

## **Copyright Warning & Restrictions**

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

**Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation**

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

THERMODYNAMIC PROPERTIES OF FORMALDEHYDE

BY

RAYMOND H. KOO

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

This thesis is to be used only with due regard to the rights of the author(s). Bibliographical references may be noted, but passages must not be copied without permission of the College and without credit being given in subsequent written or published work.

Newark, New Jersey  
1961

6076-2-15

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

NEWARK, NEW JERSEY

JUNE, 1961

42161

Library  
Newark College of Engineering

## ACKNOWLEDGEMENTS

Grateful acknowledgement is given to Dr. Joseph Joffe for his valuable guidance and advice and to Allied Chemical Corporation for the use of their calculating machine. And last, but far from least, my appreciation goes to my wife for her patience and encouragement.

TABLE OF CONTENTS

Nomenclature	iv
Summary	vi
Introduction	1
Method of Calculation	2
Results	8
Discussion	9
Appendix	
Section I    Data from Literature	12
Section II   Sample Calculations	13
Section III  Tables and Graphs	21
References	49

## NOMENCLATURE

D	= density in gm/cc
D <sub>c</sub>	= critical density in gm/cc
D <sub>r</sub>	= reduced density, D/D <sub>c</sub>
D <sub>SL</sub>	= density of saturated liquid, gm/cc
D <sub>SV</sub>	= density of saturated vapor, gm/cc
H*	= enthalpy of ideal gas in cal/g-mole
H <sub>SL</sub>	= enthalpy of saturated liquid, cal/g-mole
Δ H*	= difference between ideal enthalpies at -19°C. and a higher temperature, cal/g-mole
λ	= heat of vaporization, cal/g-mole
M	= molecular weight
P	= pressure in atmosphere
P <sub>c</sub>	= critical pressure, atm.
P <sub>r</sub>	= reduced pressure, P/P <sub>c</sub>
ϕ	= atomic and structural constant in Eq. (2) due to -CHO group.
R	= gas constant, 1.987 cal/g-mole/°K = 82.06 $\frac{(\text{cc})(\text{atm.})}{(\text{g-mole})(^\circ\text{K})}$
S*	= entropy of ideal gas, cal/g-mole/°K
S <sub>SL</sub>	= entropy of saturated liquid, cal/g-mole/°K
S <sub>SV</sub>	= entropy of saturated vapor, cal/g-mole/°K

## NOMENCLATURE (Cont'd.)

$\Delta S^*$	= difference between ideal entropies at -19°C. and a higher temperature, cal/(g-mole/°K)
T	= temperature, °K
T <sub>b</sub>	= normal boiling temperature, °K
T <sub>c</sub>	= critical temperature, °K
T <sub>r</sub>	= reduced temperature, T/T <sub>c</sub>
$\Psi(T_r), \phi(T_r)$	= functions of reduced temperatures in Eq. (5)
$\sum \Delta_T$	= sum of structural contribution in Eq. (1) due to -CHO group
V	= specific volume, cc/gm
V <sub>c</sub>	= critical volume, cc/g-mole
V <sub>SL</sub>	= specific volume of saturated liquid, cc/gm
V <sub>SV</sub>	= specific volume of saturated vapor, cc/gm
$\sum \Delta_v$	= sum of atomic and atomic group contribution to V <sub>c</sub> in Eq. (3) due to -CHO group
Z	= compressibility factor, PV/RT
Z <sub>c</sub>	= critical compressibility factor, P <sub>c</sub> V <sub>c</sub> /RT <sub>c</sub>
$\alpha_c$	= constant in Eq. (5)



## SUMMARY

The thermodynamic properties of saturated and superheated formaldehyde were evaluated at ten degree temperature intervals from  $-19^{\circ}\text{C}$ . to  $400^{\circ}\text{C}$ . and at various pressures up to 150 atmospheres.

Lydersen's correlations were used to estimate the critical constants.

Vapor pressure data were calculated using Riedel's method.

The generalized thermodynamic correlations of Hougen, Lydersen, and Greenkorn were employed to obtain values of the thermodynamic properties in the saturated and superheated regions.

The values for temperature, pressure, specific volume, enthalpy, and entropy for saturated and superheated formaldehyde are presented in the form of tables and graphs.

## INTRODUCTION

Formaldehyde is produced by the catalytic oxidation of pure, synthetic methanol.

The most important commercial use for formaldehyde is the ever-growing resin industry. When reacted with vinyls, aniline, phenols, it gives resins of both the thermosetting and thermoplastic types. These resins find very wide application in the production of molded parts for electrical appliances and varnishes.

Beside its importance in resins, formaldehyde is an outstanding reactant in the synthesis of organic chemicals, and in the modification of proteins. Its other commercial uses are in agriculture for the control of plant diseases, in disinfectants, and in the textile, leather, metal, and paper industries.

The outstanding and ever-growing importance of formaldehyde as a commercial chemical, its diversified applications and its many unique characteristics have created a definite need for a critical and systematic evaluation of the thermodynamic properties of pure monomeric gaseous formaldehyde. This investigation is presented in the hope of fulfilling this need.

## METHOD OF CALCULATION

The critical constants of formaldehyde were evaluated using Lydersen's correlations<sup>8,10</sup> based on atomic and structural contributions which could be due to either the -CHO or the -C = O group. Based on the -C = O group contribution, the calculated critical compressibility factor  $Z_c$  of formaldehyde was greater than the value of water. This was not likely, because the value of the dipole moment of water, which is 1.84<sup>15</sup>, is less than that of formaldehyde, 2.27<sup>15</sup>. Therefore, the decision was made to estimate all critical constants based on -CHO group contribution.

Calculations of the vapor pressure from -19°C. to the critical point were based on Riedel's correlation<sup>11,12</sup>.

The thermodynamic values of specific volume, enthalpy and entropy in both the saturated and superheated regions were determined from the correlations of Lydersen, Greenkorn, and Hougen<sup>9</sup>. These correlations were derived from the theory of corresponding states and evaluation of 82 different compounds for which P-V-T data and critical constants were known.

All data available for calculations in this paper are listed in Section 1.

The procedure of calculation for the establishment of the thermodynamic properties of formaldehyde was as follows:-

(A) The critical temperature was predicted using Lydersen's method<sup>8, 10</sup> which is a modification of the Guldberg rule. The Lydersen method for critical temperature relates critical temperature,  $T_c$ , to the normal boiling temperature,  $T_b$ , and  $\theta$  which

is calculated by summing atomic and structural constants that represent the component parts of the molecule. The equation used for predicating  $T_c$  was as follows<sup>9</sup>:-

$$T_c = \frac{T_b}{\theta} \quad \text{Equation (1)}$$

$$\text{where } \theta = 0.567 + \Sigma \Delta_T - (\Sigma \Delta_T)^2$$

(B) The critical pressure was evaluated by means of Lydersen's correlation which relates critical pressure to the molecular weight and  $\theta$ , an additive constant which is determined from the molecular structure. The following equation was used<sup>9</sup>:

$$P_c = \frac{M}{(\theta + 0.34)^2} \quad \text{Equation (2)}$$

(C) Lydersen's equation for critical volume,  $V_c$ , based on an earlier attempt by Schuster, was used to evaluate  $V_c$ . It is given in the form<sup>8</sup>:

$$V_c = 40 + \Sigma \Delta_V \quad \text{Equation (3)}$$

$\Delta_V$  was calculated by summation of the incremental constant due to -CHO contribution.

(D) The critical compressibility factor was obtained from the other calculated critical constants in (A), (B), and (C) through the ratio<sup>1</sup>

$$Z_c = \frac{P_c V_c}{RT_c} \quad \text{Equation (4)}$$

(E) The partial pressure of liquid formaldehyde from  $-109.4^\circ\text{C}$ . to  $-22.3^\circ\text{C}$ . has been measured by Spence and Wild<sup>14</sup>, but no vapor pressure data were available above its normal boiling point. Therefore, the vapor pressure of gaseous formaldehyde from  $-10^\circ\text{C}$ . to the critical point was evaluated using Riedel's correlation<sup>11, 12</sup>:

$$\log \frac{1}{P_r} = \phi(T_r) + (\alpha_c - 7) \psi(T_r) \quad \text{Equation (5)}$$

The value of  $\alpha_c$  was determined using the known normal boiling point of formaldehyde at 1 atmosphere.

