^o}{\beta} \tag{7}$$

Available Data

Sage and Lacey [9] [12] have determined β from experimental values of y_w and x_w for the two systems just mentioned, and also converted the solubility date of Wiebe and Gaddy [20] [21] and Bartlett [1] to β values.

These results show a considerable variation of β with the nature of the gas, indicating that the assumption of an ideal liquid solution is not valid. The values of β determined for the propane-water system from the data of Kobayaski [5] verify this conclusion. Figure 13 presents typical data of Bartlett for H_2 and N_2 and of Sage and Lacey for CH_4.

Correlation of Data

While $\frac{\beta}{P}$ varies with the gas, this variation can be generalized approximately by using pseudo reduced temperatures and pseudo reduced pressures of the vapor. Pseudo reduced temperature is the absolute temperature divided by the pseudo critical temperature, while pseudo reduced pressure is the ratio of the absolute pressure to the pseudo critical pressure. Pseudo critical properties are the molal average critical property for a mixture such as the gas-water vapor mixture. Figure 14 presents $\frac{\beta}{P}$ as a function of pseudo reduced pressure with lines of pseudo reduced temperature for the mixture. While the data for hydrogen and nitrogen [6] [20] [21] are limited to low temperatures (50° C), the data for methane and ethane go to 230° C. Figure 14 correlates the data for H_2, O_2, CH_4, and C_2H_6 reasonably well and appears to offer the most accurate method now available for predicting the mole fraction water in the gas phase.

The data of Saddington and Krase [13] and Sibbitt and Suciu [15] for the solubility of N_2 were not of particular value in preparing the generalized

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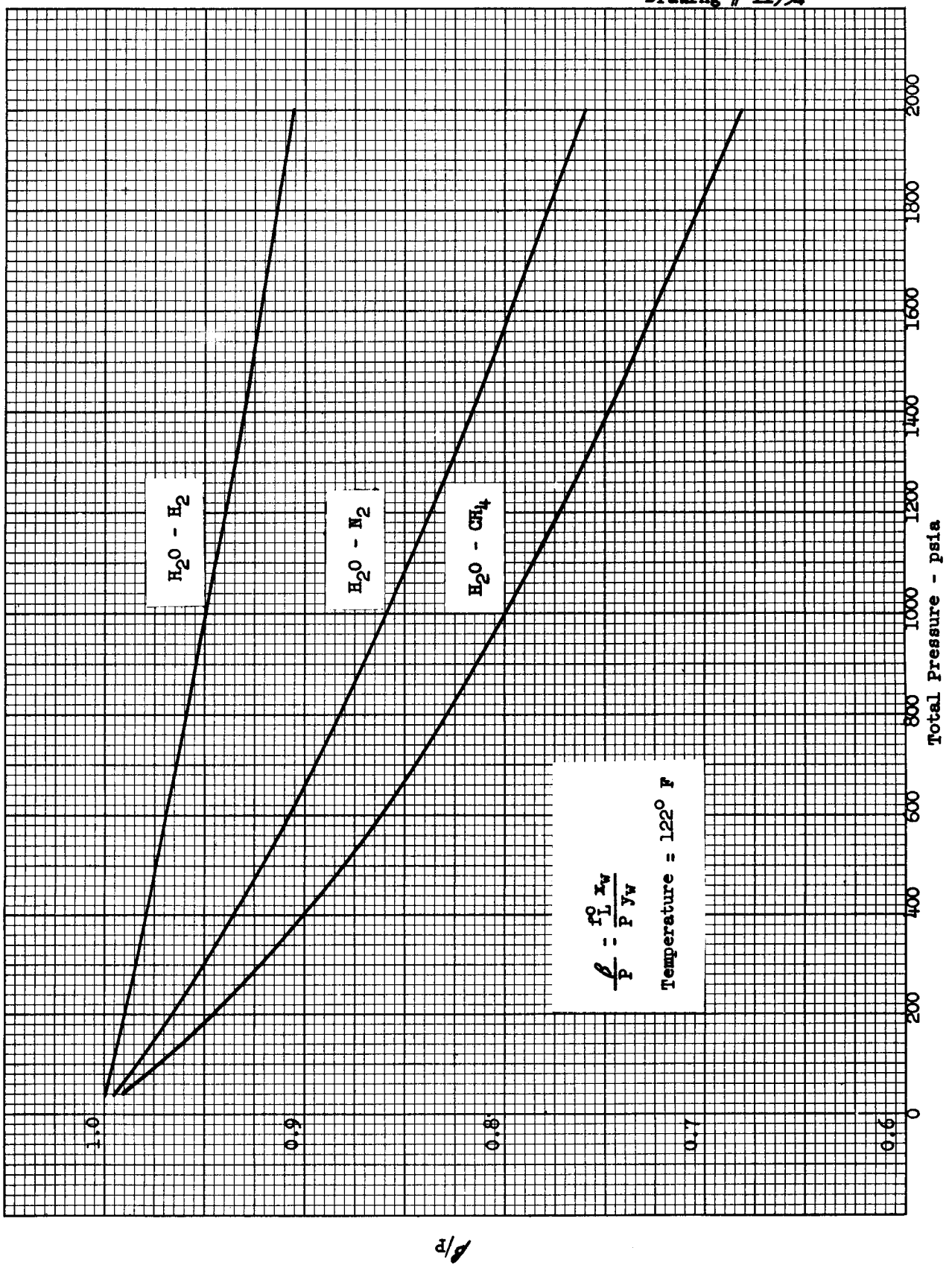

Figure 13 - β/P Plot for H_2, O_2 and CH_4

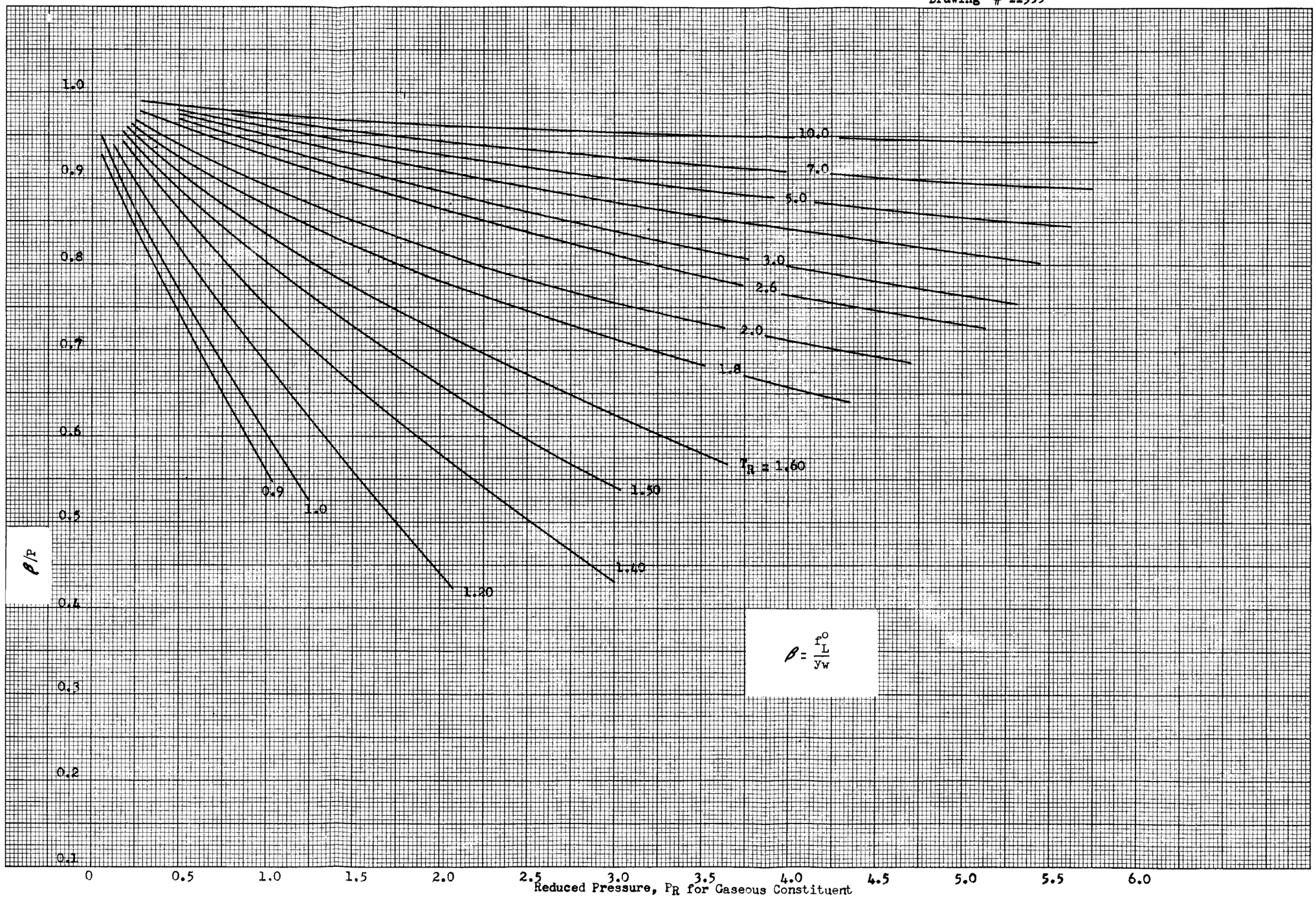

Figure 14 - β/P Correlated by Means of Reduced Temperature and Pressure

correlation of β/P because of their inconsistency. This is illustrated in Figure 15, where the available nitrogen data at 100 atm total pressure are plotted.

