Argonne National Laboratory

ON THE EQUATION OF STATE FOR
WATER AND WATER VAPOR
IN THE CRITICAL REGION

by

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NOMENCLATURE

P	Pressure, psia
V	Specific Volume, ft^3/lb
T	Absolute temperature, $459.69 + t$, °R
t	Temperature, °F
F_i	Total force on the ith molecule
F_i'	Intermolecular force on the ith molecule
r_i	Position vector for the ith molecule
U	Internal Energy, B/lb
$\phi(r)$	Intermolecular Potential energy function
r	Distance between molecules
σ	Molecular diameter
ϵ	Maximum intermolecular potential energy
μ	Dipole moment
R'	$V_c (dP_s/DT)_{T_c} = 1.1235$ $ft^3/in.^2$ °R

Abbreviations

P-V-T	Pressure, specific volume and temperature
JSME	Japan Society of Mechanical Engineers
VDI	Verein Deutscher Ingenieure, Germany
VTI	All Union Institute, Moscow
MPI	Moscow Power Institute

Subscripts

c	property at the critical point
f	property of saturated water
g	property of saturated water vapor
fg	change in property between saturated liquid state and saturated vapor state at constant temperature
s	property along the liquid-vapor saturation line

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ABSTRACT

A parametric equation of state was derived in this work for water vapor in the critical region. It is valid for pressures ranging from 3000 to 4000 psia, specific volumes from $0.8 V_c$ to $2 V_c$ and temperatures from saturation to $752°F$. The equation satisfies the following boundary conditions at the critical point,

$$(\partial P/\partial V)_{T_c} = (\partial^2 P/\partial V^2)_{T_c} = 0$$

$$(\partial P/\partial T)_{V_c} = (dP_s/dT)_{T_c}$$

$$(\partial^2 P/\partial T^2)_{V_c} = 0$$

It is superior to the previously proposed equations of state for water and water vapor in the critical region. In this respect the maximum deviation between computed and measured values of pressure of three parts in one thousand coincides approximately with the overall uncertainty in P-V-T measurements.

By utilizing certain concepts in "Clausius Theorem of the Virial" the size of water molecule was estimated as 2.61 A from P-V-T data. This is in fair agreement with other estimated values which ranged from two to five Angstroms.

CHAPTER I

INTRODUCTION

A. General

This is the final report of the program conducted by the authors at the School of Mechanical Engineering, Purdue University on the thermodynamic and transport properties of water and water vapor. These earlier

studies were concerned with pressure, specific volume and tempera-
ture,[116-119]* coefficient of volume expansion,[120] specific heat at con-
stant pressure,[121] enthalpy[122] and thermal conductivity and dynamic
viscosity.[116,117,31]

This present report gives details concerning the developments of a
semi-theoretical equation of state for water and water vapor in the critical
region, i.e. for pressures from 3000 to 4000 psia, specific volumes from
0.0400 to 0.1250 ft^3/lb and temperatures from 698 to 752°F. The equation of
state derived in this work is based on several independent sets of
P-V-T measurements. Heretofore scientific investigations have not been
completely successful in deriving reliable equations of state for water and
water vapor in the critical region.

This report is divided into five main sections. In the first section
the various conditions that must be satisfied at the critical point are out-
lined. The second section presents the development of the concepts on inter-
molecular forces. The third lists some equations of state which have been
formulated in the past thirty years. The fourth gives details of the develop-
ment of a rational P-V-T relation for water and water vapor in the critical
region. The final section gives a discussion about potential functions and
molecular parameters which may be obtained from P-V-T data.

B. Sources of References

As in the previous work, the various national steam tables[5,6,28,61
98,127,141,142,152,163,158,159,162] were found to be very useful. Various
engineering thermodynamic texts[19,129,139,140,165,166] and the physical
chemistry and physics texts by Dorsey,[20] Moelwyn-Hughes,[115]
Partington,[128] Planck[129] and Preston[131] were utilized. Considerable
effort was made to secure copies of obscure papers and reports. The more
important of these were translated from the Russian and the German into
English.

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* Numbers in parentheses refer to the references of the Bibliography.

CHAPTER II

THE CRITICAL POINT

A. General

A description is given in this chapter of some of the experiments that have been conducted to establish certain boundary conditions at the critical point. A detailed knowledge of all boundary conditions will undoubtedly lead to a better understanding of a fundamental equation of state.

B. The Critical Point

Some of the boundary conditions which must be satisfied at the critical point are as follows,

$$V_{f_g} = h_{f_g} = 0 \tag{1}$$

$$(\partial P/\partial V)_{T_c} = (\partial^2 P/\partial V^2)_{T_c} = 0 \tag{2}$$

$$(\partial P/\partial T)_{V_c} = (dP_s/dT)_{T_c} \tag{3}$$

These conditions are in reality continuity conditions.

The first condition assures the smooth or regular joining of the liquid and vapor saturation states at the critical point. According to Partington,[128] James Watt in 1783 deduced from his experiments on water that the latent heat of vaporization would vanish at some high pressure and temperature. Watt also considered that the specific volumes of saturated water and water vapor would become identical at this same condition.

It was stated in reference 117 that LaTour[96] heated water, alcohol and other fluids in sealed glass tubes and observed that the meniscus disappeared at certain temperatures. He found that the meniscus vanished, in the case of water, at a temperature of 362°C. LaTour concluded that the water substance was in one phase at this and higher temperatues. Both Watt and LaTour must be considered as the discoverers of the critical state, i.e. where $V_{f_g} = h_{f_g} = 0$.

According to Partington[128] and Preston[131] P-V-T measurements on carbon dioxide, nitrous oxide, hydrogen chloride, ammonia, ether and carbon disulphide in their respective critical regions were conducted by Andrews.[4] Andrews concluded that, at the critical point, the critical isotherm undergoes inflection, i.e. $(\partial P/\partial V)_{T_c} = (\partial^2 P/\partial V^2)_{T_c} = 0$.

Holborn and Baumann[40] demonstrated that the critical isotherm for water satisfies the conditions of Equation (2) at the critical point. They estimated that the critical temperature for water was between 374.07 and 374.62°C.

In 1891 Cailletet and Colardeau conducted P-V-T measurements along the saturation line and in the subcooled liquid and superheated vapor regions. These measurements showed that when only one phase is present, i.e. a liquid or a vapor, the pressure-temperature curves for each mass of water substance are unique. The following continuity condition at the critical point was deduced from these measurements,

$$(\partial P/\partial T)_{V_c} = (dP_s/dT)_{T_c}$$

The above condition assures the smooth joining of the critical isometric to the saturation pressure-temperature line at the critical point. Dieterici and Van der Waals[154] recognized the validity of this phenomenological condition. However Van der Waals made no provision for this condition in his equation of state.

C. Supposed Anomalies at the Critical Point.

It is not possible to deal with all of the various anomalies that have been reported with regard to the critical point. The interested reader should consult the texts by Dorsey, Preston, and Partington which contain a detailed account of most of these anomalies.

The measurements and conclusions of Callendar,[10,11] however, will be briefly discussed. Callendar concluded from his volumetric and calorimetric measurements on water in the critical region that there existed a "two phase system," between the point of meniscus disappearance, 374°C and at a supposed point of identical density, 380°C. These conclusions were criticized by Davis and Keenan,[16] and Jakob.[46] These latter investigators thought that both impurities (air) and errors in measurements invalidated Callendar's results.