(F) Specific volumes of the saturated liquid were determined from  $-10^\circ\text{C}$ . to  $141^\circ\text{C}$ . by the method of Watson<sup>2</sup>. The data required for the calculations are the critical temperature and critical compressibility factor and a single known accurate density measurement as a reference state. The liquid density at  $-20^\circ\text{C}$ . was available<sup>7</sup>, and was employed in conjunction with the reduced density table by the following equation<sup>2</sup>:

$$D_2 = \frac{D_1}{D_{r1}} \quad (D_{r2}) \quad \text{Equation (6)}$$

Specific volumes were then obtained by the reciprocals of the calculated liquid densities.

(G) Specific volumes of the saturated and superheated vapor were calculated using the generalized compressibility factors<sup>4</sup> which were derived from the correlation of Lydersen, Greenkorn and Hougen. Calculation was done using:

$$PV = ZRT \quad \text{Equation (7)}$$

(H) The saturated formaldehyde liquid at  $-19^\circ\text{C}$ . was taken as the reference point for the zero value of enthalpy and entropy.

(I) The latent heat of vaporization at the normal boiling point listed by Walker<sup>16</sup> as 5.57 Kcal/g-mole at  $-19^\circ\text{C}$ . was used to calculate the value of the latent heat of vaporization from  $-10^\circ\text{C}$ . to the critical temperature. The equation derived by Watson<sup>17</sup> was used:

$$\frac{\lambda_1}{\lambda_2} = \left[ \frac{(1 - T_{r1})}{(1 - T_{r2})} \right]^{0.38} \quad \text{Equation (8)}$$

(J) The enthalpy of the saturated vapor,  $H_{SV}$ , at 1 atm. and  $-19^\circ\text{C}$ . was determined by adding the latent heat of vaporization to the enthalpy of the saturated liquid.

(K) The molal enthalpy of the ideal gas at  $-19^\circ\text{C}$ . was obtained by adding to  $H_{SV}$  the enthalpy correction corresponding to  $-19^\circ\text{C}$ . and 1 atm. Thus,

$$H^*_3 = H_{SV} + (H^*_3 - H_{SV})$$

(L) The values of ideal enthalpy from  $-10$  to  $400^\circ\text{C}$ . were obtained by adding to  $H^*_3$  the value  $\int_{T_1}^{T_2} C_p^* dT$

where  $C_p^*$  is the molal heat capacity for ideal-gas behavior as a function of temperature, and is given by Walker<sup>16</sup> as  $(9.48 + 0.00914T - 6.4 \times 10^{-7} T^2)$  calorie per gram mole per degree Kelvin.

(M) The enthalpies of the saturated vapor from  $-10^\circ\text{C}$ . to the critical point were evaluated by correcting their enthalpy departures from ideal gas using Table 47 of Watson and et al.<sup>3</sup>.

(N) The values of enthalpy in the superheated region from  $-10^\circ\text{C}$ . to  $400^\circ\text{C}$ . and from 2 to 150 atmospheres were determined by subtracting from the values of ideal enthalpy the values of enthalpy deviations from ideality obtained from Table 50 of Watson and et al.<sup>5</sup>.

(O) The enthalpies of the saturated liquid from  $-10^\circ\text{C}$ . to the critical point were obtained directly by subtracting the latent heat of vaporization calculated in (I) from the values of the saturated vapor enthalpy.

(P) The entropies of evaporation from  $-10^{\circ}\text{C}$ . to the critical point were obtained by dividing the latent heats of vaporization in (I) by the corresponding temperatures.

(Q) The entropy of the saturated vapor  $S_{\text{SV}}$  at 1 atmosphere and  $-19^{\circ}\text{C}$ . was evaluated by adding the entropy of evaporation to the entropy of the saturated liquid at  $-19^{\circ}\text{C}$ .

(R) The molal entropy of the ideal gas  $S^*_3$  at  $-19^{\circ}\text{C}$ . was obtained by adding to  $S_{\text{SV}}$  the entropy correction  $(S^*_3 - S_{\text{SV}})$  from Table 47 of Watson and et al.<sup>3</sup>

(S) The values of ideal entropy from  $-10^{\circ}\text{C}$ . to  $400^{\circ}\text{C}$ . at the constant pressure of 1 atm. were evaluated by adding to  $S^*_3$  the value

$$\int_{T_1}^{T_2} \frac{C_p^*}{T} dT.$$

(T) The entropies of the saturated vapor from  $-10^{\circ}\text{C}$ . to the critical point were obtained by first making a pressure correction for ideal behavior, and then making a correction for lack of ideality. Thus  $S^*_5 = S^*_4 - R \ln (P_5/P_1)$ , and the entropy of the saturated vapor is obtained by subtracting  $(S^*_5 - S_5)$  from values given in Table 47 of Watson and et al.<sup>3</sup>

(U) The values of entropy in the superheated region from  $-10^{\circ}\text{C}$ . to  $400^{\circ}\text{C}$ . and from 2 to 150 atmospheres were evaluated in the same manner as in (N), except Table 52 of Watson and et al.<sup>6</sup> was used instead of Table 50.

(V) The values of the saturated liquid entropy from  $-10^{\circ}\text{C}$ . to the critical point were determined directly by subtracting the entropy of evaporation calculated in (P) from the values of the saturated vapor entropy.



## RESULTS

The calculated results for the thermodynamic properties of monomeric gaseous formaldehyde are presented in the form of tables and graphs in the Appendix.

Figure I - Vapor Pressure Data

Figure II - Enthalpy - Temperature Data

Figure III - Entropy - Temperature Data

Table I - Physical constants and equations used in the calculations

Table 2 - Thermodynamic properties of the saturated liquid and vapor from the reference temperature of  $-19^{\circ}\text{C}$ . to the critical temperature at  $10^{\circ}\text{C}$ . temperature increments. The table contains vapor pressure, specific volume, enthalpy, and entropy data.

Table 3 to

14 - Thermodynamic properties of the superheated vapor at various pressures from 1 atmosphere to 150 atmospheres and from saturated temperatures to  $400^{\circ}\text{C}$ . These tables include specific volume, enthalpy, and entropy data.

## DISCUSSION

Prior to the present correlation of the thermodynamic properties of formaldehyde, an extensive and thorough literature search was conducted. However, no correlation of the thermodynamic properties of formaldehyde was found and only limited data were uncovered from which such a correlation could be constructed.

The critical temperature and pressure were estimated by Walker<sup>16</sup> as 141°C. and 65 atm. respectively. Using Lydersen's correlation<sup>8,10</sup>, the author found the critical temperature, pressure, and volume to be 141.33°C., 66.897 atm., and 113 cc/g-mole respectively, values which are in close agreement with the findings of Walker. Based on a survey of 67 compounds, the Lydersen method has the following average accuracy<sup>10</sup>:

For calculation of	% error
$T_c$	1.3
$P_c$	4.5
$V_c$	2-5

The deviation was only 1.7% for the critical temperature estimation of acetaldehyde by the method of Lydersen.

The critical compressibility factor was estimated in the present study to be 0.222 which is less than that of water. This value is believed to be reasonably accurate, because the dipole moment of formaldehyde is greater than that of water.

No vapor pressure data on formaldehyde above its normal boiling point were located; so the Riedel correlation<sup>11</sup> was used to estimate the vapor pressure over the temperature range of -10°C. to 141°C. The Riedel method was chosen because it requires the minimum data of only critical temperature, critical pressure, and one boiling point which were reasonably

predicted and given. Moreover, most of the other methods are not recommended for values of  $Z_c$  less than 0.23 or boiling point less than 250°K. This method of vapor pressure correlation has  $\pm 10\%$  accuracy.