Figure 14 has been used to prepare Figures 16 and 17, which are applicable for the system $2H_2:1O_2$ - water. Figure 16 shows the ratio of the computed concentration y_w to the ideal concentration determined from equation (4); i.e.,

$$\frac{y_{Comp.}}{y_{Ideal}} = \frac{f_L^o}{\beta P} \tag{8}$$

In preparing this figure the pseudo critical temperature and pressure were first evaluated on the basis of an assumed value of y_w. Then β at the given P and T was read from Figure 14. This value for β was employed in equation (8) to determine $y_{Comp.}/y_{Ideal}$. The fugacity of pure liquid water, f_L^o, was computed by first determining the fugacity at the vapor pressure from a generalized $\frac{f}{P}$ chart (Perry, Chemical Engineers' Handbook, p. 536) and then correcting for the effect of pressure on the liquid fugacity by the expression:

$$\ln f_L^o/f_{v.p.}^o = \frac{1}{RT} \int_p^P V_L \, dp \tag{9}$$

It is observed that at high temperatures and low pressures the computed value of y_w is essentially equal to the ideal result based upon the perfect gas assumption.

Figure 18 is a plot similar to Figure 16, based upon the experimental data for the methane-water system.

Figure 17 is a plot of the computed y_w values as a function of temperature and pressure for the two moles H_2 to 1 mol O_2 mixture. Similar charts for

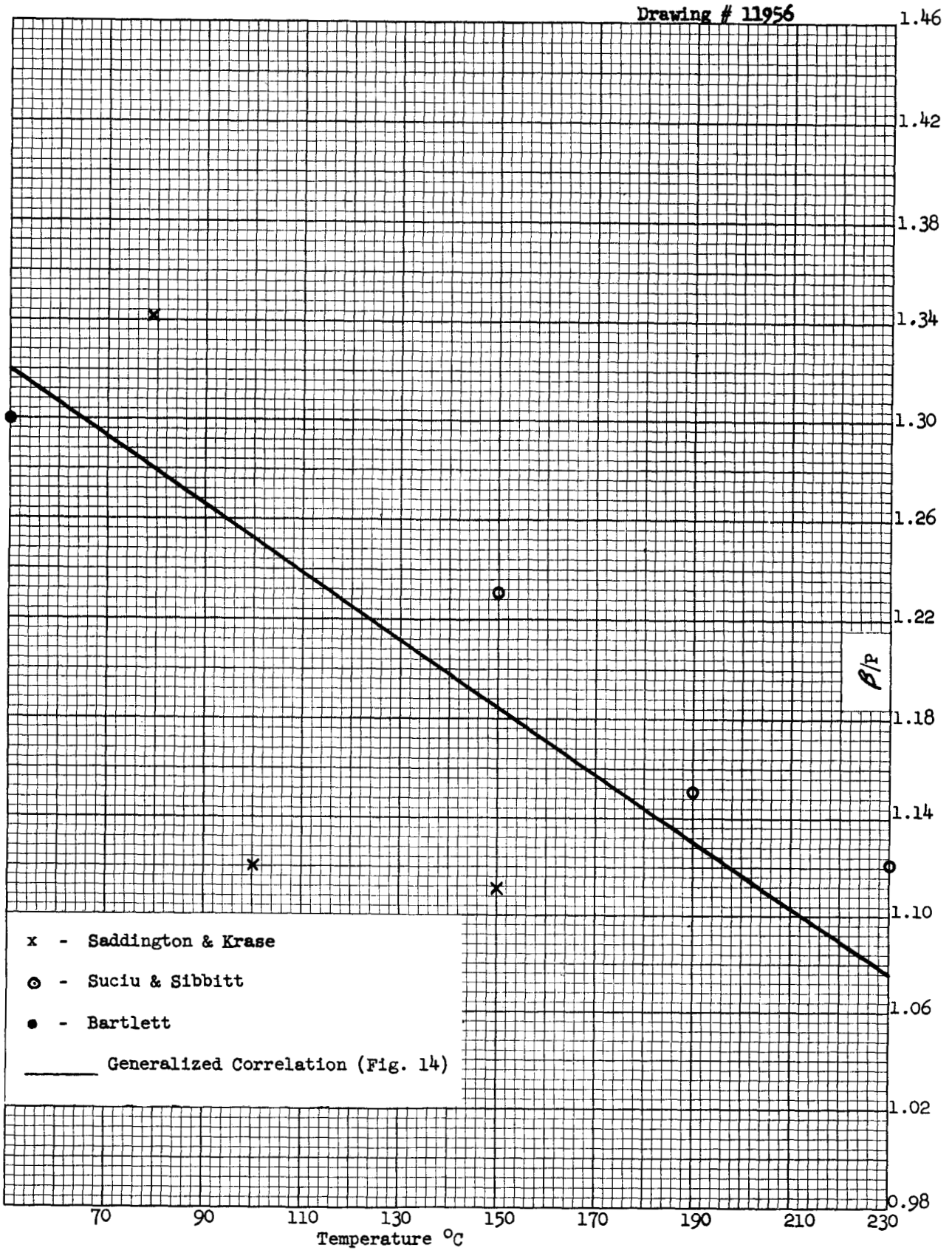

Figure 15 - Comparison of β/P for N_2-H_2O System at 100 Atmospheres

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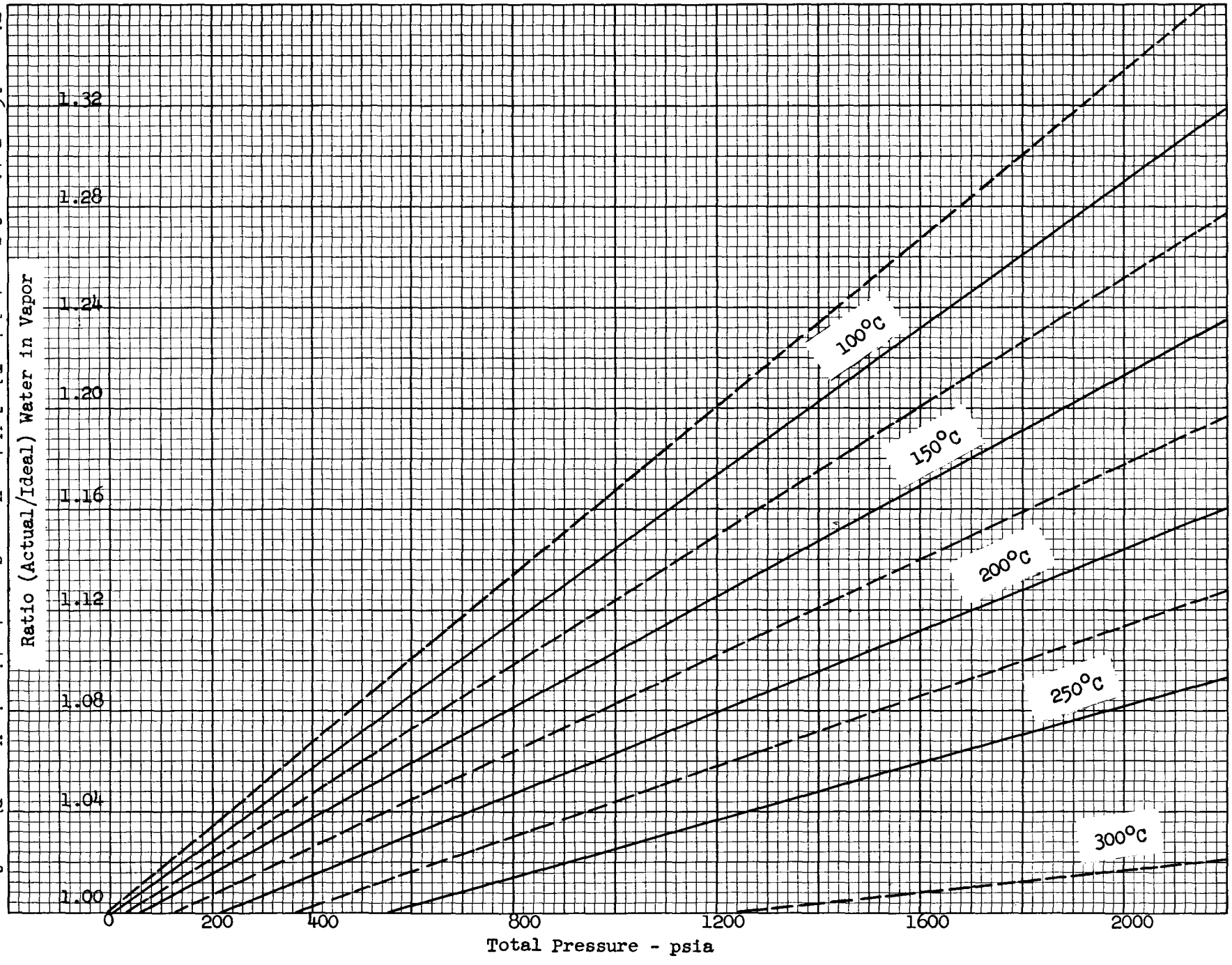


Figure 16 - Ratio of Computed to Ideal Water Vapor Concentration in Vapor Phase for $2H_2:O_2-H_2O$ System