Subsequently, careful experiments showed that in the case of water, there was only one phase present at temperatures which exceed the temperature of meniscus disappearance. Some of the investigators who studied this were Eck,[22,23] Egerton and Callendar[24] Havlicek and Miskovsky,[35] Jakob and Fritz,[47] Koch,[92] Osborne et al.[125] and Riesenfeld and Chang.[132]

D. Summary

1. The boundary conditions at the critical point are in reality phenomenological laws.

2. The anomalous measurements of Callendar could not be reproduced by Eck, Egerton and Callendar, Havlicek and Miskovsky, Jakob and Fritz, Koch, Osborne et al. and Riesenfeld and Chang. The concept of the critical point for water substance is based on these subsequent measurements.

CHAPTER III

INTERMOLECULAR FORCES

A. Gene ral

The so-called perfect gas equation, PV= RT, may be derived from kinetic theory by assuming that a perfect gas is comprised of noninteracting molecules which behave elastically upon impact. The deviation of the P-V-T behavior of a real gas from that of a perfect gas may be attributed to the existence of interaction (both attractive and repulsive) between mole-cules. The supposed clustering of molecules causes further deviation be-tween the actual and ideal behavior of P-V-T.

Some molecules are more complex in structure than other molecules. Further the water molecule due to its atomic electronic structure possesses a strong electric dipole. Consequently the forces of attraction between such molecules (polar molecules) is a function of both distance and the respective angles of orientation and inclination.

It is theoretically possible to derive the P-V-T relation for any sub-stance from a knowledge of the intermolecular potential function. However, due to mathematical difficulties such calculation of P-V-T relations are re-stricted at present mainly to dilute gases and solids.

B. Intermolecular Forces

The existence of attractive and repulsive forces was first deduced by Boscovich during the eighteenth century.[109] Unfortunately Boscovich had no experimental data with which to test or modify his hypothesis.

Apparently Clausius in proving the now famous "Theorem of the Virial" assumed the existence of both intermolecular attraction and repul-sion.[14] Clausius proved that the mean kinetic energy of a system or as-sembly of molecules is equal to the virial of the forces, i.e.

$$\frac{1}{2} \overline{\Sigma m U^2} = -\frac{1}{2} \overline{\Sigma \vec{r_i} \cdot F_i} \tag{4}$$

where r_i is the position of the ith molecule and F_i is the intermolecular and external force on the ith molecule.

Van der Waals,[154,155] in deriving his now well known equation of state, took into account attraction between molecules but neglected repulsion.*

* Due to the assumed incompressibilities of the molecules the Van der Waal equation implies infinite repulsion at the instant of an encounter between molecules.

He made the following interesting statements about the possible variation of the molecular diameter with temperature. "Does the temperature influence the limiting distance of approach of the molecules during an encounter? Are the molecules of a body larger at higher temperature? On account of the uncertainty of the answers to these questions I have neglected the effect of a possible expansion of the molecules, and further researches must show how far this is justifiable."

Maxwell[109] analyzed the P-V-T measurements on carbon dioxide of Andrews.[4] He found that along a given isotherm ($30.92°C$), the pressure-specific volume product, PV, decreases with increasing values of density, $1/V$. This behavior he attributed to the existence of attractive forces between molecules. He further found that PV decreases to a minimum value and then subsequently increases very rapidly as the density increases. This latter variation he attributed to the existence of finite repulsive forces between the molecules.

Schofield some sixty years later[143] deduced similar general characteristics about the intermolecular potential. He considered, for example, that $(\partial U/\partial V)_T \, dV$ was the energy necessary to vary the separation of molecules during an isothermal expansion or compression. The name cohesion was given to the term, $(\partial U/\partial V)_T$. By means of the following thermodynamic relation $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$, the cohesion for a number of gaseous substances was evaluated by utilizing the P-V-T data of Amagat. Schofield concluded that molecules cannot be considered as rigid spheres. Futhermore he concluded that the force between two molecules is repulsive at small intermolecular separations and attractive at large intermolecular separations.

C. Summary

1. The concepts of intermolecular forces have been gradually refined over a period of some two hundred years.

2. The analyses of Maxwell and Schofield tended to show that the force between two molecules is repulsive at small intermolecular separations and attractive at large intermolecular separations.

CHAPTER IV

PREVIOUS EMPIRICAL EQUATIONS OF STATE FOR
WATER VAPOR

A. General

This section briefly summarizes various equations of state which
have been proposed for water vapor during the past twenty-five years.
Wherever possible reasons for the failure of the empirical equations
have been noted. The empirical form of the existing formulation illus-
trates the lack of success in applying the theory of an equation of state
in the dense gas region.

The equations described here are not valid in the critical region,
i.e. the region of interest of this report. The possible exceptions to this
are the Juza and Keyes equations of state.

B. Previous Empirical Equations

The various empirical equations that have been proposed during the
past twenty-five years are given in Table 1.

The equation of state of Keyes et al.[70] was essentially derived
from their P-V-T measurements.[71] They state that "the equation is
valid to 10 cm³/gram at saturation pressure and temperature but is not
reliable along the saturation line to smaller specific volumes. At higher
temperatures, however, the pressures corresponding to somewhat smaller
specific volumes may be reliable."

Keyes et al. further state that "the theory of the equation of state
is not at a stage where a suitable expression for high pressures may be
derived. Moreover the natural form of the equation of state comes from
the theory giving P as a function of V and T, or what amounts to the same
thing, B as a function of V and T." It may be seen from Table 1 that Keyes
et al. arbitrarily and out of convenience made B a function of temperature
and pressure.

The authors of this report think that there is a fundamental reason
for the failure of the equation of Keyes et al. in the critical region. Their
equation may be rewritten as

$$PV = RT \left\{ \frac{1}{1 - B/V} \right\} \tag{5}$$

According to the Binomial Theorem[13] the term $1/(1 - B/V)$ may be ex-
panded as a power series in specific volume provided that the absolute
value B/V is less than unity. With this restriction one obtains,