In the absence of any experimental data, the heat capacity data for formaldehyde were calculated by Walker<sup>16</sup> based on spectroscopic measurements. These data can be represented by the following equation as a function of temperature between 0 to 400°C.

$$C_p = 9.48 + 0.00914T - 6.4 \times 10^{-7} T^2$$

The accuracy of the above equation is not known. However, formaldehyde possesses no internal rotation and this fact makes the use of the principles of statistical mechanics possible for predicting accurate heat capacity and absolute entropy for the ideal gaseous state from spectroscopic measurements. For this reason, the results obtained by using the above heat capacity equation to calculate the enthalpy and entropy of the ideal gas are believed to have satisfactory accuracy.

The generalized correlations of Lydersen, Greenkorn, and Hougen<sup>9</sup> were used to obtain the values of the specific volume, enthalpy and entropy in both the saturated and superheated regions. These correlations were based on the theorem of corresponding states which proposes that all pure gases manifest the same compressibility factors and departures from ideal gas behavior of enthalpy and entropy when measured at the same reduced conditions of pressure and temperature and at the same value of  $Z_c$ .

The specific volumes of the saturated liquid were evaluated by the method of Watson<sup>2</sup>. This method is not sensitive to errors in  $D_c$  or  $Z_c$ . The average error in estimating liquid densities by this method is about 1%.

The generalized compressibility factors were employed in calculating the specific volume in the saturated and superheated vapor regions. The average deviation of experimental values of  $Z$  from tabulated values varies from zero at low pressures to 2.5% in the critical region and to 2.0% at high pressures.

The values of the latent heat of vaporization were determined by the Watson method<sup>17</sup>. This method is capable of predicting data at all conditions up to the critical with errors generally less than 5% in magnitude.

Corrections for departures from ideality of enthalpy and entropy were made using the generalized factors presented by Hougen, Watson, and Ragatz<sup>1</sup>. The accuracy for these corrections for non-ideality is not available. However, it is believed they are reasonably reliable, especially with the introduction of a third parameter  $Z_c$  by Lydersen and et al.<sup>9</sup>

The present investigation was the basis for the compilation of tables of the thermodynamic properties for formaldehyde. Although the values of these properties were mostly derived from generalized correlations and empirical equations, it is the author's opinion that these data are well within engineering accuracy requirements for design work. Nevertheless, reliable experimental thermodynamic data should be used in preference to the data presented in this paper whenever they are available.

APPENDIX

SECTION I

DATA FROM LITERATURE

TABLE I

The following data were available for monomeric gaseous formaldehyde:

Molecular weight <sup>13</sup>	30.03
Formula <sup>13</sup>	CHOH
Normal Boiling Point <sup>13</sup>	-19.2°C.
Melting Point <sup>16</sup>	-118°C.
Heat of Formation, 18°C. <sup>16</sup>	28 Kcal/mole
Free Energy, 25°C. <sup>16</sup>	-27 Kcal/mole
Heat of Combustion <sup>18</sup>	134.1 Kcal/mole'
Latent Heat of Vaporization, -19°C. <sup>16</sup>	5.57 Kcal/mole
Trouton's Constant, -19°C. <sup>16</sup>	21.9 cal/mole/°K
Liquid Density, -20°C. <sup>7</sup>	0.8153 gm/cc
Heat Capacity of ideal gas, -19°C. to 400°C. <sup>16</sup>	
$C_p^* = 9.48 + 0.00914T - 6.4 \times 10^{-7}T^2$ cal/mole/°K	
Partial pressure of liquid formaldehyde <sup>16</sup>	
$\log_{10} P \text{ atm.} = -1429/T + 1.75 \log T - 0.0063T + 3.0177$	
where T is °K.	

SECTION II

SAMPLE CALCULATIONS



The critical properties were calculated as follows:

(A) Critical pressure  $P_c$  by Lydersen's method<sup>8,10</sup>

$$P_c = \frac{M}{(\Phi + 0.34)^2}$$

where  $P_c$  = critical pressure in atmosphere

$M$  = molecular weight = 30.03

$\Phi$  = atomic and structural constant  
= 0.33

$$P_c = \frac{30.03}{(0.33 + 0.34)^2} = 66.897 \text{ atm.}$$

(B) Critical temperature  $T_c$  by Lydersen's method<sup>8,10</sup>

$$T_c = \frac{T_b}{0.567 + \sum \Delta_T - (\sum \Delta_T)^2}$$

where  $T_c$  = critical temperature in °K

$T_b$  = normal boiling point = 253.96°K

$\Delta_T$  = structural contribution from  
-CHO group = 0.048

$$T_c = \frac{253.96}{0.567 + 0.048 - (0.048)^2} = 414.49^\circ\text{K}$$

(C) Critical volume by Lydersen's method<sup>8</sup>

$$V_c = 40 + \sum \Delta_V$$

where  $V_c$  = critical volume in cc/g-mole

$\Delta_V$  = atomic and atomic group contribution to  $V_c$  = 73 for -CHO group

$$V_c = 40 + 73 = 113 \text{ cc/gm-mole}$$

(D) Critical compressibility factor

$$Z_c = \frac{P_c V_c}{RT_c}$$

where  $Z_c$  = critical compressibility factor

$P_c$  = critical pressure = 66.897 atm.

$V_c$  = critical volume = 113 cc/g-mole

$T_c$  = critical temperature = 414.49°K

$R$  = gas law constant = 82.06  $\frac{\text{cc-atm.}}{\text{g-mole}^\circ\text{K}}$

$$Z_c = \frac{(66.897)(113)}{(82.06)(414.49)} = 0.2220$$

Vapor pressures were calculated by Reidel Correlation <sup>11,12</sup>

$$\log \frac{P_c}{P} = \Phi(T_r) + (\alpha_c - 7) \Psi(T_r)$$

where  $P_c$  = critical pressure in atmosphere

$P$  = pressure in atmosphere

$\Phi(T_r)$  and  $\Psi(T_r)$  are as functions  
of  $T_r$

$T_r$  = reduced temperature =  $\frac{T}{T_c}$

The constant  $\alpha_c$  was calculated based on the normal boiling point of 253.96°K at one atm.

$$T_r = \frac{253.96^\circ\text{K}}{414.49^\circ\text{K}} = 0.613$$

$$\log \frac{66.897}{1} = 1.851 + (\alpha_c - 7) (0.326)$$

$$\alpha_c = 6.903$$

Therefore, the general equation for vapor pressure calculations is

$$\log \frac{P_c}{P} = \phi(T_r) - (0.097) \psi(T_r)$$

$$\text{at } 10^\circ\text{C. } T_r = \frac{283.16}{414.49} = 0.6831; \quad \phi(T_r) = 1.348;$$

$$\psi(T_r) = .224$$

$$\log P_c - \log P = 1.348 - (0.097) (.224)$$

$$P = 3.156 \text{ atm.}$$

Saturated liquid volumes were determined by the following method <sup>2</sup>:

$$D_2 = \frac{D_1}{D_{r1}} (D_{r2})$$

where  $D_1$  = accurate measurement of density at  $T_{r1}$

and  $P_{r1}$

$$= 0.8153 \text{ gm/ml at } -20^\circ\text{C.}$$

$D_2$  = desired density at  $T_{r2}$  and  $P_{r2}$

$D_{r1}$  = reduced density at  $-20^\circ\text{C.} = 2.9821$

$$\text{at } 10^\circ\text{C. } T_r = 0.683 \quad D_{r2} = 2.8546$$

$$D_{SL} = \frac{0.8153}{2.9821} (2.8546)$$

$$D_{SL} = 0.7804 \text{ gm/cc}$$

$$\text{Specific Volume} = 1.2814 \text{ cc/gm}$$

Saturated vapor volumes were calculated using compressibility factors

$$V_{SV} = \frac{ZRT}{PM}$$

where

$V_{SV}$  = specific volume of saturated vapor, ml/gm

Z = compressibility factor at T°K

R = gas law constant =  $82.06 \frac{\text{cc-atm.}}{\text{g-mole } ^\circ\text{K}}$

T = temperature of gas in °K

P = pressure of gas in atm.

M = molecular weight of CH<sub>2</sub>O = 30.03 gm.

at 10°C.