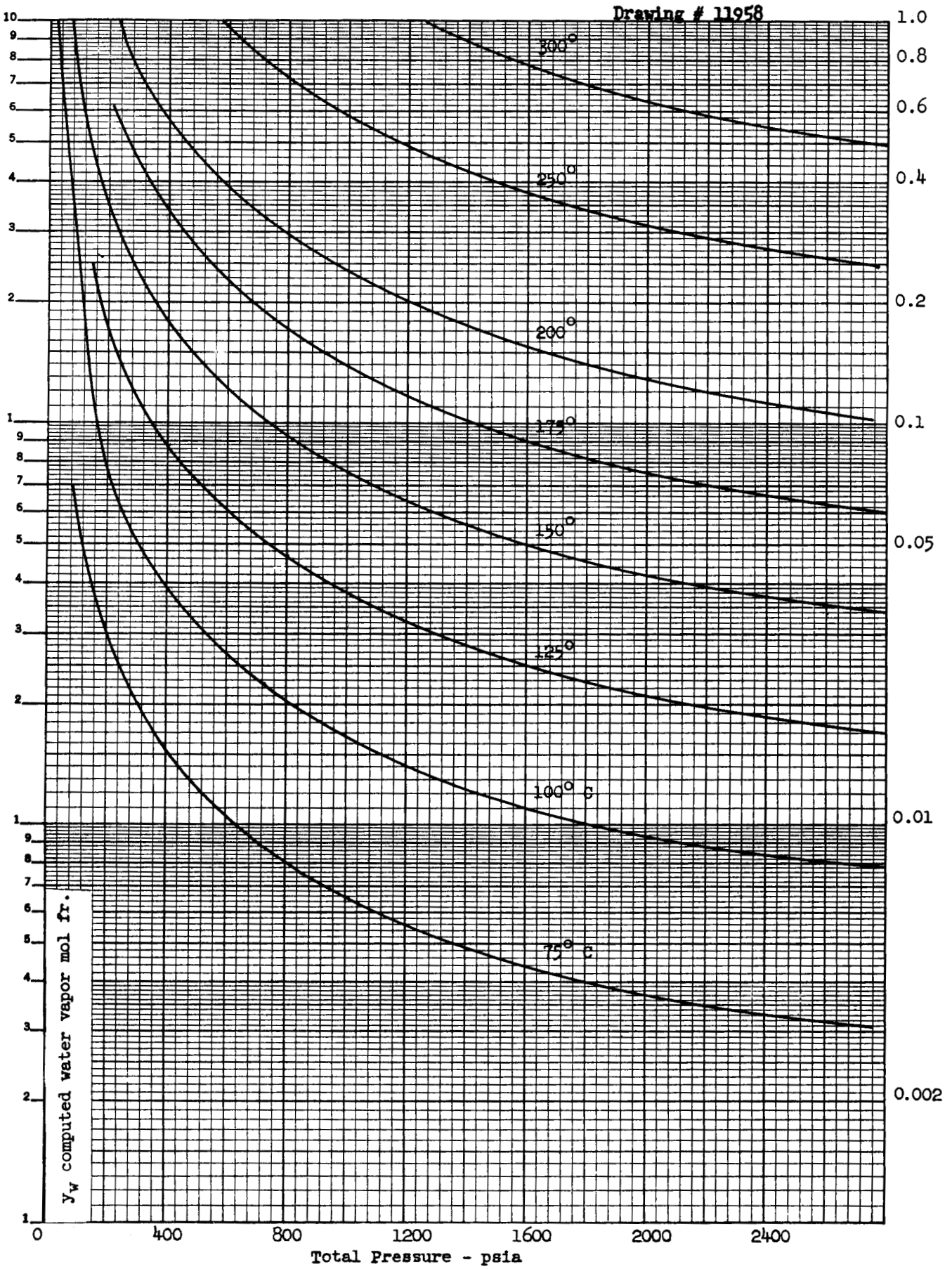


Figure 17 - Computed Mol Fraction Water in Vapor Phase of $2H_2:O_2$-H_2O System

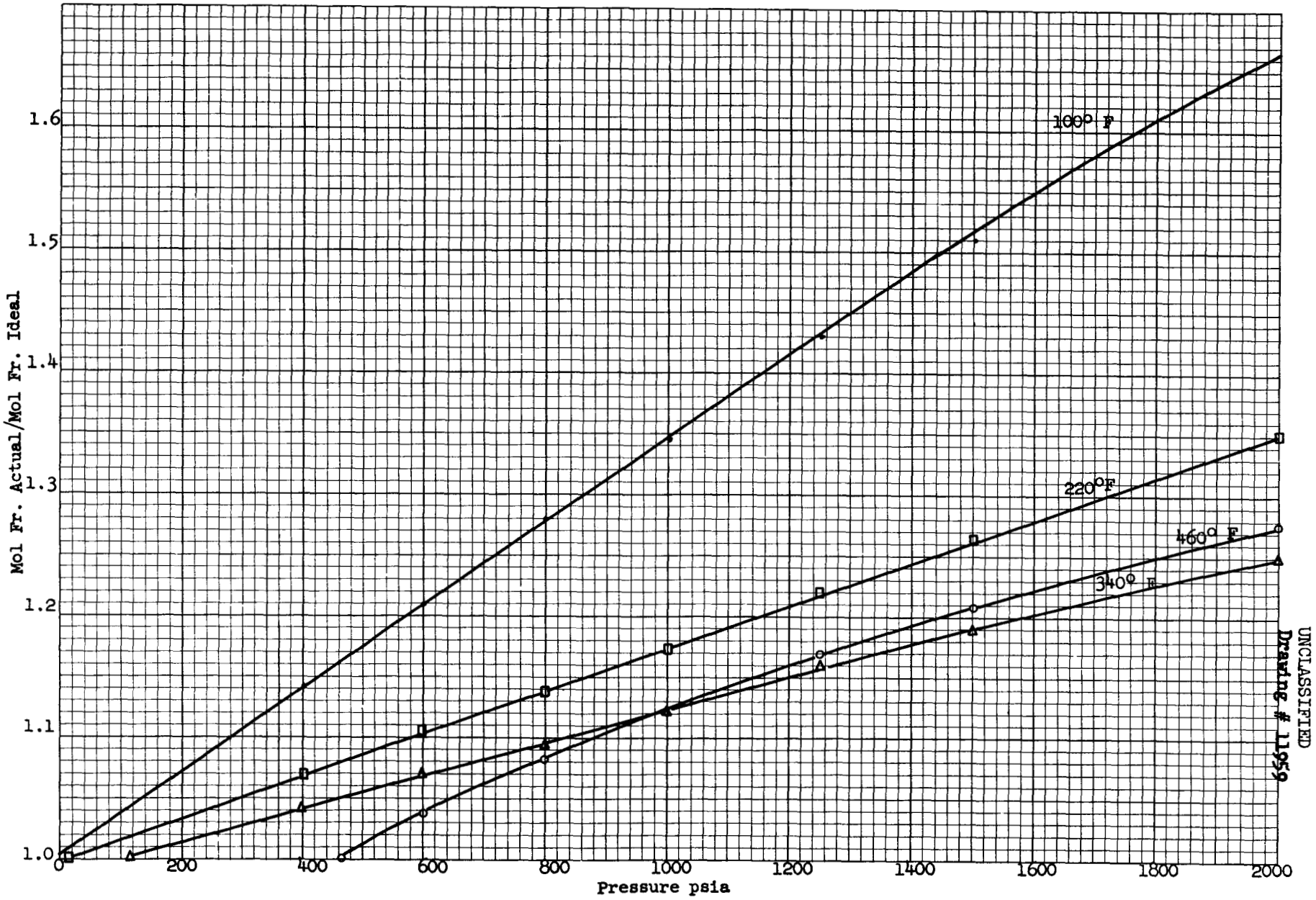


Figure 18 - Ratio of Actual to Ideal Water Vapor Concentrations in Vapor Phase for CH_4-H_2O System

other combinations of gases with water could be prepared in the same way. However, the generalized β/P chart should not be used for gases of higher molecular weight than ethane. For example, the data of Kobayaski [5] for propane-water near the three phase critical are not correlated by Figure 14, presumably because of the more nearly equal boiling points of water and propane.

Sibbitt and Suciu [15] measured the mole fraction water vapor in the vapor phase of the H_2-water system at 1000 psia total pressure. This information can be used to check the β/P chart for a system which is similar to the $2H_2 - O_2$-water system. The following table shows a comparison of the mole fraction water vapor obtained experimentally, from the perfect gas law, and from the β/P chart.

Table II

Comparison of Water Vapor Concentrations

Total pressure = 1000 psia

t-°C	Mole Fraction Water in Vapor		
	Exper. Suciu	Ideal	β/P Chart
100	-	0.0147	0.0168
150	0.077	0.069	0.075
200	0.228	0.226	0.235
250	0.588	0.580	0.591

This discussion has been limited to gases and pure water. When salts are dissolved in the liquid phase, the concentration of water in the equilibrium gas phase will be reduced. This reduction may be estimated by multiplying the concentration of water over the salt-free system by the ratio of the vapor pressure of salt solution to the vapor pressure of pure water at the same temperature.