$$PV = RT \left\{ 1 + B/V + (B/V)^2 + --- \right\} \tag{6}$$

Table 1

EMPIRICAL EQUATIONS OF STATE

Investigator(s)	Equation of State	Constants or Parameters
Keyes, Smith and Gerry, Ref. 70, 1936	$P = \dfrac{RT}{V - B}$ where $B = B_0 \left[1 + B_0 g_1(t) \, (tP) + B_0^3 g_2(t) \, (tP)^3 - B_0^{12} g_3(t) \, (tP)^{12} \right]$ $B_0 = 1.89 - 2641.62$ $g_1(t) = 82.546 \, t - 1.6246 \times 10^5 \, t^2$ $g_2(t) = 0.21828 - 1.2697 \times 10^5 \, t^2$ $g_3(t) = 3.635 \times 10^{-4} - 6.768 \times 10^{64} \, t^{24}$	P = int atmospheres V = cm^3/gram T = °K R = 4.55504 t = $1/T$
Plank, R. Ref. 130, 1936	$P = \dfrac{RT}{V - b} + \displaystyle\sum_{n=2}^{5} A \, n/(V - b)^n$	A n are functions of temperature b is a constant
Koch, W. Ref. 94, 1937	$V = \dfrac{RT}{P} - \dfrac{A}{(T/100)^{2.82}} - P^2 \left[\dfrac{B}{(T/100)^{14}} + \dfrac{C}{(T/100)^{31.6}} \right]$ $R = 47.06$ $A = 0.9172$ $B = 1.3088 \times 10^{-4}$ $C = 4.379 \times 10^7$	P = kg/m^2 V = m^3/Kg T = °K
Juza, J. Ref. 50, 1938	$V = \dfrac{RT}{P} - \left[A(T) + B(T)\left(\dfrac{P}{10^6}\right) + C(T)\left(\dfrac{P}{10^6}\right)^4 \right]$ $A(T) = \dfrac{0.102}{(T/100)^2} + \dfrac{0.046}{[(T-220)/100]^2} - 0.000438$ $B(T) = \dfrac{2.655}{(T/100)^8} - 0.000062$ $C(T) = \dfrac{2.9 \times 10^{14}}{(T/100)^{22}} - \dfrac{3.78 \times 10^{13}}{(T/100)^{21}}$	P = Kg/m^2 V = m^3/Kg T = °K R = 47.05
Leib, E. F. Ref. 100, 1940	$PV/RT = x/(e^x - 1)$ $x = 2.5433 \times 10^6 / VT^3$	P = Kg/m^2 V = m^3/Kg T = °K R = 47.05
Tanishita, Ref. 149, 1944	$V = \dfrac{RT}{P} + \dfrac{A}{(T/100)^{2.7}} + \dfrac{BP + CP^5}{(T/100)^{8.4}} + \dfrac{DP^5}{(T/100)^{30.5}} + \dfrac{EP^{25}}{(T/100)^{147}}$ where $A = -0.668$ $B = -437/P - 6.31 \times 10^{-3}$ $C = 1.89 \times 10^{-29}$ $D = -1.6 \times 10^{-10}$ $E = -3.26 \times 10^{-43}$	P = Kg/m^2 V = m^3/Kg T = °K R = 47.06
Keyes, F. G. Ref. 72, 1949	$\log \dfrac{RT}{PV} = \log \dfrac{\omega}{V} + \dfrac{\psi \omega}{V^2}$ $\omega = V - \delta$ $\delta = 2.0624 \exp(-0.38/V)$ $\psi = \psi_0 (1 + \psi_1/V + \psi_2/V^2)$ $\psi_0 = 1260.17 \, \tau \exp 74240 \, \tau^2$ $\tau = 1/T$	P = int. atm. V = cm^3/g T = °K R = 4.55465 For $T < T_c$ $\psi_1 = 305.6 \psi_0 \tau \exp[14.848 \times 10^4 \tau^2]$ $\psi_2 = 0$ For $T > T_c$ $\psi_1 = (479.76 + 141500 \, \tau) \psi_0 \tau$ $\psi_2 = \dfrac{75.364 - 27.505 \psi_0}{\psi_0^3}$
Timrot, D. L. Ref. 152, 1952	$V = \dfrac{RT}{P} - \left[A(T) + B(T) \, P + C(T) \, P^2 + D(T) \, P^{3.8} + E(T) \, P^8 \right]$	P = Kg/cm^2 V = m^3/Kg T = °K R = 47.053
Vukalovich, M. P. Ref. 158, 1951	$PV = RT \left[1 - A(T)/V + B(T,V)/V^2 \right]$ $A(T) = 0.039995 \, T + 63.2 + \dfrac{10005}{(T/100)^{2.468}}$ $B(T,V) = \dfrac{8.941}{(T/100)^{2.468}} - \left(1 - \dfrac{22.70}{T^{0.5}} \right)\left(1 + \dfrac{0.0069}{V} - \dfrac{35.57}{(1000V)^3} \right)\left(\dfrac{85014}{(T/100)^{5.936}} \right)$	

<div align="center">Table 1 (Cont'd.)</div>

Investigator(s)	Equation of State	Constants or Parameters
Vukalovich, M. P. Ref. 160, 1956	$PV = RT\left[1 - \sum_{n=1}^{4} (\beta_n V^{-n})\right]$ $B_1 = 0.00100 + \frac{73.80}{RT} - 691091\, T^{-3.0937} \exp\left(\frac{Tc}{T}\right)$ $B_2 = -.0017277 \exp .007511\, T$ $B_3 = 0.11882 \times 10^{-5} \exp(-.00575\,T) - 10^{-8} \exp\left[-0.3501 \times 10^{-10}(T/100)^9\right]$ $B_4 = -0.26401 \times 10^{-9} \exp(-.00316\,T) + 1.5116 \times 10^{-11}$ $\exp\left[2.8521 \times 10^{-7}(T-673.16)^2 - 1.7781 \times 10^{-11}(T-673.16)^4\right]$	P = Kg/m3 V = m3/Kg T = °K R = 47.060
Juza, J. Ref. 53, 1958	$P = \frac{-RT}{V-b} - \frac{1}{V^2}\left[A + \frac{B}{T^5} + \frac{C}{T^8} + \frac{D}{f(T)}\right]$ b, A, B, C and D are functions of specific volume (under modification) f(T) is a function of temperature (under modification)	P = Kg/cm2 V = m3/Kg T = °K R = 47.05
Horlock, J. H. Ref. 45, 1956	$\frac{PV}{T} = 84.6 - 4.3\left(\frac{P'}{400}\right)^{1.35}\left(\frac{1060}{T}\right)^{5.85}$	P = lb/ft2 V = ft3/lb T = °R P' = lb/in2

If B is assumed to be a function of V and T, Equation (6) is a special form of the well known virial expansion of Onnes[124] i.e.

$$PV = RT\left\{1 + A_1(T)/V + A_2(T)/V^2 + \cdots\right\} . \tag{7}$$

At the pressure and temperature condition corresponding to 10 cm^3/g on the saturation line, $RT/PV \simeq 1.90$. Consequently $B/V = 1 - RT/PV \simeq -0.9$. At lower specific volumes ($V < 10$ cm^3/g) the values of RT/PV exceeds two and at the critical point and in the critical region it can approach values as high as four. It is reasonable to conclude that the failure of the Keyes et al. equation is probably related to the fact that it occurs in that part of the critical region where $|B/V| > 1$.

It was stated previously that Equation (6) is a special form of the Onnes virial equation of state. Consequently it appears that the convergence of the virial equation of state in the critical region is doubtful.

According to Schmidt[140] the fifth order polynomial equation of Plank[130] may be used to accurately describe the properties of water vapor in the critical region. Schmidt made no specific mention of a definite application of the Plank equation. Recently, however, Rombusch[135] found that the Plank equation reproduced pressure values for the critical isotherm of water vapor only to within three per cent.

The equation of state of Koch[94] was derived from the P-V-T values adopted at the TIC.[5] Timrot[150] showed that specific volumes computed from the Koch equation were in good agreement with those adopted along the saturation line at the TIC for pressures only to about 100 atmospheres. It may be concluded that Koch's equation is definitely not valid in the region of interest of this report.

Juza[50] derived his equation of state from the calorimetric measurements of Havlicek and Miskovsky[35] Koch[91] and Egerton and Callendar.[25] The equation is not valid in the region of interest of this report.

Leib[98,99,100] utilized the P-V-T data adopted at the TIC[5] to derive his equation of state. Some concepts of statistical mechanics were used to derive the equation. According to Leib, the equation is valid in that part of the superheated vapor region where $P \leq P_c$ and $V \geq 2 V_c$.

In 1944 Tanishita[149] derived an empirical P-V-T formulation for superheated water vapor.* The equation, which was subsequently used for the construction of the 1955 J.S.M.E. tables,[6] is not valid in the critical region.

The equation of state derived by Keyes[72] in 1949 was based on his P-V-T measurements.[71] It was used to compile values for various thermodynamic functions in references 26, 27 and 36.

Keyes noted that at very large values of specific volume and at high temperatures the equation becomes identical in form to Dieterici's[18] equation, i.e.

$$P = \frac{RT}{V - \beta} \, e^{-A_0 T/V}$$

He further found marked similarity between the form of his present equation, the equation of Beattie and Bridgeman,[7] and the equation he used some forty years ago[66] for the pressure-volume-temperature relation of ammonia.