Z = 0.9318 at  $Z_c = 0.222$  and  $T_r = 0.683$

$$V_{SV} = \frac{(0.9318)(82.06)(283.16)}{(3.16)(30.03)}$$

$$V_{SV} = 228.142 \text{ ml/gm}$$

The saturated liquid at -19°C. was taken as the reference state

$$H_{SL} = 0$$

$$S_{SL} = 0$$

The saturated vapor at -19°C. 16

$$H_{SV} = 5.57 \text{ Kcal/g-mole}$$

$$S_{SV} = 21.9 \text{ cal/g-mole } ^\circ\text{K}$$

The ideal gas enthalpy and entropy at -19°C. and 1 atm. were calculated as follows<sup>3</sup>:

$$\text{at } T_r = 0.613 \text{ and } Z_c = 0.222$$

$$\left(\frac{H^* - H}{T_c}\right) = 0.1947$$

$$H^* - H_{SV} = (0.1947)(414.49)$$

$$H^* = 5570 + 80.701 = 5650.701 \text{ cal/g-mole}$$

$$(S^* - S_{SV}) = 0.2292$$

$$S^* = 21.9 + 0.2292 = 22.1292 \text{ cal/g-mole } ^\circ\text{K}$$

The ideal gas enthalpy and entropy from  $-19^{\circ}\text{C.}$  to  $400^{\circ}\text{C.}$   
at 1 atm. were evaluated as represented by following relations<sup>16</sup>:

at  $10^{\circ}\text{C.}$

$$\Delta H^* = \int_{254.16}^{283.16} (9.48 + 0.00914T - 6.4 \times 10^{-7}T^2) dT$$

$$\Delta H^* = 344.757$$

$$H^* = H^*_{-19^{\circ}\text{C.}} + 344.757$$

$$= 5995.458 \text{ cal/g-mole}$$

at  $10^{\circ}\text{C.}$

$$\Delta S^* = \int_{254.16}^{283.16} \left( \frac{9.48}{T} + 0.00914 - 6.4 \times 10^{-7}T \right) dT$$

$$\Delta S^* = 1.265$$

$$S^* = S^*_{-19^{\circ}\text{C.}} + 1.265$$

$$= 22.1292 + 1.265$$

$$= 23.3942 \text{ cal/g-mole } ^{\circ}\text{K}$$

Correcting the deviation of the enthalpy from ideality<sup>5</sup>

for saturated vapor at  $10^{\circ}\text{C.}$ :

where  $T_r = 0.683$  and  $Z_c = 0.222$

$$\left( \frac{H^* - H}{T_c} \right) = 0.4361$$

$$(H^* - H) = 180.759$$

$$H_{SV} = H^*_{10^{\circ}\text{C.}} - 180.759$$

$$H_{SV} = 5814.699 \text{ cal/g-mole } ^{\circ}\text{K}$$

Correcting the entropy of the ideal gas at 1 atm. to the entropy of the ideal gas at the pressure corresponding to 10°C. <sup>1,6</sup>

where the saturated pressure corresponding to 10°C. is 3.16 atm. Therefore,

$$S^*_2 = S^*_1 - 1.987 \ln \frac{P_2}{P_1}$$

$$S^*_2 = 23.3942 - 1.987 \ln \frac{3.16}{1}$$

$$S^*_2 = 21.1092 \text{ cal/g-mole } ^\circ\text{K}$$

Correcting for ideality for the saturated vapor at +10°C. <sup>3</sup>

where  $T_r = 0.683$  and  $Z_c = 0.222$

$$(S^*_2 - S) = 0.4637$$

$$S_{SV} = S^*_2 - 0.4637$$

$$S_{SV} = 20.6455 \text{ cal/g-mole } ^\circ\text{K}$$

Saturated liquid enthalpies and entropies were determined as follows <sup>17</sup>:

at 10°C. 
$$\frac{\lambda_1}{\lambda_2} = \left[ \frac{(1-T_{r1})_1}{(1-T_{r2})_2} \right]^{0.38}$$

where  $\lambda_1$  and  $\lambda_2$  = heat of vaporization at

-19°C. and 10°C. respectively

$T_{r1}$  and  $T_{r2}$  = reduced temperature at

-19°C. and 10°C. respectively

$$\frac{\lambda_1}{\lambda_2} = \left[ \frac{1-0.613}{1-0.683} \right]^{0.38} = 1.0784$$

$$\lambda_2 = \frac{5570}{1.0784} = 5165.059 \text{ cal/g-mole}$$

$$\Delta S_2 = \frac{\lambda_2}{T_2}$$

$$\Delta S_2 = \frac{5165.059}{283.16} = 18.241 \text{ cal/g-mole } ^\circ\text{K}$$

$$\text{at } 10^{\circ}\text{C. } H_{\text{SL}} = H_{\text{SV}} - \lambda_2$$

where  $H_{\text{SL}}$  = saturated liquid enthalpy

$H_{\text{SV}}$  = saturated vapor enthalpy

$$H_{\text{SL}} = 5814.699 - 5165.059$$

$$H_{\text{SL}} = 649.64 \text{ cal/g-mole}$$

$$\text{at } 10^{\circ}\text{C. } S_{\text{SL}} = S_{\text{SV}} - \Delta S_2$$

where  $S_{\text{SL}}$  = saturated liquid entropy

$S_{\text{SV}}$  = saturated vapor entropy

$$S_{\text{SL}} = 20.6455 - 18.2410$$

$$S_{\text{SL}} = 2.4045 \text{ cal/g-mole } ^{\circ}\text{K}$$

Values of enthalpy and entropy for the superheated vapor were evaluated by the following procedure<sup>5,6</sup>:

at  $10^{\circ}\text{C.}$  and 2 atm., where  $T_r = 0.683$ ,  $Z_c = 0.222$

and  $P_r = 0.0299$

Correcting the deviation of the enthalpy from ideality

$$\left( \frac{H^* - H}{T_c} \right) = 0.2676 \text{ cal/g-mole } ^{\circ}\text{K}$$

$$H^* - H = 110.909 \text{ cal/g-mole}$$

$$H = H^* - 110.909$$

$$H = 5884.549 \text{ cal/g-mole}$$

Correcting the deviation of the entropy as a function of pressure<sup>1</sup>.

$$S^*_2 = S^*_1 - 1.987 \ln \frac{P_2}{P_1}$$

where  $S^*_1$  at  $10^{\circ}\text{C.}$  and 1 atm. = 23.3942 cal/g-mole  $^{\circ}\text{K}$

$$S^*_2 = 23.3942 - 1.987 \ln \frac{2}{1}$$

$$S^*_2 = 22.0170 \text{ cal/g-mole } ^{\circ}\text{K}$$

Correcting the deviation of the entropy from ideality<sup>6</sup>

$$(S^*_2 - S) = 0.3414$$

$$S = S^*_2 - 0.3417$$

$$S = 21.6756 \text{ cal/g-mole } ^\circ\text{K}$$

Specific volumes in the superheated region were determined by the following method<sup>4</sup>:

at 10°C. and 2 atm. where  $T_r = 0.683$  and  $P_r = .0299$   
from reference 7 at  $Z_c = .222$