EFFECT OF DISSOLVED SALT ON BOILING POINTS

Dissolved salts increase the temperature at which a liquid will boil at a given pressure; the effect is often called a boiling point elevation. Data have been reported for various solutions such as NaOH and H_2SO_4 (Perry, p. 173) and are generally correlated by means of Duhring line charts. Limited data are available for the vapor pressure lowering of saturated UO_2SO_4 solutions at temperatures from 25 to 70° C [16]. These data at concentrations from 8.1 to 9.1 normal have been interpolated for concentration and extrapolated for temperature by employing a chart of log $\frac{\text{V.P. } H_2O}{\text{V.P. soln}}$ versus $\frac{1}{T}$ with the NaOH data used as a guide. Figure 19 gives the estimated boiling point elevations of UO_2SO_4 solutions and the vapor pressure (bubble point pressure) for these solutions at 250° C.

The concentrations are given as grams of uranium per liter of solution at 250° C and were related to solution normality as shown in Table III.

Table III

Methods of Expressing UO_2SO_4 Concentrations

gms U / liter soln at 30° C	gms U / liter soln at 250° C	density of solution 30° C gm/cc	density of solution 250° C gm/cc	Normality N
37.1	30	1.05	.85	0.34
121	100	1.155	.955	1.02
236	200	1.31	1.11	2.00
348	300	1.46	1.26	2.93
457	400	1.60	1.40	3.84

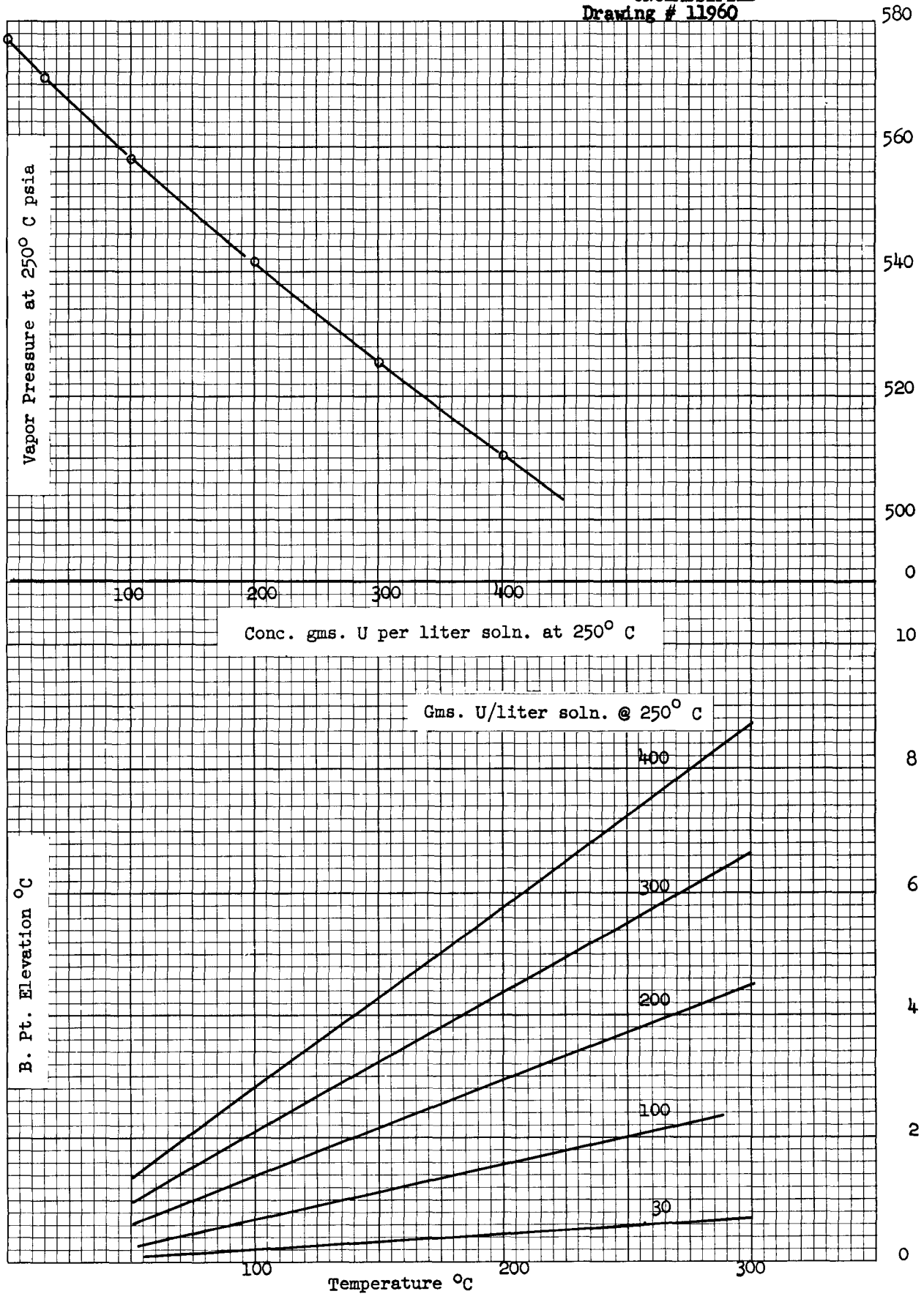


Figure 19 - Estimated Effect of Concentration on the Boiling Points of Uranyl Sulphate Solutions

TEMPERATURE CHANGE UPON EXPANSION OF SATURATED VAPORS OF H_2-O_2-H_2O

The enthalpy change is zero for the adiabatic expansion of a gas through a throttling valve when the outlet velocity returns to the inlet velocity. The temperature change for a gas at constant enthalpy is related to the deviation of the gas from the ideal gas law; it is zero for an ideal gas. The effect of pressure on the enthalpy of a gas may be computed from compressibility factors by equation (10).

$$\Delta H_T = \int_{P_1}^{P_2} - \frac{RT^2}{P} \left(\frac{\partial Z}{\partial T}\right)_P dP \qquad (10)$$

where

ΔH_T = increase in enthalpy at constant temperature

R = gas constant

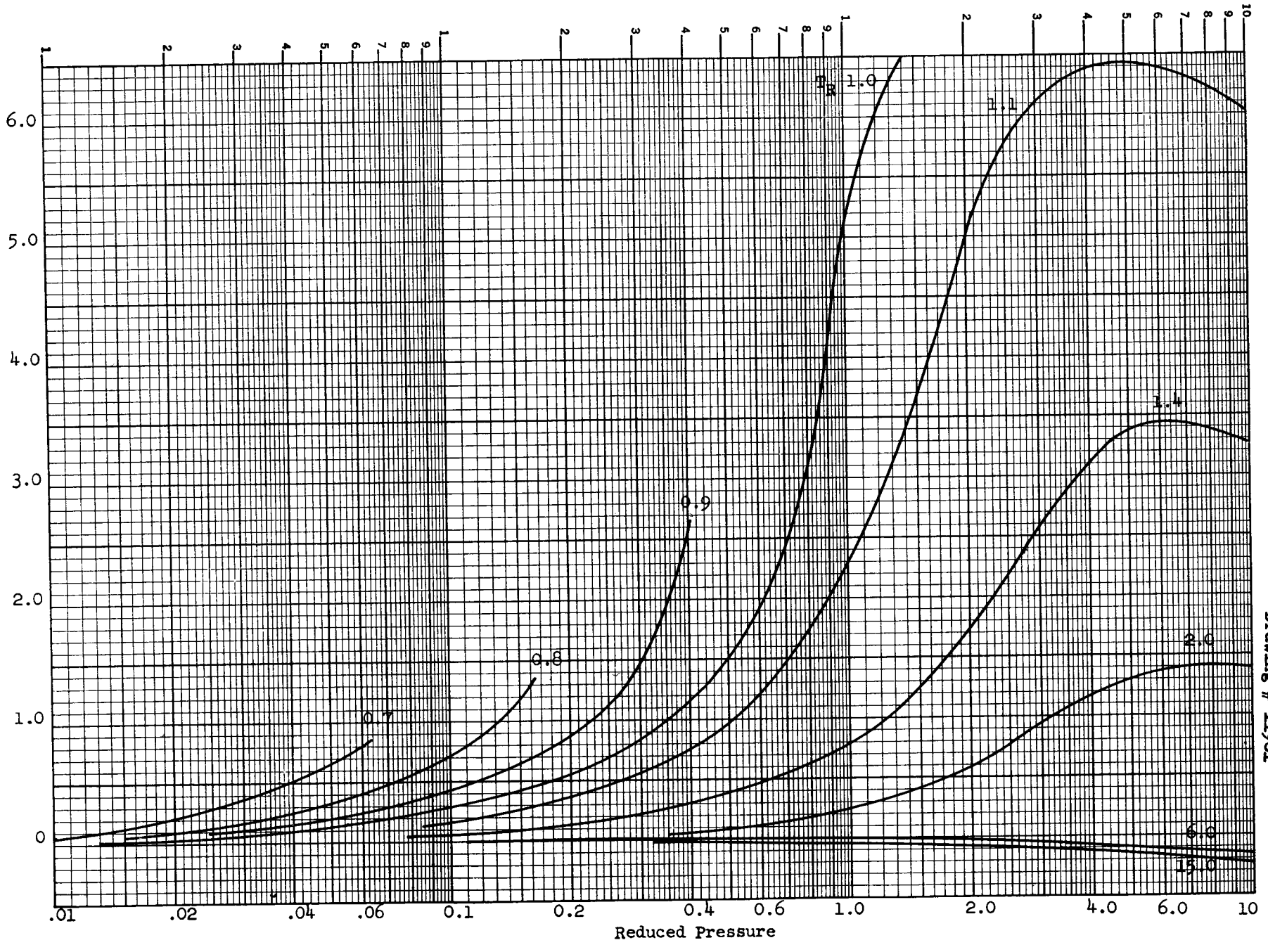
T = absolute temperature

P = absolute pressure

Z = compressibility factor in PV = ZnRT

The effect of pressure on the enthalpy has been correlated on the basis of reduced pressure and reduced temperature (Perry, p. 568) and has been very useful for hydrocarbon gases. The correlation permits computation of temperature changes upon expansion when specific heat data are available at atmospheric pressures.