Keyes[72] observed that the critical isotherm computed from the $t > t_c$ equation lies below the critical isotherm computed from the $t < t_c$ equation, to the extent of 1.5 atmospheres (22 psia). In addition he found that $(\partial^2 P/\partial T^2)_V$ does not assume the value of zero for the critical isotherm at the critical specific volume. Keyes concluded that "an element in the equation of state may have eluded recognition."

Since 1949, Keyes has amended his equation of state several times.[73,74,75,76] Keyes[74] utilized the recent P-V-T measurements of Kirillin et al.[77,81] and of Holser and Kennedy[41,42,43] to derive values for the second virial coefficient. Keyes concluded that the consistency of the Kirillin data above 500°C (932°F) was not satisfactory.

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*The writers of this report are of the opinion that Tanishita employed the TIC values[5] to evaluate the constants in his equation.

In 1952 Timrot[152] derived two empirical equations of state from his[150,151] and other* experimental measurements of specific heat at constant pressure. The first equation is valid in the subcritical and super-critical regions where the specific heat is less than 1.0 B/lb°F. The second equation of state describes the region near the saturation line as well as in the supercritical region where the specific heat has values in the range 1 to about 4 B/lb°F. The form of the second equation will not be given since it was not explicitly given in the 1952 Timrot tables.

These two equations were used to compute values for the various thermodynamic properties of water vapor in the Timrot steam tables.[152,153] In the region of interest of this report the values in the Timrot tables were derived by Vargaftik[156,157] by an undisclosed graphical method.

According to Romadin[134] Vukalovich initiated much theoretical research[158-162] on the thermodynamic properties of water vapor since 1935. The equation of state derived by Vukalovich and used in his 1952 steam tables is based on the hypothesis of association of molecules into double and triple complexes. He assumed that the individual molecules combine purely mechanically into these higher complexes.

Vukalovich's equation of state is not valid in the region of interest here. He stated that in the critical region water vapor consists not only of double and triple complexes but also of higher ordered complexes. Thus Vukalovich implied that the 1952 equation is not valid in the critical region because these higher associations were not taken into consideration.

In 1956 Vukalovich[160,161,162] derived an equation of state which was claimed to take into account associations of up to five molecules. It is similar in form to the virial equation.[124] Even the 1956 equation is not valid in the critical region.

The equation of state proposed by Juza[51,52,53,54,55] is based solely on the calorimetric measurements of Havlicek and Miskovsky. Juza stated the equation satisfied the following conditions at the critical point,

$$(\partial P/\partial V)_{T_c} = (\partial^2 P/\partial V^2)_{T_c} = 0$$

$$(\partial P/\partial T)_{V_c} = (dP_s/dT)_{T_c}$$

$$(\partial^2 P/\partial T^2)_{V_c} = 0$$

The last condition is the mathematical statement for a straight line rela-tionship between pressure and temperature along the critical isometric.

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*Although no specific mention was made it is thought that Timrot used the measurements in references 35, 90 and 91.

In the region of specific volumes, $V > V_c$ the values obtained from Juza's equation of state were in good agreement with the smoothed P-V-T values of references 116 and 119. However for specific volumes, $V < V_c$ the agreement was only fair. In view of this analysis it is reasonable to conclude that the empirical equation of Juza is satisfactory in that part of the critical region where the specific volume is greater than the critical specific volume.

Horlock's equation of state[45] represented the specific volume of superheated water vapor to within one and one-half per cent for pressures from 200-2000 psia and temperatures from 400 to 1000°F. Evidently Horlock employed some of the ideas proposed by Callendar.[10,11]

In 1958 Kirillin[83,84] outlined the techniques which were utilized by various investigators to derive P-V-T formulations. He was critical of the values derived by Keyes[74] for the second virial coefficient. Furthermore he found that Keyes' graphical extrapolation to zero density was unrealistic since at extremely low densities the majority of the experimental points along various isotherms were lower, or below that, of the extrapolating lines.

Kazavachinsky et al.[56-60,64,65] have done considerable research on the development of an equation of state for superheated water vapor. They evidently utilized the P-V-T measurements of Keyes,[71] Timrot,[150] Holser and Kennedy,[43] Kirillin[87] and Osborne et al.[125] In the region of interest of this report the equation has not been completely verified or compared with all of the available P-V-T and calorimetric measurements. Kazavachinsky[59] stated for example that, "It is necessary to note that the deviations between the values of specific heat obtained by the equation and the data of others does not exceed two per cent. However upon approach to the saturation curve (for subcritical temperatures) and the maximum (for supercritical temperatures) the deviations become larger and reach six to twelve per cent on the various maxima."

Kazavachinsky attributed the above deviation to the fact that measurements of specific heat possess large errors in this region. However since the largest computed value of specific heat is 6.00 B/lb°F it is reasonable to assume that their equation may be in need of adjustment in the vicinity of the critical point.

C. Summary

1. Of the many equations of state proposed only in the equations proposed by Keyes and Juza was an effort made to ensure that the various boundary conditions at the critical point were even approximately satisfied.

2.   The equation of state proposed by Juza is thought by the present authors to represent measurements to within experimental uncertainty in the region for which specific volumes exceed the critical specific volume.

3.   Further theoretical and experimental research is needed in order to derive an equation of state for water vapor in the critical region.

CHAPTER V

A DEVELOPMENT OF AN APPROXIMATE EQUATION OF STATE
FOR WATER VAPOR IN THE CRITICAL REGION

A. General

The approach taken by the authors of this report to develop an equation of state was both rational and empirical. It was a rational approach since due regard was given to the various boundary conditions which must be satisfied at the critical point. On the other hand it was empirical since independent precise sets of volumetric measurements were utilized.

B. Experimental Data Utilized

The experimental P-V-T values utilized are essentially those which were considered most precise in references 117 and 118. Specifically along the saturation line the pressure-temperature measurements of Egerton and Callendar,[24] Osborne et al.[126] and Smith et al.[144] were chosen and considered as a single body of measurements. This data was used to obtain a most probable value for the derivative $(dP_s/dT)_{T_c}$.

There have been a number of independent sets of P-V-T measurements undertaken on subcooled water and superheated water vapor. The P-V-T measurements utilized in this region were those of Havlicek and Miskovsky,[35] Holser and Kennedy,[43] Keyes et al.[71,145] and Kirillin et al.[78,79,81,82,85,86,87] In all of these investigations, it may safely be stated, that pressures were measured to within one part in one thousand, specific volume to within two parts in one thousand and temperatures to within 0.1°C. Measurements of other investigators were not utilized solely due to the fact that errors in their measurements of pressure specific volume and temperature exceeded the above mentioned limits of error.

C. Development of the P-V-T Formulation

The starting point of the development of the equation of state of this work was an examination of PV - V isotherms in the critical region. Figure 1 is a small-scale reproduction of a PV - V plot in which the above values were drawn accurately to within a few parts in ten thousand.

One of the remarkable features of Figure 1 is the almost identical manner in which the pressure-specific volume product, PV, varies with the specific volume, V, along various isotherms.

After a very detailed study of Figure 1 it was concluded that for any given specific volume, the change in the pressure-specific volume product with temperature is invariant to a first approximation. Consequently

for the range of P-V-T of Figure 1 the following relation is valid to a first approximation,

$$[\partial(PV)/\partial T]_V = R' = \text{constant} \tag{8}$$

Such invariance, even to within first approximation, is noteworthy.