$$Z = \text{compressibility factor} = 0.9814$$

$$\text{since } V = \frac{ZRT}{PM}$$

$$V = \frac{(0.9814)(82.06)(283.16)}{(2)(30.03)}$$

$$V = 379.69 \text{ cc/gm.}$$



SECTION III

TABLES AND GRAPHS

TABLE 2

THERMODYNAMIC PROPERTIES OF SATURATED FORMALDEHYDE

<u>TEMP.</u> °C.	<u>PRES-</u> <u>SURE</u> atm.	<u>SPECIFIC VOLUME</u>		<u>ENTHALPY</u>		<u>ENTROPY</u>	
		ml. per gm. <u>Liquid</u> <u>Vapor</u>		cal/g-mole <u>Liquid</u> <u>Vapor</u>		cal/g-mole/°K <u>Liquid</u> <u>Vapor</u>	
-19	1.0	1.2280	671.731	0	5570.000	0	21.9
-10	1.48	1.2420	466.158	196.959	5652.395	0.7342	21.4642
0	2.20	1.2600	321.414	426.584	5736.909	1.6045	21.0445
10	3.16	1.2814	228.142	649.640	5814.699	2.4045	20.6455
20	4.41	1.3047	166.386	873.116	5891.134	3.2058	20.3228
30	6.01	1.3295	123.598	1097.186	5958.046	4.0578	20.0408
40	8.10	1.3576	92.420	1333.301	6013.973	4.7766	19.7236
50	10.55	1.3868	71.1728	1542.133	6043.143	5.4261	19.3541
60	13.55	1.4246	55.306	1759.530	6072.345	6.0484	18.9934
70	17.10	1.4707	43.248	1984.558	6086.178	6.6908	18.6438
80	21.31	1.5224	34.008	2230.240	6090.254	7.3744	18.3044
90	26.26	1.5683	26.913	2424.196	6076.654	7.9131	17.9701
100	31.99	1.6443	20.894	2682.800	5992.366	8.6654	17.5344
110	38.43	1.7559	16.417	2923.674	5910.269	9.2263	17.0213
120	46.51	1.9315	12.355	3182.257	5745.534	9.9258	16.4458
130	55.42	2.1604	9.0778	3491.501	5516.956	10.7101	15.7340
141	66.89	3.7629	3.7629	4384.230	4384.230	12.820	12.820

TABLE 3

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT ONE ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
-19	694.52	5650.70	22.129
-10	719.11	5756.82	22.536
0	746.44	5875.65	22.986
10	773.76	5995.46	23.394
20	793.75	6116.12	23.819
30	820.67	6237.87	24.233
40	847.57	6360.65	24.634
50	874.47	6482.99	25.028
60	901.46	6608.30	25.398
70	929.00	6732.09	25.768
80	956.58	6857.81	26.130
90	984.10	6985.50	26.479
100	1011.90	7109.15	26.838
110	1040.12	7241.20	27.162
120	1067.45	7371.27	27.500
130	1095.45	7501.20	27.840
141	1126.89	7646.13	28.177
150	1150.60	7764.00	28.467
160	1177.78	7898.88	28.787
170	1204.91	8030.71	29.085
180	1233.40	8165.65	29.394
190	1260.71	8299.95	29.691

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT ONE ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole /°K</u>
200	1288.03	8438.67	29.988
210	1319.92	8572.15	30.270
220	1343.45	8713.68	30.537
230	1371.28	8850.10	30.814
240	1398.62	8990.35	31.091
250	1425.96	9127.67	31.372
260	1453.30	9269.85	31.629
270	1480.63	9412.05	31.906
280	1507.97	9555.10	32.167
290	1535.31	9698.20	32.423
300	1562.65	9842.15	32.690
310	1590.07	9988.70	32.906
320	1617.63	10136.80	33.167
330	1645.23	10273.16	33.424
340	1672.84	10432.15	33.640
350	1700.40	10580.60	33.886
360	1727.75	10736.10	34.127
370	1755.09	10881.50	34.373
380	1782.43	11034.00	34.603
390	1809.78	11185.10	34.839
400	1837.07	11329.10	35.065

TABLE 4  
THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT TWO ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
0	364.35	5754.63	21.234
10	379.69	5884.55	21.676
20	391.32	6012.38	22.130
30	404.92	6141.96	22.574
40	418.54	6272.90	23.005
50	432.18	6403.09	23.429
60	445.88	6535.65	23.827
70	459.92	6663.79	24.215
80	474.01	6794.07	24.595
90	487.98	6925.45	24.959
100	502.29	7054.85	25.340
110	516.54	7195.30	25.678
120	530.24	7330.03	26.029
130	544.51	7463.01	26.376
141	560.05	7609.53	26.721
150	572.57	7730.02	27.019
160	586.58	7866.84	27.346
170	600.37	8001.41	27.651
180	614.66	8139.08	27.970
190	628.42	8274.13	28.268

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT TWO ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
200	642.06	8415.28	28.571
210	655.90	8550.14	28.856
220	670.22	8692.92	29.126
230	684.02	8830.46	29.406
240	697.83	8971.58	29.684
250	711.57	9109.71	29.967
260	725.40	9252.81	30.225
270	739.16	9395.56	30.503
280	752.92	9538.92	30.766
290	766.69	9682.30	31.024
300	780.46	9826.55	31.291
310	794.16	9973.49	31.509
320	807.83	10122.21	31.771
330	821.50	10259.23	32.028
340	835.16	10418.85	32.245
350	848.84	10567.92	32.492
360	862.62	10724.23	32.734
370	876.34	10870.33	32.980
380	890.05	11023.56	33.212
390	903.77	11175.40	33.448
400	917.41	11319.96	33.675

TABLE 5

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT FIVE ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole /°K</u>
-19			
0			
10			
20			
30	155.82	6014.83	20.383
40	161.46	6153.24	20.824
50	167.18	6290.66	21.290
60	172.98	6430.55	21.716
70	178.85	6568.04	22.132
80	184.81	6706.56	22.542
90	190.64	6844.54	22.930
100	196.79	6981.77	23.344
110	202.67	7126.01	23.698
120	208.53	7267.07	24.065
130	214.36	7402.30	24.424
141	220.89	7547.77	24.784
150	226.15	7676.83	25.093
160	232.07	7817.89	25.431
170	237.81	7955.85	25.749
180	243.60	8098.75	26.075
190	249.21	8236.29	26.379

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT FIVE ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole /°K</u>
200	254.95	8380.56	26.690
210	260.71	8517.77	26.981
220	266.43	8662.24	27.251
230	272.00	8800.74	27.533
240	277.58	8942.81	27.812
250	283.16	9081.79	28.096
260	288.75	9225.83	28.355
270	294.32	9369.23	28.635
280	299.92	9513.07	28.902
290	305.50	9656.92	29.164
300	311.08	9801.66	29.436
310	316.60	9949.32	29.656
320	322.03	10099.33	29.920
330	327.46	10237.72	30.179
340	332.89	10398.66	30.398
350	338.26	10548.95	30.646
360	343.76	10706.03	30.889
370	349.22	10852.84	31.137
380	354.72	11006.81	31.370
390	360.23	11159.36	31.608
400	365.64	11304.88	31.836



TABLE 6  
THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT TEN ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
-19			
0			
10			
20			
30			
40			
50	78.510	6136.00	19.409
60	81.650	6280.05	19.911
70	84.843	6422.37	20.363
80	88.088	6568.23	20.809
90	91.238	6710.51	21.226
100	94.710	6856.33	21.684
110	98.337	7002.84	22.073
120	101.163	7151.52	22.462
130	104.287	7293.85	22.844
141	107.801	7449.88	23.226
150	110.607	7588.06	23.545
160	113.719	7737.16	23.907
170	116.733	7882.17	24.237
180	119.739	8032.40	24.574
190	122.661	8178.85	24.888

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT TEN ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
200	125.672	8326.62	25.208
210	128.698	8467.46	25.509
220	131.619	8614.87	25.789
230	134.481	8754.73	26.080
240	137.337	8896.23	26.367
250	140.200	9034.96	26.658
260	143.099	9178.75	26.926
270	145.947	9324.19	27.211
280	148.816	9472.87	27.480
290	151.692	9621.40	27.742
300	154.574	9770.99	28.017
310	157.399	9921.93	28.240
320	160.164	10072.81	28.507
330	162.930	10212.23	28.769
340	165.699	10374.13	28.991
350	168.453	10524.50	29.242
360	171.192	10682.64	29.486
370	173.932	10830.36	29.736
380	176.654	10985.30	29.970
390	179.396	11138.85	30.209
400	182.120	11285.42	30.438

TABLE 7  
THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT TWENTY ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
-19			
0			
10			
20			
30			
40			
50			
60			
70			
80	39.330	6171.88	18.746
90	41.099	6364.23	19.208
100	43.212	6581.79	19.731
110	45.129	6772.24	20.176
120	47.139	6918.27	20.618
130	49.027	7083.43	21.053
141	51.070	7279.75	21.502
150	52.535	7398.45	21.850
160	54.345	7571.46	22.248
170	56.054	7730.64	22.618
180	57.666	7890.04	22.970
190	59.224	8045.06	23.322