To compute the temperature change for gases containing large concentrations of water, the generalized reduced temperature - reduced pressure plot for $\Delta H/T$ may be expected to be generally satisfactory. Figure 20 has been drawn



$\frac{\Delta H}{T}$ for expansion

Figure 20 - Effect of Pressure on Enthalpy

using information from Perry, p. 568, but the low reduced temperature curves are based upon the data for water since there was some differences between the water data and the generalized plot. This plot may be used for pure substances on a reduced temperature - reduced pressure basis or for mixtures on a pseudo reduced temperature and pseudo reduced pressure basis. Specific heat data are plotted at atmospheric pressure on Figure 21.

The behavior of saturated steam may be read directly from the Mollier diagram of the steam tables. The temperature drop upon expanding steam at constant enthalpy is shown on Figure 22. It may be seen that steam at 1000 psia and 285° C enters the two phase region upon expansion and leaves it at 135 psia. Thus steam follows the saturation curve for the most part but becomes superheated at low pressures, as shown at several temperatures.

The behavior of pure hydrogen may be computed from compressibility data or obtained from Figure 20. Deming and Shupe [3] computed the Joule-Thomson coefficients $(dT/dP)_H$ for hydrogen, but they appear to be in error by a factor of 41. Hydrogen is at high reduced temperatures and hence the compressibility factor decreases with rise in temperature even at low pressures. Pure hydrogen would increase at 11° C from 250° C upon expansion from 1000 psia to 14.7 psia as shown on Figure 22.

The effect of pressure on the enthalpy of mixtures may be computed from Figure 20 when the pseudo critical temperature and pseudo critical pressure are used. The pseudo critical is the molal average critical property computed from the analysis of the mixture and the critical conditions of the pure constituents.

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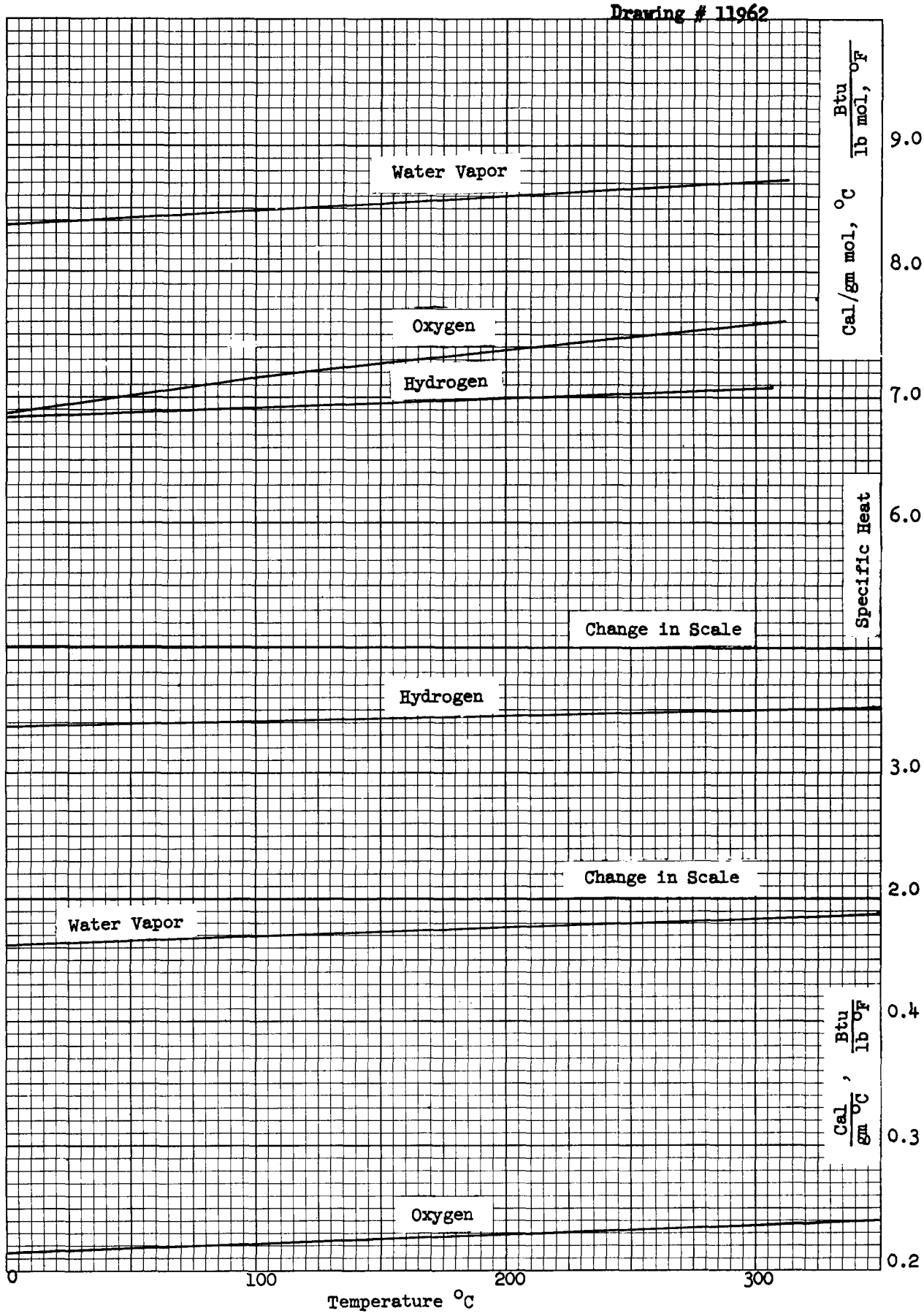

Figure 21 - Specific Heats of H_2, O_2 and H_2O Vapor

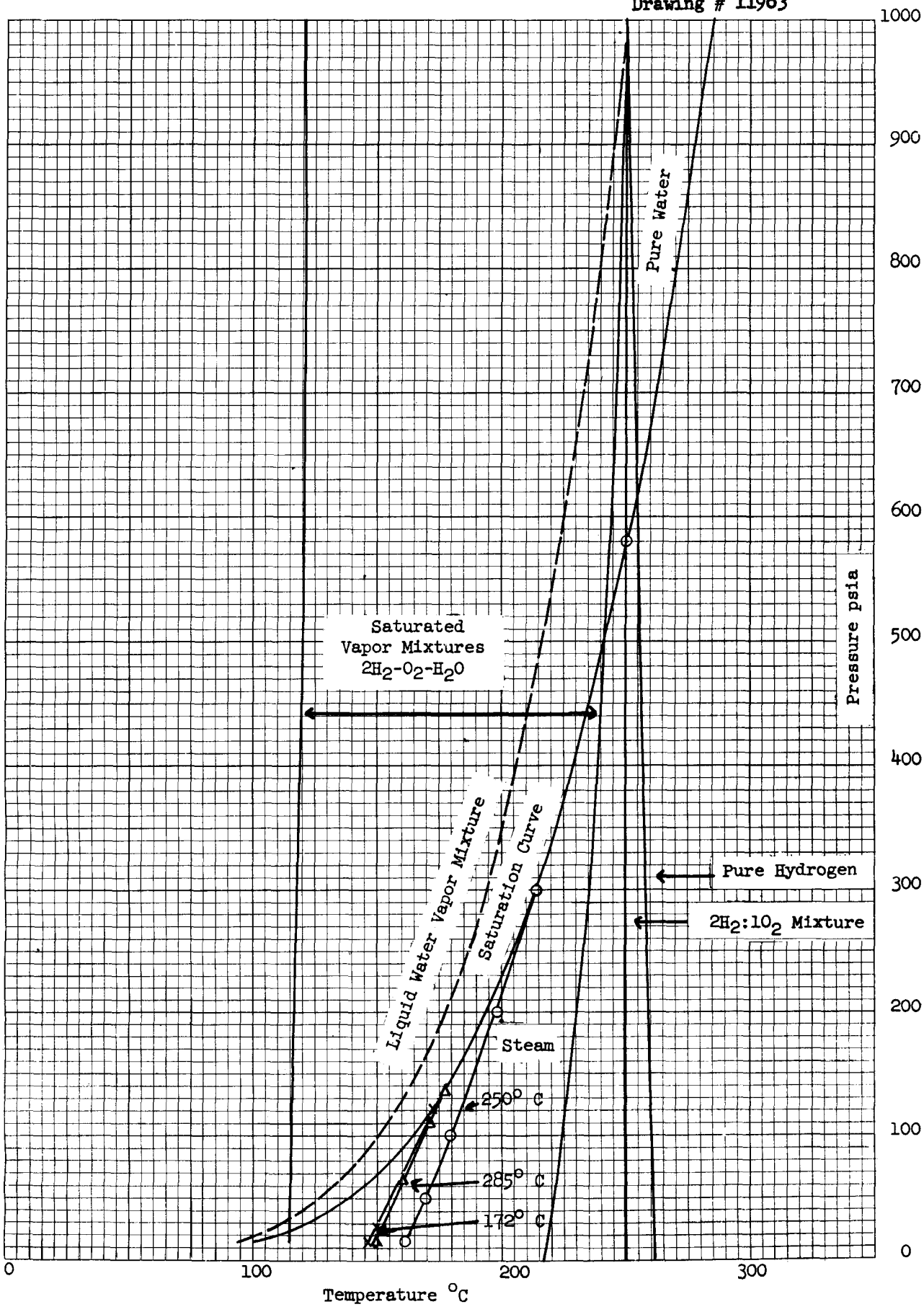

Figure 22 - Temperature Change Upon Expansion at Constant H

The temperature change upon expanding saturated mixtures of $2H_2$-O_2-H_2O from 1000 psia to 14.7 psia has been computed for a series of saturation temperatures. The mixture composition is taken as having water at a mol fraction equal to its vapor pressure divided by the total pressure; the hydrogen-oxygen ration is taken as 2.0. The results of the computations are plotted on Figures 22 and 23.