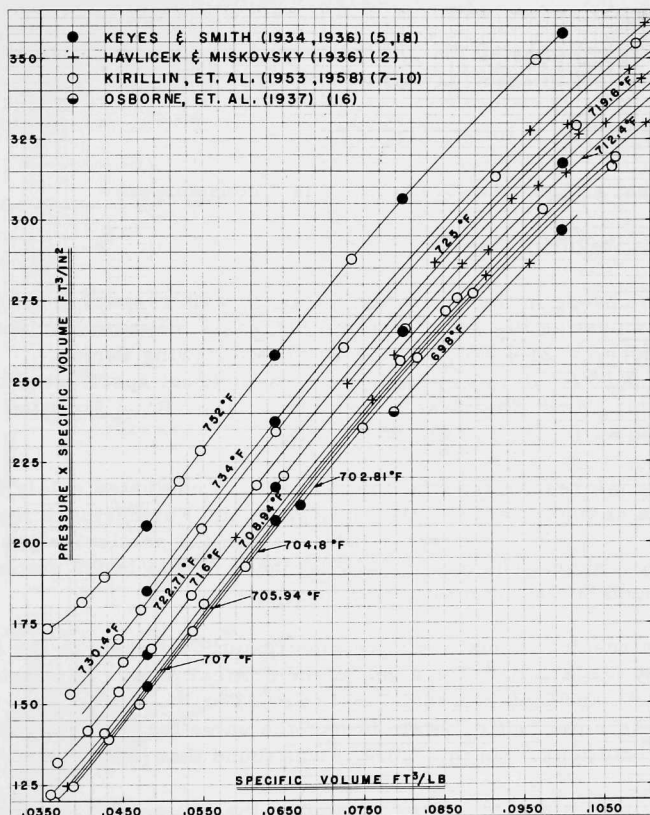
Fig. 1. PV - V Isotherms in the Critical Region

For a perfect gas (PV = RT) the change in the pressure-specific volume product with temperature along <u>any</u> constant specific volume is identically equal to the gas constant R. In view of this it would be of interest to determine the relation, if any, between the perfect gas constant R for water vapor with the constant, R', of Equation (8).

The next step in the development of the equation of state of this work was the evaluation of the constant R'. In view of what has been stated previously, Equation (8) certainly is valid along the critical specific volume line from the critical temperature to 752°F. Thus the following relation may be written,

$$[\partial(PV)/\partial T]_{V_c} = V_c(\partial P/\partial T)_{V_c} = R' \quad . \tag{9}$$

In Chapter II it was noted that the following boundary condition at the critical point must be satisfied by an equation of state

$$(\partial P/\partial T)_{V_c} = (dP_s/dT)_{T_c} \quad . \tag{3}$$

The constant of Equation (9) becomes as a consequence

$$R' = V_c(dP_s/dT)_{T_c} \quad . \tag{10}$$

The change in the saturation pressure with respect to temperature along the saturation line at the critical point was measured in this work as, $(dP_s/dT)_{T_c} = 21.4 \pm 0.1$ lb/in.^{2} °F. The following value, 0.0525 ± 0.0005 ft^3/lb was estimated for the critical specific volume in reference 116. Utilizing these values the constant R' in Equation (9) may be evaluated as 1.1235 ± 0.016 ft^3/in.^{2} °R.

It is interesting that the constant R' was evaluated solely from parameters of water vapor at the critical point. Furthermore the constant R' is some ninety per cent larger in value than the particular gas constant, R, for water vapor. The physical significance of this latter statement has not been found by the authors of this report.

The results of this work are significantly different to the concepts proposed by Dieterici[18] for a gas at the critical point. Partington states for example that "Dieterici found that $(\partial P/\partial T)_{V_c} = R/2V_c$, i.e., the value of $(\partial P/\partial T)_V$ in the critical state is half the value for an ideal gas under the same conditions." In this work it was found that $(\partial P/\partial T)_{V_c} \simeq 1.9R/V_c$.

The next step in the development of the equation of state of this work consisted of the verification of Equation (9). It was noted in references 116 and 117 that Keyes et al.[71] in 1936 and Timrot[150] in 1950 conducted precise P-V-T measurements along various isometrics in the critical region. Figure 2 is a small-scale reproduction in which the above measurements were plotted with the pressure-specific volume product as the ordinate, the temperature as the abscissa and with the specific volume as a parameter.

The striking feature of Figure 2 is that the isometrics ranging from 0.0400 to 0.1200 ft^3/lb appear to be parallel. Furthermore it may be seen that for the specific volumes ranging from 0.0400 to 0.0800 ft^3/lb the slopes

to a first approximation invariant to temperatures as high as 825°F (440°C). However for specific volumes greater than 0.1000 ft/lb the slopes evidently are no longer invariant for temperatures higher than 752°F (400°C).
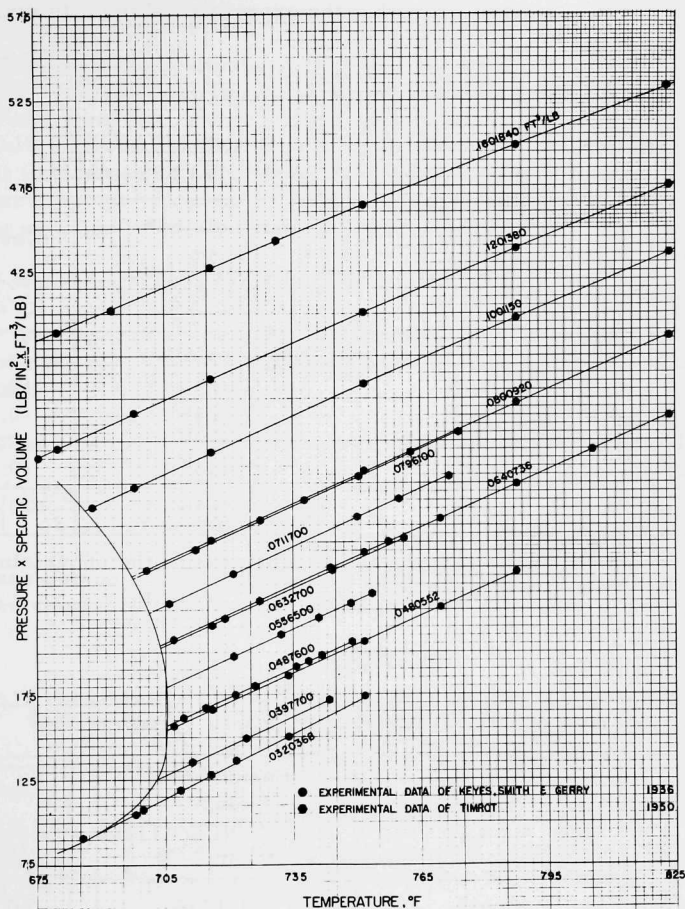

Fig. 2. Experimental Pressure-Volume-Temperature
Relation for Water Vapor

The slopes of Figure 2 were evaluated by the method described in reference 120. Comparisons between the 'measured values' of the slopes along with the formulated value of this work, $V_c(dP_s/dT)_{T_c}$ = 1.1235 ± 0.016 ft^3/in.^{2} °R are given in Tables 2 and 3. The average values

obtained for $[\partial(PV)/\partial T]_V$ from the Keyes and the Timrot data are in excellent agreement with the formulated value of 1.1235 ft^3/in.^{2} °R. It is noteworthy that the individual measured values obtained from the Keyes data do not deviate from the above formulated value by more than 0.0135 ft^3/in.^{2} °R, i.e. entirely within the experimental uncertainty in the formulated value.