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT TWENTY ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
200	60.826	8198.28	23.649
210	62.383	8351.66	23.966
220	63.937	8507.61	24.264
230	65.433	8653.55	24.567
240	66.965	8802.52	24.866
250	68.485	8947.80	25.169
260	70.042	9099.05	25.450
270	71.564	9249.09	25.744
280	73.078	9400.43	26.021
290	74.592	9551.48	26.292
300	76.120	9703.72	26.574
310	77.624	9857.52	26.802
320	77.085	10012.21	27.069
330	80.567	10155.70	27.331
340	82.046	10321.49	27.553
350	83.520	10476.16	27.805
360	84.973	10635.39	28.049
370	86.412	10783.81	28.299
380	87.863	10939.63	28.534
390	89.363	11094.00	28.773
400	90.766	11242.73	29.006

TABLE 8

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT THIRTY ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
-19			
0			
10			
20			
30			
40			
50			
60			
70			
80			
90			
100	26.013	6227.11	18.076
110	27.337	6423.74	18.666
120	28.756	6662.13	19.262
130	30.164	6860.24	19.785
141	31.709	7077.49	20.300
150	32.882	7226.24	20.687
160	34.216	7416.45	21.130
170	35.474	7611.28	21.516
180	36.671	7746.22	21.902
190	37.860	7910.36	22.268

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT THIRTY ATM,

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
200	38.992	8071.87	22.622
210	40.103	8235.61	22.961
220	41.221	8398.69	23.276
230	42.318	8553.76	23.593
240	43.412	8708.93	23.905
250	44.491	8859.89	24.220
260	45.614	9017.45	24.514
270	46.677	9172.49	24.816
280	47.713	9328.39	25.098
290	48.751	9483.51	25.373
300	49.799	9640.72	25.659
310	50.833	9796.93	25.893
320	51.845	9951.37	26.170
330	52.901	10094.53	26.443
340	53.940	10260.15	26.676
350	54.973	10423.19	26.937
360	55.982	10585.32	27.189
370	56.972	10737.06	27.450
380	57.971	10895.28	27.693
390	58.980	11052.51	27.942
400	59.955	11201.61	28.171

TABLE 9  
THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT FORTY ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole /°K</u>
-19			
0			
10			
20			
30			
40			
50			
60			
70			
80			
90			
100			
110			
120	19.168	6280.41	17.922
130	20.550	6563.28	18.605
141	22.003	6818.87	19.213
150	22.960	7006.37	19.670
160	24.106	7215.02	20.178
170	25.141	7398.25	20.624
180	26.129	7578.78	21.047
190	27.136	7757.84	21.447

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT FORTY ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
200	28.074	7926.81	21.823
210	29.010	8096.35	22.164
220	29.904	8264.82	22.486
230	30.761	8427.77	22.820
240	31.629	8591.23	23.149
250	32.488	8750.10	23.480
260	33.390	8916.32	23.791
270	34.231	9078.00	24.106
280	35.047	9237.21	24.397
290	35.882	9396.68	24.682
300	36.711	9557.42	24.978
310	37.511	9718.06	25.220
320	38.284	9877.35	25.503
330	39.073	10025.73	25.782
340	39.864	10195.91	26.020
350	40.596	10359.28	26.286
360	41.436	10520.58	26.540
370	42.209	10675.10	26.803
380	42.995	10836.72	27.049
390	43.785	10997.35	27.299
400	44.542	11147.98	27.533



TABLE 10

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT FIFTY ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole /°K</u>
-19			
0			
10			
20			
30			
40			
50			
60			
70			
80			
90			
100			
110			
120			
130	14.041	6046.45	17.086
141	15.774	6461.19	18.013
150	16.831	6693.87	18.632
160	17.944	6953.91	19.271
170	18.857	7175.68	19.798
180	19.721	7392.68	20.284
190	20.606	7587.49	20.718

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT FIFTY ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
200	21.393	7767.25	21.118
210	22.222	7949.22	21.489
220	23.008	8125.98	21.831
230	23.755	8286.85	22.171
240	24.513	8455.70	22.512
250	25.257	8617.06	22.853
260	26.049	8787.42	23.176
270	26.772	8956.97	23.500
280	27.482	9122.82	23.801
290	28.192	9287.47	24.095
300	28.914	9454.22	24.400
310	29.610	9620.12	24.650
320	30.280	9784.51	24.939
330	30.969	9938.69	25.225
340	31.653	10114.67	25.470
350	32.329	10278.79	25.742
360	32.979	10448.05	25.999
370	33.616	10605.47	26.267
380	34.264	10770.61	26.517
390	34.915	10934.35	26.771
400	35.530	11088.71	27.008

TABLE 11

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT SEVENTY FIVE ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
-19			
0			
10			
20			
30			
40			
50			
60			
70			
80			
90			
100			
110			
120			
130			
141	4.2020	4241.96	12.082
150	5.9412	5076.02	14.636
160	8.3855	6046.95	16.696
170	9.6979	6495.72	17.744
180	10.716	6821.02	18.478
190	11.636	7100.34	19.073

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT SEVENTY FIVE ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole /°K</u>
200	12.378	7336.21	19.606
210	13.127	7554.78	20.059
220	13.809	7761.67	20.444
230	14.411	7950.06	20.822
240	15.008	8139.92	21.205
250	15.781	8322.83	21.585
260	16.222	8516.53	21.951
270	16.784	8697.81	22.306
280	17.320	8874.64	22.630
290	17.857	9050.19	22.946
300	18.410	9227.84	23.274
310	18.948	9403.69	23.544
320	19.403	9577.36	23.850
330	19.897	9741.53	24.156
340	20.390	9927.34	24.420
350	20.874	10100.82	24.710
360	21.338	10280.61	24.978
370	21.790	10447.52	25.264
380	22.253	10622.61	25.528
390	22.717	10796.17	25.796
400	23.157	10956.63	26.046

TABLE 12

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT ONE HUNDRED ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
-19			
0			
10			
20			
30			
40			
50			
60			
70			
80			
90			
100			
110			
120			
130			
141	2.7618	4230.98	12.197
150	3.0069	4603.74	13.116
160	3.9303	5221.47	14.685
170	4.8931	5879.66	16.035
180	5.9088	6342.44	17.066
190	6.9114	6706.35	17.866

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT ONE HUNDRED ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole /°K</u>
200	7.5946	6987.23	18.462
210	8.3230	7242.15	19.002
220	8.9723	7475.28	19.453
230	9.5352	7685.88	19.877
240	10.084	7893.69	20.287
250	10.616	8092.76	20.691
260	11.208	8304.16	21.085
270	11.706	8501.07	21.462
280	12.165	8693.02	21.809
290	12.644	8881.72	22.147
300	13.100	9075.40	22.498
310	13.538	9261.32	22.785
320	13.925	9439.47	23.100
330	14.333	9608.37	23.415
340	14.743	9798.03	23.687
350	15.139	9976.32	23.985
360	15.520	10157.10	24.258
370	15.888	10324.88	24.550
380	16.266	10501.01	24.820
390	16.647	10675.32	25.094
400	16.994	10840.04	25.348

TABLE 13  
THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT 125 ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
-19			
0			
10			
20			
30			
40			
50			
60			
70			
80			
90			
100			
110			
120			
130			
141	2.6119	4082.19	11.737
150	2.8093	4379.51	12.439
160	3.1266	4829.39	13.479
170	3.5224	5329.26	14.627
180	3.9664	5848.80	15.798
190	4.5186	6276.97	16.726