The computations for 250° C are included as an example: 250° C = 523° K = 482° F = 942° R. Vapor pressure of water = 576 psia; total pressure, 1000 psia.

Constituent	Mol Fr.	Tc°R	Pseudo Crit. Temp.	P_c Psia	Pseudo Crit. Press Psia	Cp	Cp x Mol Fr.
H_2	.283	60	16.9	188	53	7.0	1.97
O_2	.141	278	39.2	730	103	7.4	1.04
H_2O	.576	1165	672 / 728° R	3206	1848 / 2004 psia	8.6	4.95 / C_p = 7.96

Reduced temperature = 942/728 = 1.3; Reduced pressure = 1000/2004 = 0.5

$\Delta H/T$ from Figure 20 = 0.5; ΔH = 0.5 x 523 calories/gm mol

The enthalpy absorbed in lowering the temperature is 261 cal/gm mol. The temperature decrease is $\frac{261}{7.96}$ = 33° C.

The temperature decreases for a series of $2H_2$:O_2 vapors saturated with water at various temperatures when expanding from 1000 psia to 14.7 psia are plotted on Figure 23.

If saturated liquid water were expanded it would have a temperature relationship shown by the saturation curve of Figure 22; a mixture of liquid water and saturated vapor when expanded would lie at temperatures lower than the saturation curve for pure water as long as liquid were present. A mixture of 8.3 lbs. of water and 1.98 lbs. of vapor (20 cu. ft. $2H_2$ and O_2, S.T.P.) when expanded from 1000 psia to 14.7 psia would be at 201° F (94° C) with

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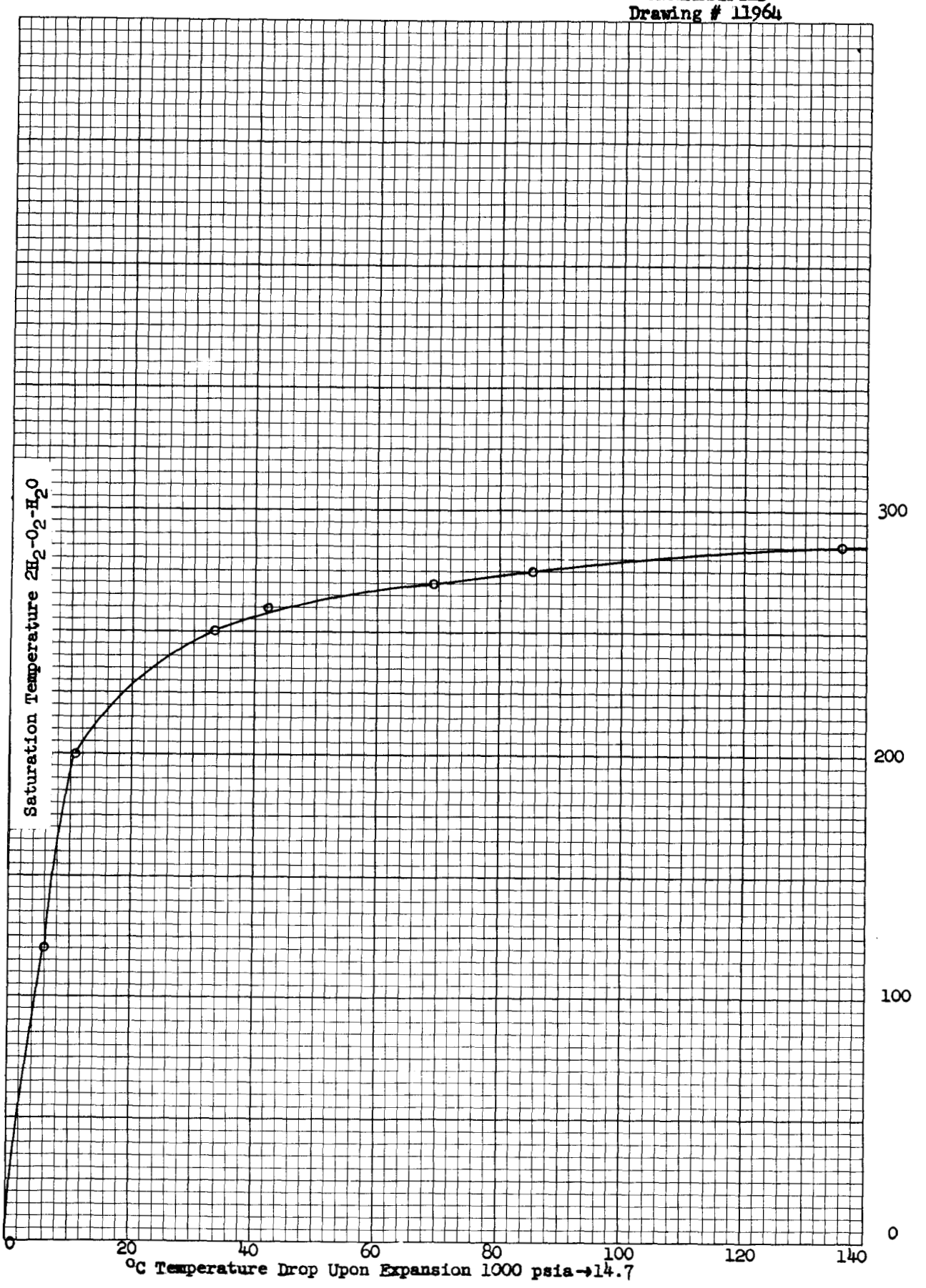

Figure 23 - Temperature Drop Upon Expanding Saturated Vapors of $2H_2$-O_2-H_2O System to Atmospheric Pressure

5.3 pounds of water remaining as liquid and the vapor containing 19% of H_2 and O_2. The dotted curve on Figure 22 shows the general nature of the final conditions when expanding the above mixture of water and vapor from 1000 psia and 250° C to 14.7 psia.

APPENDIX I

METHOD OF KRICHEVSKY AND KASARNOVSKY [7] FOR CORRELATION OF SOLUBILITY DATA

The thermodynamic relationship derived by Krichevsky and Kasarnovsky [7] for correlating solubility data appears to be suitable for gas-water systems. Their equation may be derived as follows:

The partial molal free energy of a constituent dissolved in a liquid at constant temperature and concentration may be expressed by equation 11.

$$d\bar{F}_{2_{T,N}} = \bar{v}_2 \, dP \tag{11}$$

N = concentration of constituent

$\bar{F}$ = free energy of constituent in liquid

$\bar{v}_2$ = partial molal volume of constituent in liquid

P = pressure

T = temperature

By definition, the partial molal free energy is related to the fugacity by equation (12):

$$d\bar{F}_2 = RTd \ln \bar{f}_2 \tag{12}$$

R = gas constant

$\bar{f}_2$ = partial molal fugacity of constituent

These two equations may be equated and put in integral form with integration between the limits of conditions at zero solubility at the vapor pressure of water to the conditions at some higher pressure, P.

$$\int_{\bar{f}_{2S}}^{\bar{f}_2} RT \, d\ln \bar{f}_2 = \int_{P_s}^{P} \bar{v}_2 \, dP \tag{13}$$

where $\bar{f}_{2S}$ = partial molal fugacity of constituent at the saturation pressure of the water or solvent.

p_s = vapor pressure of water at T

Formal integration requires that the temperature remain constant and that partial molal volume of the dissolved constituent ($\bar{v}_2$) in the liquid state remain constant and unaffected by pressure (P) and changes in concentration (N). The integrated form is given by equation 14.

$$\ln \bar{f}_2/f_{2S} = \frac{\bar{v}_2}{RT} (P - p_s) \tag{14}$$

Henry's Law is practically always valid at low pressure for low concentrations of gas and is given by equation (15).

$$\bar{f}_{2S} = K_H N_2 \tag{15}$$

K_H = Henry's Law constant

N_2 = mol fraction of constituent in liquid

The elimination of the $\bar{f}_{2S}$ between equations (14) and (15) yields equation (16).

$$\text{Log } \bar{f}_2/N_2 = \log K_H + \frac{\bar{v}_2}{RT} (P - p_s) \tag{16}$$

This equation may be further simplified by incorporating p_s in a modified Henry's Law constant K_M:

$$\log K = \log K_M + \frac{\bar{v}_2 p_s}{2.303\ RT} \tag{17}$$

The final equation with a modified Henry's Law constant then becomes:

$$\log \bar{f}_2/N_2 = \log K_M + \frac{\bar{v}_2 P}{2.303\ RT} \tag{18}$$

The partial molal fugacity $\bar{f}_2$ is the same in the vapor as in the liquid at phase equilibrium. The value for $\bar{f}_2$ may be obtained for ideal solutions by equation (19) from the mol fraction of the constituent in the gas phase and the fugacity of the pure constituent in the gas phase f_2^o

$$\bar{f}_2 = y_2 f_2^o \tag{19}$$

Equations (16) or (18) may be used to correlate solubility data. At a given temperature, the concentration of gas (N_2) is known as a function of pressure (P). The fugacity of the gaseous constituent must be known and the mol fraction of the gaseous constituent in the gas, the product of which yields $\bar{f}_2$ when assuming ideal solutions. The data are plotted as log $\bar{f}_2/N_2$ versus $\frac{P}{2.303\ RT}$ or $\frac{P - p_s}{2.303\ RT}$ and should describe a straight line of slope $\bar{v}_2$ and intercept log K_M or log K. Extension of the line, extends the pressure range. Krichevsky and Kasarnovsky found this method very satisfactory for correlating the solubility of N_2 and H_2.