Table 2

COMPARISON BETWEEN FORMULATED AND MEASURED SLOPES
ACCORDING TO P-V-T DATA OF KEYES et al.[71]

Specific Volume V, ft^3/lb	Measured Slope $\alpha = [\partial(PV)/\partial T]_V$, ft^3/in.^{2}-°R	Formulated* Slope $R' = V_c(dP_s/dT)T_c$, ft^3/in.^{2}-°R	Deviation $\alpha - R'$, ft^3/in.^{2}-°R
0.04806	1.1195	1.1235	-0.0040
0.06407	1.1280	1.1235	+0.0045
0.08009	1.1170	1.1235	-0.0065
0.10012	1.1330	1.1235	+0.0095
0.12014	1.1100	1.1235	-0.0135
Averages	1.1215	1.1235	-0.002

*Formulated by the authors of this work where the uncertainty
in R' is estimated as ±0.016.

Table 3

COMPARISON BETWEEN FORMULATED AND MEASURED SLOPES
ACCORDING TO THE P-V-T DATA OF TIMROT[150]

Specific Volume V, ft^3/lb	Measured Slope $\alpha = [\partial(PV)/\partial T]_V$, ft^3/in.^{2}-°R	Formulated* Slope $R' = V_c(dP_s/dT)T_c$, ft^3/in.^{2}-°R	Deviation $\alpha - R'$, ft^3/in.^{2}-°R
0.03977	1.1280	1.1235	+0.0045
0.04876	1.1240	1.1235	+0.0005
0.05565	1.1300	1.1235	+0.0065
0.06327	1.1190	1.1235	-0.0045
0.06391	1.1480	1.1235	+0.0245
0.07117	1.1420	1.1235	+0.0185
0.07961	1.1270	1.1235	+0.0035
Averages	1.1311	1.1235	+0.0077

*Formulated by the authors of this work where the uncertainty in R'
is estimated as ±0.016.

With the exceptions of the 0.06391 and 0.07117 ft³/lb isometrics the individual slopes obtained from the Timrot data are in excellent agreement with the formulated value. The plausible reason that can be given for the disagreement, in the case of the above two isometrics, is that the actual measurements are in error.

The foregoing analysis indicates that the slopes of the isometrics from 0.0400 to 0.1200 ft³/lb and temperatures from saturation to 752°F are constant and invariant to a first approximation.

It is interesting to note that the relation deduced in this work is somewhat different to that derived by Timrot.[152] Timrot derived the following equation from his measured isometrics,[150]

$$(\partial P/\partial T)_V = 100/(V + 0.000407)$$

where P is in kg/cm², T is in °K and V is in m³/kg. The equation, reportedly, represents the slopes of his isometrics in the critical region near the saturation line.

Timrot's equation may be rewritten in the following form

$$\left\{\frac{\partial(PV)}{\partial T}\right\}_V = \frac{100}{1 + 0.000407/V} \tag{11}$$

The values obtained for $\left\{\partial(PV)/\partial T\right\}_V$ from Equation (11) along with the measured values of Figure 2 are given in Table 4.

Table 4

COMPARISON OF $(\partial PV/\partial T)_V$ AS MEASURED AND AS
COMPUTED ACCORDING TO TIMROT'S EQUATION

Specific Volume ft³/lb	$(\partial(PV)/\partial T)_V$		Deviation
	According to Timrot Data ft³/in.²-°R	According to Timrot Eq'n. ft³/in.²-°R	Meas'd-Comp'd Measured ft³/in.²-°R
0.03977	1.128	1.090	+0.034
0.04876	1.124	1.119	+0.0044
0.05565	1.130	1.136	-0.0053
0.06327	1.119	1.150	-0.029
0.06391	1.148	1.152	-0.0035
0.07117	1.142	1.162	-0.0175
0.07961	1.127	1.173	-0.0407

The results of Table 4 indicate that the apparent dependence of $(\partial(PV)/\partial T)_V$ with specific volume as obtained by Timrot's equation is not borne out by his measurements. If $\{\partial(PV)/\partial T\}_V$ is considered as a function of specific volume, it would not be as exaggerated as that suggested by Timrot's equation.

In view of Figure 2 <u>interesting conclusions</u> may be drawn with regard to the pressure-temperature relation along the critical specific volume line. For specific volumes from 0.0400 to 0.0800 ft^3/lb, which encompass the critical volume, $V_c = 0.0525$ ft^3/lb, the isometrics are linear at temperatures as high as 825°F. The maximum deviation between the experimental and smooth value of PV is entirely within two parts in one thousand. It may be concluded therefore that deviations from the straight line are entirely within experimental uncertainty. Thus the critical isometric is, within experimental uncertainty, linear in pressure and temperature up to at least 825°F, i.e. some 120°F above the critical temperature.

Amirkhanov and Karimov[2,3] conducted C_V measurements on water and water vapor for temperatures to 716°F (380°C). They were able to conclude that the condition $(\partial C_V/\partial V)_T = 0$, and hence $(\partial^2 P/\partial T^2) = 0$, occurred always at the critical specific volume. In view of this and our own analysis it is reasonable to deduce that the equation of state must satisfy the condition $(\partial^2 P/\partial T^2)_{V_c} = 0$ to at least 825°F (440°C).

It should be emphasized that the condition $(\partial^2 P/\partial T^2)_{V_c} = 0$ is not peculiar to water substance only. For example Young concluded from his P-V-T measurements[164] on isopentane, that the condition $(\partial^2 P/\partial T^2)_V = 0$ is valid in the neighborhood of the critical point. Furthermore Michels, Bijl and Michels[114,115] analyzed their C_V measurements on CO_2 in the critical region[112,113] and found the condition $(\partial^2 P/\partial T^2)_{V_c} = 0$ persisted to at least some 110°C above the critical temperature.

Michels, Bijl and Michels state that "a kinetic explanation of the phenomenon, $[(\partial^2 P/\partial T^2)_{V_c} = 0]$ might be based on the assumption of group formation. The decreased association with increase of temperature would lead to a production of heat of dissociation and therefore to an apparent increase of C_V. A theory in agreement with the theoretical facts should lead to the conclusion that $(\partial U_a/\partial T)_V$ is a maximum at the critical density." It is interesting to note that G. V. Ry[138] found that this was not fulfilled when association was confined to the formation of double molecules.

The next basic step in our development of an approximate equation of state was to reduce all of the P-V-T measurements in Figure 1 to one common isotherm. Integrating Equation (9) at constant specific volume and choosing the critical temperature as a base temperature we may write

$$(PV)_T - (PV)_{T_c} = R'(T - T_c) \tag{12}$$

Equation (12) may be arranged in the following form

$$(PV)_T - R'(T - T_c) = (PV)_{T_c} \quad . \tag{13}$$

The first term on the left hand side of Equation (13) gives the pressure-specific volume product at a temperature T. The second term on the left hand side may be looked upon as a correction factor which, when added algebraically to the first term, yields the pressure specific volume product, at the same specific volume V, along the critical isotherm.

Equation (13) was used to reduce all the data of Figure 1 along with the data of Osborne et al.[126] and Timrot[150] to a single curve. A small-scale reproduction of the curve drawn through the 'reduced experimental data' is given in Figure 3. In the large majority of the cases, the deviations of the reduced experimental PV product from the smooth curve were less than two parts in one thousand. There were few experimental values which deviated from the smooth curve by more than two parts in one thousand. However, no deviations of more than five parts in one thousand were found.

Figure 4 gives a comparison between the computed and experimental P-V-T values along various isotherms. This diagram was constructed by utilizing the parametric curve of Figure 3 in conjunction with Equation (13).