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT 125 ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole / °K</u>
200	5.0744	6577.75	17.365
210	5.7425	6869.96	17.976
220	6.3368	7127.13	18.455
230	6.8370	7363.43	18.934
240	7.3364	7597.35	19.393
250	7.8189	7820.46	19.842
260	8.3624	8055.90	20.287
270	8.8066	8273.53	20.697
280	9.2093	8475.85	21.063
290	9.6109	8676.14	21.420
300	10.032	8879.36	21.792
310	10.411	9074.40	22.093
320	10.740	9259.80	22.419
330	11.087	9436.78	22.745
340	11.433	9634.73	23.029
350	11.772	9819.24	23.337
360	12.087	10008.72	23.622
370	12.393	10183.97	23.931
380	12.706	10367.55	24.214
390	13.024	10549.73	24.501
400	13.314	10717.36	24.760



TABLE 14

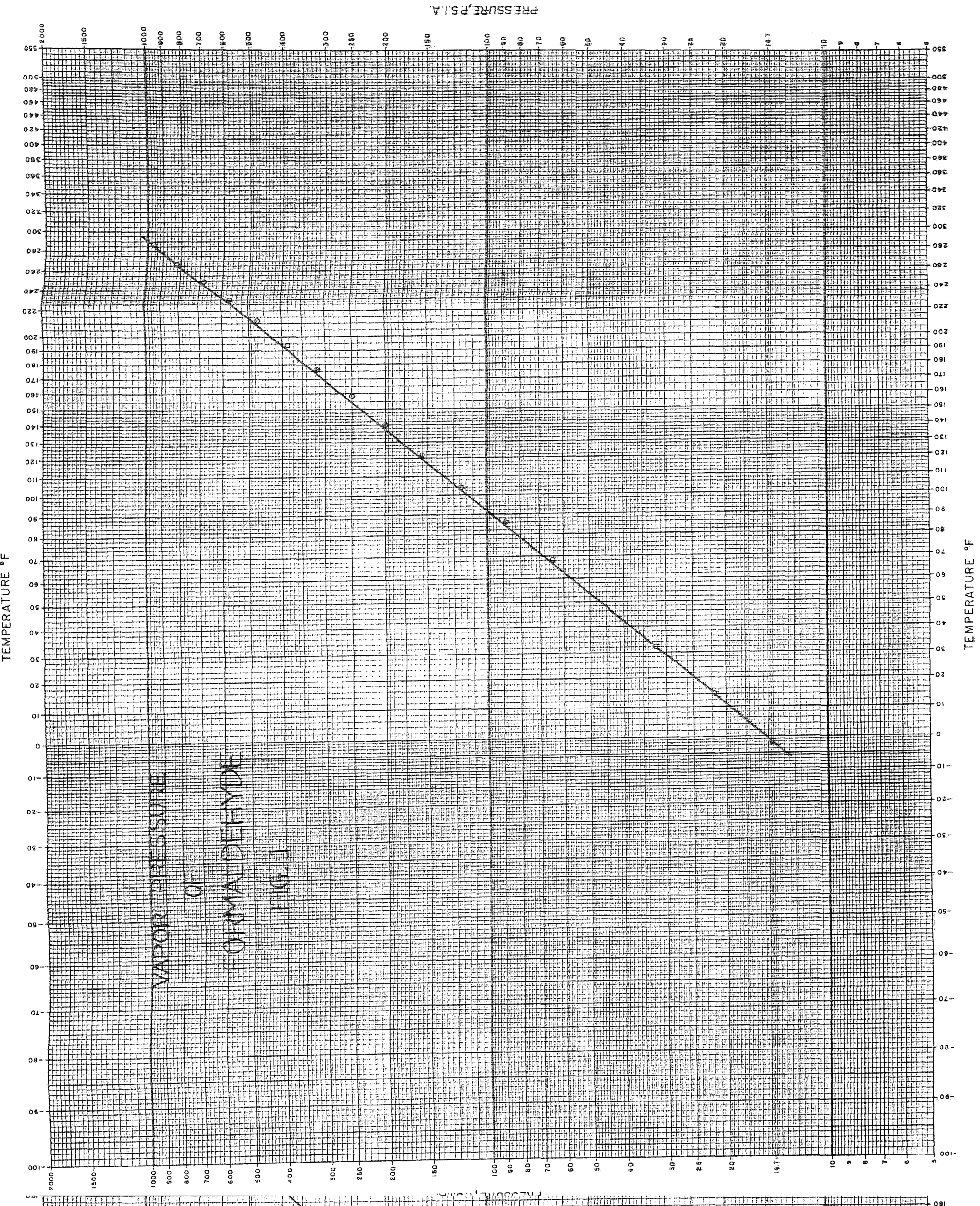
THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT 150 ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
-19			
0			
10			
20			
30			
40			
50			
60			
70			
80			
90			
100			
110			
120			
130			
141	2.5243	4024.17	11.423
150	2.6639	4309.06	12.108
160	2.8712	4707.54	13.027
170	3.1045	5144.83	14.034
180	3.4081	5619.21	15.098
190	3.7911	6045.29	16.035

THERMODYNAMIC PROPERTIES OF SUPERHEATED FORMALDEHYDE  
AT 150 ATM.

<u>TEMP.</u> <u>°C.</u>	<u>SPEC. VOLUME</u> <u>cc/gm</u>	<u>ENTHALPY</u> <u>cal/g-mole</u>	<u>ENTROPY</u> <u>cal/g-mole/°K</u>
200	4.1823	6353.52	16.787
210	4.6446	6635.38	17.272
220	5.0713	6894.62	17.772
230	5.4645	7132.16	18.243
240	5.8871	7372.30	18.712
250	6.2972	7602.46	19.171
260	6.7583	7848.25	19.628
270	7.1373	8069.62	20.053
280	7.6817	8285.20	20.443
290	7.8216	8497.93	20.822
300	8.1797	8714.82	21.216
310	8.4997	8921.05	21.536
320	8.7719	9115.99	21.874
330	9.0581	9302.91	22.215
340	9.3445	9510.39	22.511
350	9.6252	9703.60	22.832
360	9.8891	9895.58	23.121
370	10.143	10072.9	23.436
380	10.404	10258.6	23.725
390	10.669	10443.2	24.018
400	10.945	10615.0	24.284