Kobayashi [5] also found it an excellent tool for extending propane solubility in water from 3000 to 10,000 pounds per square inch after having proved the method from data on methane and ethane to this pressure.

Extrapolation or interpolation of temperatures may be accomplished by plotting $\bar{v}_2$ and K as a function of temperature. One must know the gas fugacity at the new temperature as well as the concentration of gas in the vapor phase to predict the solubility from the modified Henry's Law constant and the partial molal volume.

The correlation procedure was not successful for the H_2 data at high temperatures because they were not of sufficient accuracy. However, the nature

of the results will be shown for the method is believed to be the best correlation tool now available for extending the pressure range of accurate data.

Table IV presents the computations for two isotherms of the H_2 solubility data [17]. Figure 24 is a plot of equations (16) and (18). The fugacity data for H_2 vapor were obtained from Deming and Shupe [2] [3]. The water vapor concentration (y_1) was obtained from the correlation given earlier in this report.

It should be noted that $\bar{v}_2$ is the slope of the curves and when it is zero, Henry's Law becomes exact and there is no partial volume of the dissolved gas in the liquid. Krichevsky and Kasarnovsky [7] and Kobayaski [5] found smooth values of $\bar{v}_2$ as a function of temperature for the gases investigated.

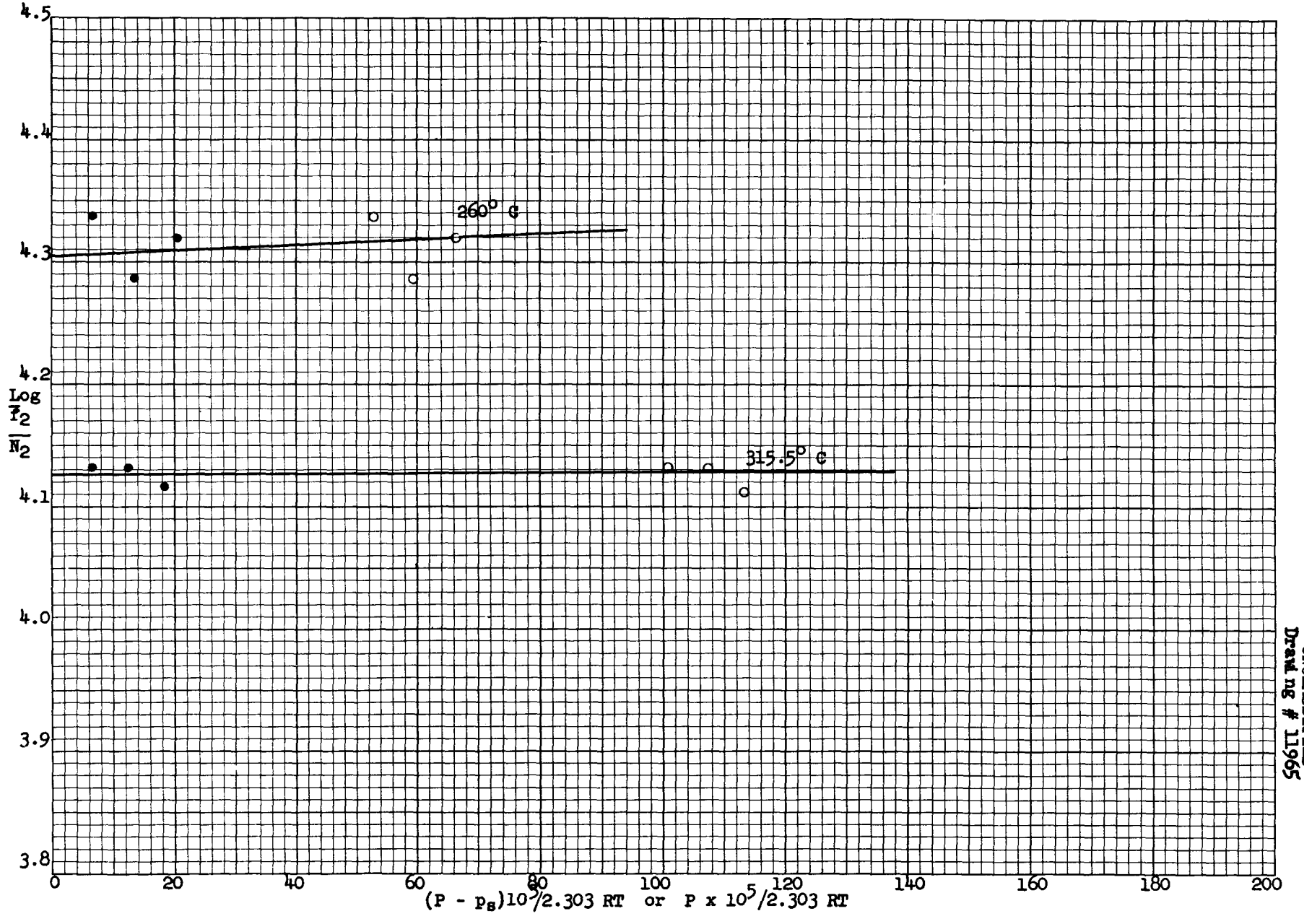

Figure 24 - Krichevsky and Kasarnovsky Correlation of Solubility for H_2 in Water

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TABLE IV

COMPUTATIONS FOR KRICHEVSKY AND KASARNOVSKY CORRELATION

total press. atm.	total press. psia	vapor press. H_2O psia	$\frac{P \times 10^5}{2.303\ RT}$ cc/mol	$\frac{(P-p_s)10^5}{2.303\ RT}$ cc/mol	Mol Fr. in Liquid $N_2 \times 10^3$	Mol Fr. H_2O in Vapor, y_1	Mol Fr. H_2 in Vapor, y_2	f_2^o atm	$\bar{f}_2$ atm	log $\bar{f}_2/N_2$
				Temperature 500° F, 260° C, 533° K						
53.2	780.0	680.8	52.6	6.73	0.313	.864	.136	54.2	7.37	4.373
60.0	880.8	680.8	59.5	13.5	0.730	.770	.230	61.4	14.12	4.286
66.8	980.8	680.8	66.1	20.2	1.003	.695	.305	68.5	20.9	4.320
				Temperature 600° F, 315° 5C, 588° 5K						
111.8	1643	1543	100.5	6.61	0.521	0.939	0.061	116	7.07	4.132
118.8	1743	1543	106.9	12.2	1.06	0.885	0.115	123.8	14.33	4.131
125.5	1843	1543	113.0	18.3	1.61	0.839	0.161	131.2	21.1	4.117

APPENDIX II

RELATIVE VOLATILITIES OF O_2, N_2, H_2, He, Xe, and Kr IN WATER

In evaluating the relative concentrations of volatile gases in the gas phase in equilibrium with the liquid solution, a knowledge of relative volatilities is desirable. The relative volatility of gas 1 to gas 2 is defined as:

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \tag{20}$$

where y = mole fraction of the component in the vapor

x = mole fraction of the component in the liquid

To obtain an approximate knowledge of the α values, Henry's and Dalton's Laws may be assumed. Then

$$Py_1 = K_1 x_1 \tag{21}$$

$$\alpha_{12} = \frac{K_1}{K_2} \tag{22}$$

where K represents the Henry's Law constant.

Figure 6 shows Henry's Law constants based upon the low pressure solubility data. The results for H_2 and N_2 were taken from Figures 3 and 5. The values for xenon and krypton were taken from the work of van Antropoff[19] and Valentiner [18] listed in the Handbook of Chemistry and Physics. The data for helium is from Wiebe and Gaddy [22] and Perry [10], while that for nitrogen is based upon Wiebe and Gaddy [20] and Saddington and Krase [13].

Figure 25 represents the relative volatilies (with respect to hydrogen) evaluated from Figure 6 using equation (22).