The deviations between the computed and experimental values of pressure of Figure 4 is entirely within five parts in one thousand. The overall uncertainty in pressure due to the combined uncertainty in pressure, specific volume and temperature is about three parts in one thousand. Consequently it would appear that the parametric equation of state reproduces measurements to within their respective experimental uncertainty. In the region of interest of this report there are only five points which have deviations between three and five parts per one thousand.

Even though the parametric curve of Figure 3 is empirical it would be convenient to obtain a formulation from it. Details of this will now follow.

Let

$$f(V) = PV - R'(T - T_c) \tag{14}$$

The assumption will be made that f(V) may be expanded in Taylor's series about the critical point. Equation (14) becomes

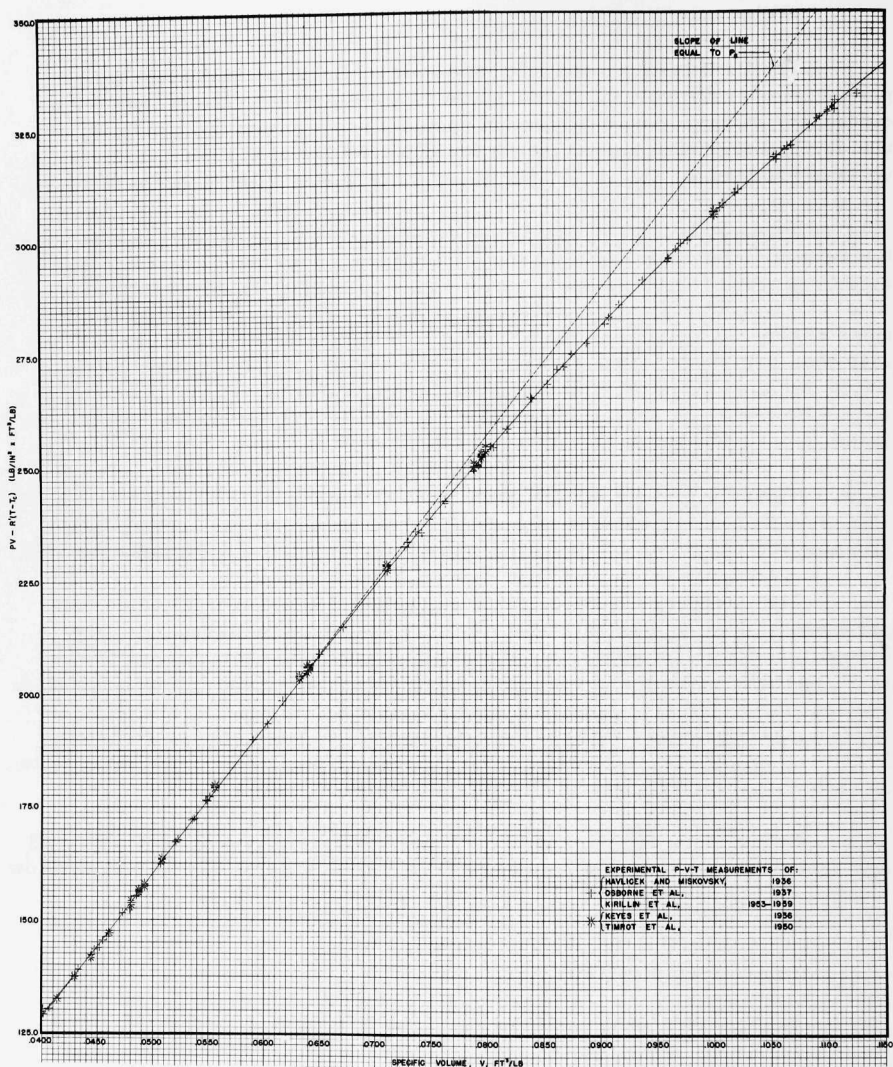$$f(V_c) + f'(V_c)[V - V_c] + f''(V_c)[V - V_c]^2 + ------ = PV - R'(T - T_c) \tag{15}$$

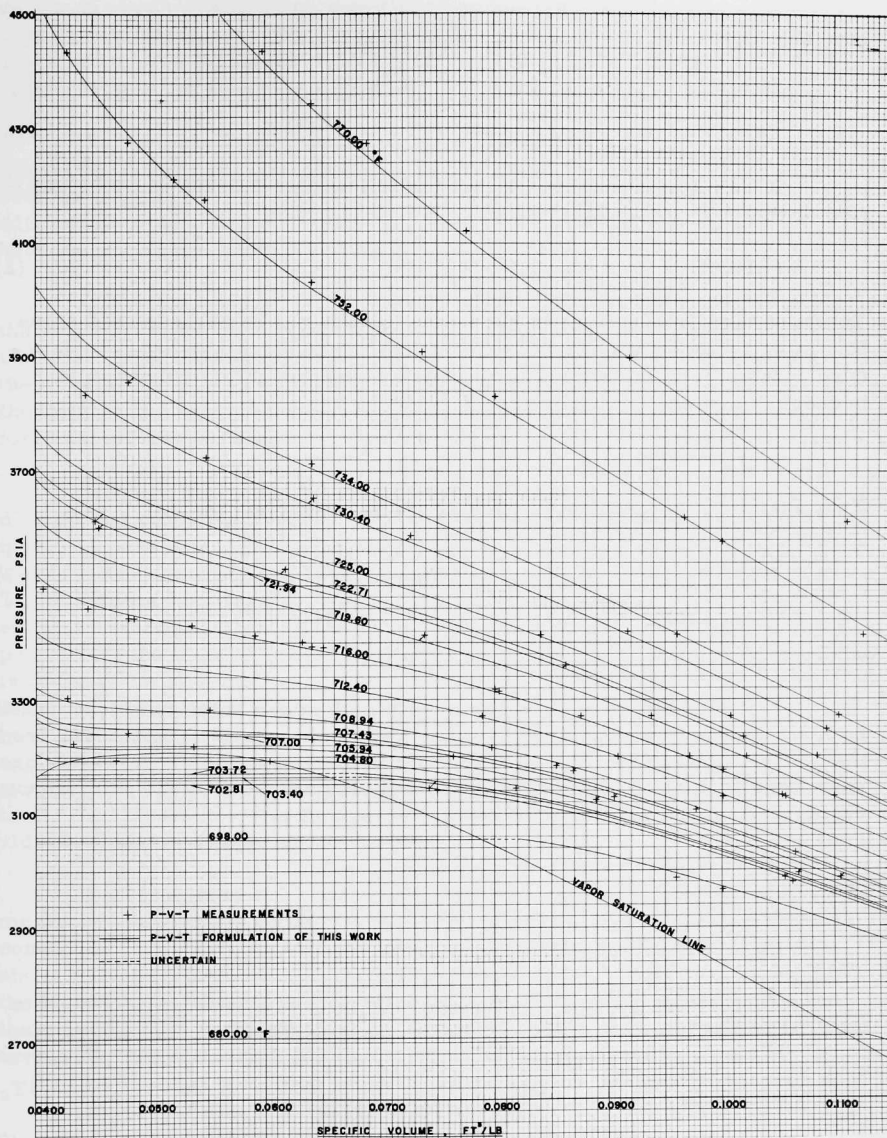Fig. 3. Variation of $(PV)_{T_c}$ with V in the Critical Region

Fig. 4. Comparison Between Computed and Derived Data Along
Various Isotherms

It is evident from Figure 3 that $f(V_c) = P_c V_c$. Thus Equation (15) may be written as

$$P_c V_c + f'(V_c)[V - V_c] + f''(V_c)[V - V_c]^2 + \text{------} = PV - R'(T - T_c) \quad .$$

$$(16)$$

It was stated previously that the following condition must be satisfied at the critical point,

$$(\partial P/\partial V)_{T_c} = 0 \quad . \tag{2}$$

To satisfy this condition it is necessary that $f'(V_c)$ be assigned the value P_c. It will also be recalled that, $(\partial^2 P/\partial V^2)_{T_c} = 0$, is another boundary condition which must be satisfied. Because of this latter condition it is necessary that the coefficient of $(V - V_c)^2$ be zero, i.e.

$$f''(V_c) = 0 \quad .$$

Thus Equation (16) may be written as the following series,

$$PV - P_c V - R'(T - T_c) = \sum_{n=3}^{n} a_n [V - V_c]^n \tag{17}$$

where n takes on integer values up to infinity.