VAPOR PRESSURE  
OF  
FORMALDEHYDE  
FIG. 1



# ENTHALPY-TEMPERATURE CHART FOR FORMALDEHYDE

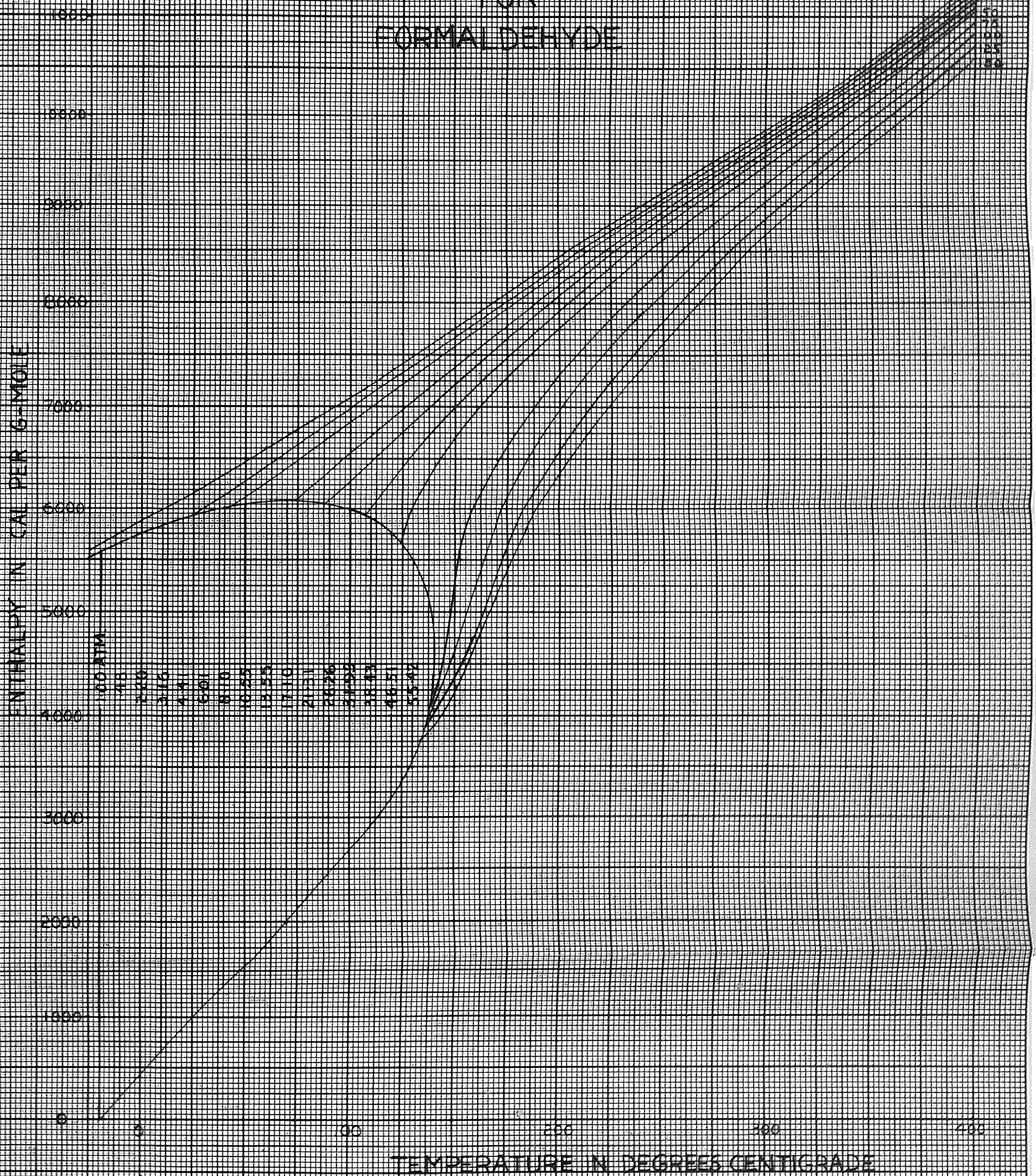


FIG. 2

ENTROPY-TEMPERATURE CHART  
FOR  
FORMALDEHYDE

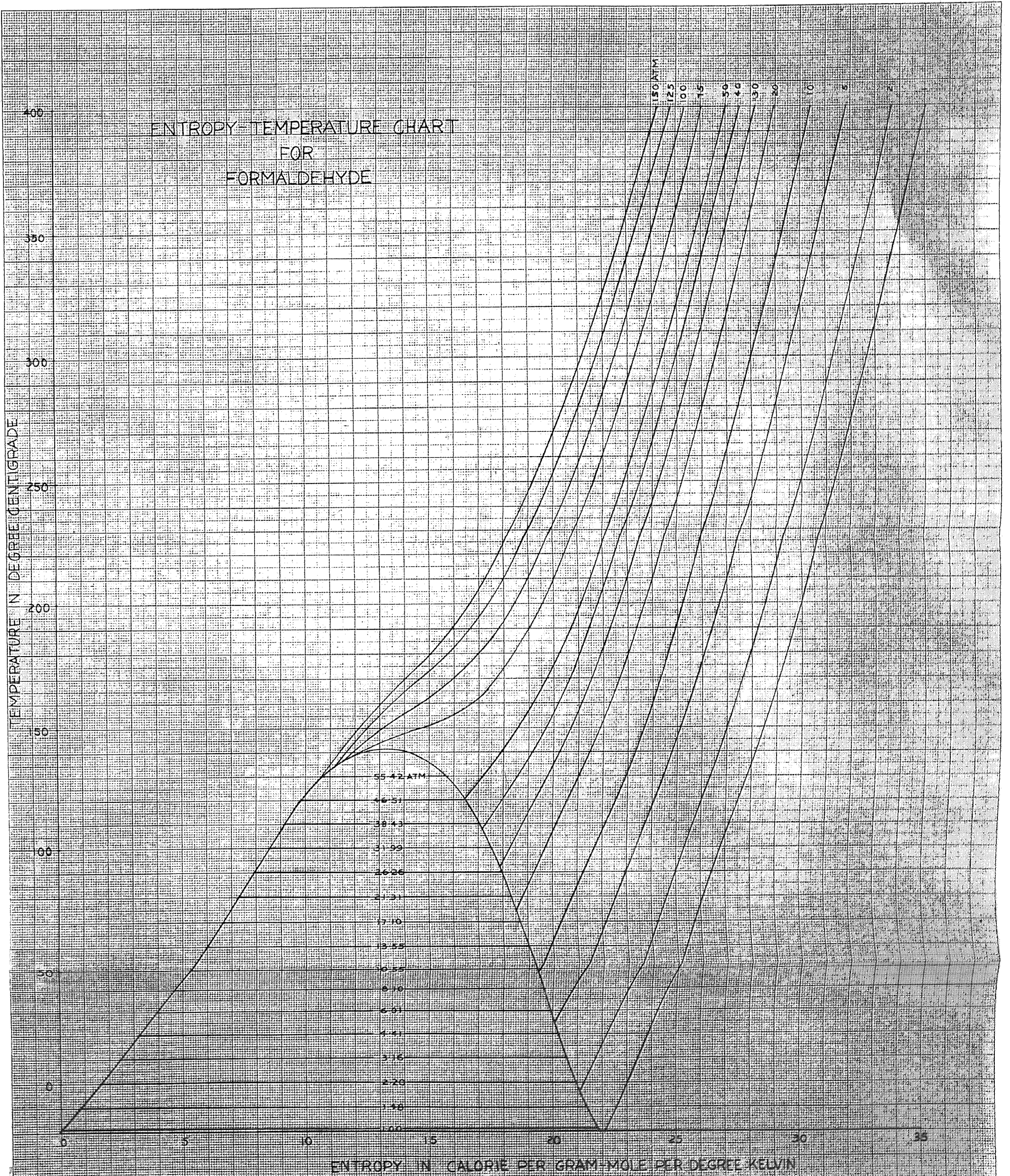


FIG. 3

## REFERENCES

- (1) Hougen, O.A., Watson, K.M., and Ragatz, R. A., Chemical Process Process, Part II, 2nd Edition, New York: John Wiley and Sons, 1959, p. 570, p. 549.
- (2) Ibid, p. 577.
- (3) Ibid, pp. 582-5.
- (4) Ibid, pp. 588-591.
- (5) Ibid, pp. 595-8.
- (6) Ibid, pp. 607-610.
- (7) Kehule, A., Ber., 25, (3), 2432 (1892).
- (8) Lydersen, A. L., Estimation of Critical Properties of Organic Compounds, Coll. Eng., Univ. Wisconsin, Eng. Expt. Sta. Rept. 3, Madison, Wis., April 1955.
- (9) Lydersen, A. L., Greenkorn, R. A., and Hougen O. A., "Generalized Thermodynamic Properties of Pure Fluids", University of Wisconsin, Eng. Exp. Sta. Rept. 4, Madison, Wis., Oct. 1955.
- (10) Reid, Robert C., and Sherwood, Thomas K., The Properties of Gases and Liquid, New York: McGraw-Hill Book Company, Inc., 1958, pp. 7-33.
- (11) Ibid, pp. 71-83.
- (12) Reidel, L., Chem. - Ing. - Tech. 26:83 (1954).
- (13) "Selected Values of Properties of Hydrocarbons and Related Compounds", American Petroleum Inst. Res. Project 44, Oct. 31, 1954, Table 209 a - E
- (14) Spence, R., and Wild, W., J., J. Chem. Soc., 1935, 338-340.
- (15) Syrkin, Y. K., and Dyatkina, M. E., Structure of Molecules and The Chemical Bonds, New York: Interscience Publisher, Inc., 1950, 206, 217.

## REFERENCES

- (16) Walker, J. Frederic, Formaldehyde, 2nd Edition, New York: Reinhold Publishing Corporation, 1953, pp. 36, 37.
- (17) Watson, K. M., Ind. Eng. Chem., Vol. 35, 1943, pp 398-406.
- (18) Wartenberg, H. V., and Lerner-Steinberg, B., Angew. Chem., 38, 591-2 (1925).