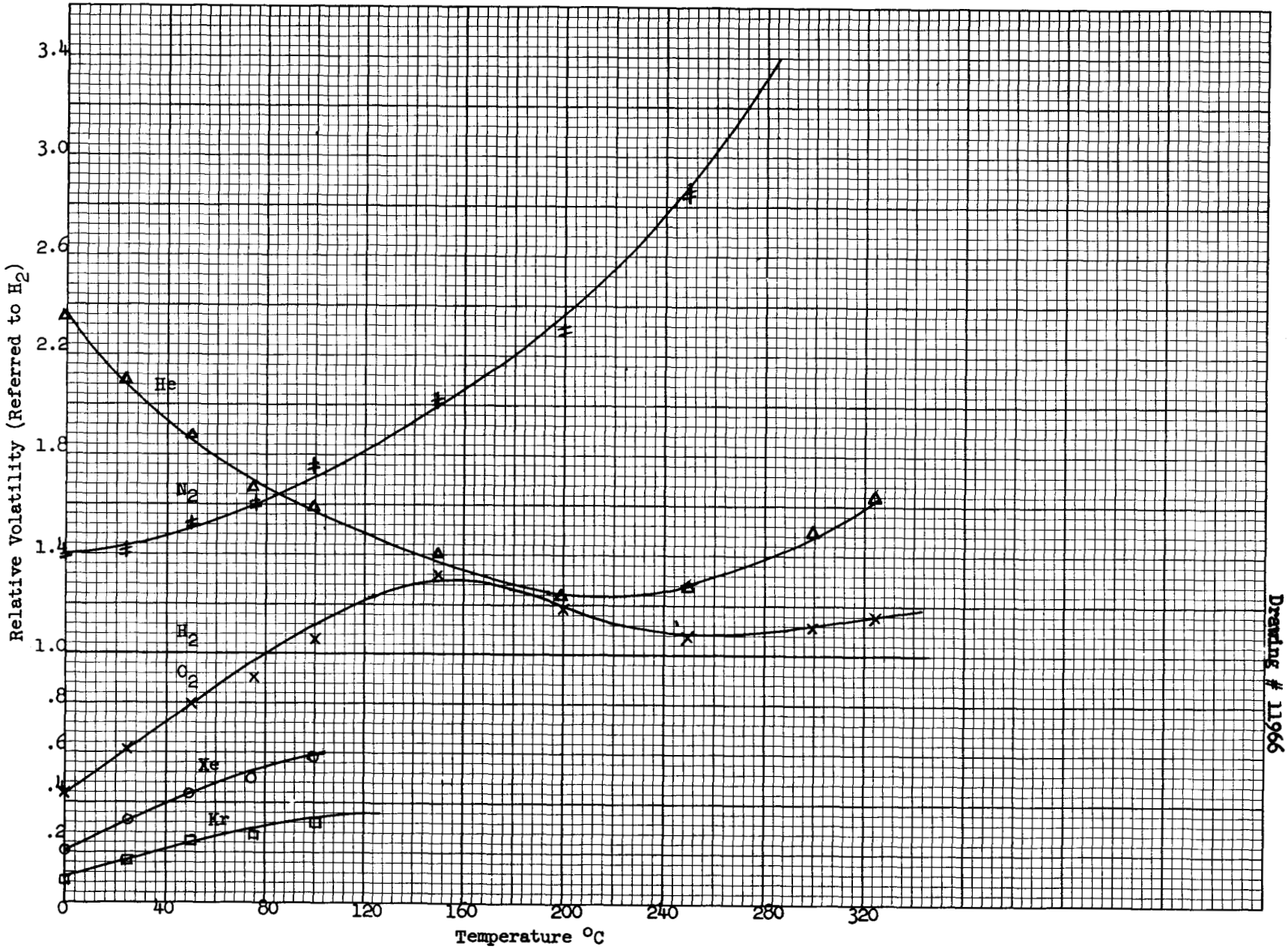

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Figure 25 - Approximate Relative Volatilities of Various Gases in Water

APPENDIX III

EFFECT OF DISSOLVED SALT ON GAS SOLUBILITY

A theory for the effect of salt concentration on the solubility of gases in water has been developed from thermodynamic considerations. By proper integration of the Duhem equation (see Appendix I) Krichevsky and Kasarnovsky derived the following expression for the solubility of a gas in pure water.

$$\ln \frac{\bar{f}_2}{N_2} = \ln K + \frac{\bar{v}_2}{RT} (P - p_s) \tag{23}$$

where $\bar{f}_2$ is the fugacity of the gas in the vapor phase, N_2 its mole fraction in the liquid phase, and $\bar{v}_2$ its partial volume in the liquid phase. The only assumption in this equation is that the partial volume, $\bar{v}_2$, is independent of temperature and pressure. If equation (23) is applied to a salt solution (constant composition) at the same temperature and total pressure the result would be

$$\ln \frac{\bar{f}_2'}{N_2'} = \ln K' + \frac{1}{RT} \bar{v}_2' (P - p_s') \tag{24}$$

where N_2' represents the solubility of the gas in the salt solution. Subtracting equation (24) from (23) gives an expression for the ratio of the solubilities of the gas in the salt solution and in water, N_2'/N_2; i.e.,

$$\ln \frac{N_2'}{N_2} = \ln K - \ln K' + \frac{1}{RT} \left[\bar{v}_2 (P - p_s) - \bar{v}_2' (P - p_s') \right] + \ln \frac{\bar{f}_2'}{\bar{f}_2} \tag{25}$$

The ratio $\bar{f}_2'/\bar{f}_2$ represents the ratio of the fugacities of the hydrogen in the vapor phase. If the vapor phase is an ideal gas,

$$\bar{f}_2' = f^o y'$$

$$\bar{f}_2 = f^o y$$

where f^o is the fugacity of the pure gas at the temperature and total pressure of the system. Hence the ratio may be written

$$\frac{\bar{f}_2'}{\bar{f}_2} = \frac{y'}{y} = \frac{1-y_w'}{1-y_w} = \frac{P-p_s'}{P-p_s} \tag{26}$$

where the last equality follows from the assumption of perfect gas behavior. This assumption is not serious because it is made for both the water and salt solution cases and the results employed in ratio form. Hence equation (25) becomes

$$\ln \frac{N_2'}{N_2} = \ln \frac{K}{K'} + \ln \frac{P - p_s'}{P - p_s} + \frac{1}{RT} \; \bar{v}_2 \, (P - p_s) - \bar{v}_2' \, (P - p_s') \tag{27}$$

The last term of the preceding expression is exactly zero if Henry's Law applies for $\bar{v}_2$ and $\bar{v}_2'$ are both zero. Even if Henry's Law does not hold, $\bar{v}_2$ and $\bar{v}_2'$ are probably about the same in magnitude so that the term would be small. Likewise $\frac{P - p_s'}{P - p_s}$ is approximately unity. Significant deviations will occur only at high temperatures and low total pressures where $P - p_s$ and $P - p_s'$ will be small, and at high salt solutions where p and p' are significantly different. In both cases the magnitude of the terms will depend primarily upon the solution concentration rather than temperature and pressure. Hence the last two terms of equation (27) are small and can be adequately represented by a function of salt concentration. Similarly the ratio of the Henry's Law constants is dependent primarily on the nature and concentration of the salt and only to a minor extent upon the temperature level. Therefore an approximate expression for the ratio of the solubility of a gas in salt solution to that in pure water is

$$\ln \frac{N_2'}{N_2} = f \text{ (nature of salt, concentration)} \tag{3}$$

This means that a plot of solubility ratio versus salt concentration should be approximately independent of pressure and temperature. Also, if the concentration variable employed is normality the spread of the curves for different salt solutions should be a minimum.

The more general equation (27) can be used as a general method for correlating solubility of gases in salt solutions. A plot of solubility data as $\ln f_2/N_2$ vs. $P - p_s$ as described in Appendix II for both water and aqueous salt solutions at one temperature would permit the evaluation of $\bar{v}_2'$, $\bar{v}_2$ and K and K'. Then equation (27) can be employed to evaluate the ratio $\frac{N_2'}{N_2}$ at any pressure and temperature.

APPENDIX IV

SOLUBILITY OF GASES IN HEAVY WATER

Since the solubility of gases in heavy water, deuterium oxide, may be desired, the literature was surveyed for such data. The only information found was the solubility of carbon dioxide in deuterium oxide at 25° C and one atmosphere.* The Ostwald coefficients are reported as 0.821 ± .007 for H_2O and 0.819 ± .005 for D_2O at 25° C. The Ostwald coefficients are the volumes of gas at 25° C and one atmosphere dissolved in one volume of liquid at 25° C. Thus the solubility of CO_2 in D_2O may be taken to be the same as for H_2O on a volume basis. The solubility of gas per gram of D_2O will equal the solubility in H_2O times $\frac{(\text{density of } H_2O)}{(\text{density of } D_2O)}$ or $\frac{.997}{1.104} = .903$ at 25°C.

Until better information is available, this procedure of multiplying the solubility of a gas in H_2O by the ratio of the densities to obtain the solubility per gram D_2O is suggested.

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* Curry, J. and Hazelton, C. L., J. Am. Chem. Soc. 60, 2771 (1938).

NOMENCLATURE

P = total pressure

p_s = vapor pressure or saturation pressure

K = Henry's Law constant

P_H = total pressure - vapor pressure

N = normality of solution

N_2 = mol fraction of solute (gas) in solvent (water)

N_2' = mol fraction of solute (gas) in solvent (salt solution)

y = mol fraction in vapor

x = mol fraction in liquid

f_L^o = fugacity of pure liquid

f_v^o = fugacity of pure vapor

$\beta = \frac{f_L^o x_w}{y_w}$

T = temperature

R = gas constant

V = volume

H = enthalpy

Z = compressibility factor

$\bar{F}$ = partial free energy

$\bar{v}$ = partial molal volume

$\bar{f}$ = partial molal fugacity

α = relative volatility

Subscripts

1 constituent (1) (sometimes water)

2 constituent (2)

w water

v.p. vapor pressure

s - at saturation or vapor pressure

M on K = modified Henry's Law constant

It should be noted that both N and x have been used for mol fraction in the liquid phase.

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