Utilizing the results of Figure 3 a fifth order polynomial was fitted by least squares. The specific volume range which was selected was from the critical specific volume to a specific volume of 0.1100 ft^3/lb. For pressure in psia, specific volume in ft^3/lb and temperatures in °F, the following values were found for the coefficients, a_3, a_4 and a_5,

$$a_3 = -2.38539 \times 10^5$$

$$a_4 = 38.21000 \times 10^5$$

$$a_5 = -386.574 \times 10^5 \quad .$$

It would be highly desirable to determine if the above coefficients possessed any physical significance. A study of Equation (17) shows that the coefficients are related to the higher ordered derivatives of pressure with respect to specific volume at the critical point, i.e. $a_3 = (\partial^3 P/\partial V^2)_{T_c}$, $a_4 = (\partial^4 P/\partial V)_{T_c}$ and $a_5 = (\partial^5 P/\partial V^5)_{T_c}$.

There is a considerable amount of uncertainty about the magnitude and the sign of the third, fourth and higher ordered derivatives of pressure with respect to specific volume at the critical point. Part of this uncertainty

is due to the fact that some theories, notably that of Mayer and Mayer,[110,111] predict that there is a two phase region encompassed by the temperature T_m at which the miniscus disappears and the temperature T_C where $(\partial P / \partial V)_{T_C} = (\partial^2 P / \partial V^2)_{T_C} = 0$.

For such a theory there would be a small region of specific volumes where the isotherms between T_m and T_C possess horizontal portions. Consequently between T_m and T_C all of the ordered derivatives of pressure with respect to specific volume are zero. This is usually called the "derby hat" theory of the critical region.

Mayer and Mayer[111] state that "experimental evidence indicates that the difference $(T_C - T_m)$ is 10 to 15°C for some materials." Presumably this statement took into account the results of Callendar[10] who found that the difference in $T_C - T_m$ was about 6°C for water vapor. It should be noted though that the measurements of Callendar could not be reproduced. Therefore his conclusion about value of $T_C - T_m$ must be ignored.

Wentorf and Boyd[163] conducted P-V-T measurements on carbon dioxide and sulfur hexafluoride. The precision of these measurements is highly impressive. These measurements tended to show that isotherms within a few one hundredths of a degree above the critical temperature, T_m, possessed horizontal portions. They concluded that "there is some evidence lending support to the Mayer theory of the critical phenomena, especially in the case of sulfur hexafluoride. However, the anomalous region is found to be so small that for most purposes the temperature of meniscus disappearance, T_m and the temperature, T_C, at which $(\partial P / \partial V)_T$ and $(\partial^2 P / \partial V^2)_T$ are both zero are the same. The theory of Mayer is strictly applicable only to simple molecules whose fields of forces are spherically symmetric; carbon dioxide and sulfur hexafluoride do not exactly meet these requirements. Experiments of xenon are planned; these should provide data better suited for comparison with theory."

Subsequent to the work of Wentorf and Boyd,[163] P-V-T measurements on xenon were conducted by Habgood and Schneider.[33,34] They concluded that there was no obvious region of flat, horizontal isotherms above the critical point. Thus their measurements offered no support for the Mayer-Harrison theory.[110,111] Habgood and Schneider stated further that "at the critical point, T_C, the third and fourth derivatives of pressure with respect to specific volume appears to be zero."

In view of the preceding discussion it may be concluded that there may be an experimental basis for the Mayer-Harrison theory of the critical point. Consequently, what remains to be considered are the values and sign of the third, fourth and higher order derivatives of pressure with respect to specific volume at the critical point. Landau and Lifshitz[97] consider for example that $(\partial^3 P / \partial V^2)_{T_C}$ must be negative. Rossini[136]

considers that $(\partial^4 P/\partial V^4)_{T_c}$ is the first derivative which is not zero and that it changes sign at the critical point. The results of this work indicate that $(\partial^3 P/\partial V^3)_{T_c} < 0$ while $(\partial^4 P/\partial V^4)_T > 0$ in the case of water. This is in agreement with both Landau and Lifshitz and Rossini. However, in view of the empirical nature of Equation (17), the values obtained for $(\partial^3 P/\partial V^3)_{T_c}$, $(\partial^4 P/\partial V^4)_{T_c}$ and $(\partial^5 P/\partial V^5)_{T_c}$ may have little if any physical significance since if primary data is accurate to at least one part in one thousand then upon successive differentiation the accuracy is reduced by an order of magnitude for each successive derivative.

The shortcomings of Equation (17) is that it is only valid in the region encompassing the critical point i.e. $V_c < V < 2 V_c$. If the equation is used for larger values of specific volume it will yield erroneous results. Furthermore Equation (17) is not in a rational form in so far as at large values of V, the series $\Sigma a_n (V - V_c)^n$ is divergent.

If an equation of state is rational, it would yield the perfect gas equation at sufficiently large values of specific volume. Consequently, a more realistic formulation would have the following form

$$PV - R'(T - T_c) = \sum_n a_n/V^n \qquad (18)$$

where

$$n = 0, 1, 2, 3, \text{--------}$$

It was thought though, that there would be considerable difficulty in satisfying certain boundary conditions at the critical point with such a form. Moreover even though the above form is suggested from the Virial equation of state our previous analysis showed that such an infinite series might be divergent at the critical point and also in the critical region.

D. Summary

1. The slope of the critical isometric was determined in this work to be,

$$(\partial P/\partial T)_{V_c} = 1.9 R/V_c \quad .$$

This is significantly different to that originally proposed by Dieterici, i.e. $(\partial P/\partial T)_{V_c} = R/2 V_c$.

2. Analyses of P-V-T measurements made along isometrics showed that the following boundary condition is valid for temperatures to at least 825°F (440°C),

$$(\partial^2 P/\partial T^2)_{V_c} = 0 \quad .$$

Apparently this boundary condition is typical of other substances besides water.

3.   A parametric equation of state was derived in this work for specific volumes from 0.0400 to 0.1200 ft³/lb, and temperatures from saturation to about 752°F. The following analytical formulation was derived from the parametric curve for specific volumes ranging from the critical specific volume to about twice the critical specific volume.

$$PV - P_c V - R' (T - T_c) = \sum_{n=3}^{5} a_n (V - V_c)^n$$

4.   It is recommended that further work be carried out on the development of an equation of state. Specifically it would be highly desirable to amend the equation of state of this work so as to make the derivative, $\{\partial(PV)/\partial T\}_V$, a function of specific volume and temperature. In the critical region the functional dependence on specific volume and temperature would be small. Nonetheless if it is evaluated highly accurate calorimetric properties could be computed.

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CHAPTER VI

POTENTIAL FUNCTIONS AND MOLECULAR
PARAMETERS FROM P-V-T MEASUREMENTS

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A. General

This present chapter discusses certain aspects of a theoretical equation of state for an imperfect gas. It should be mentioned at the outset though that the theory of the equation of state cannot be developed without a more comprehensive knowledge about the nature of interaction of electrons, atoms and molecules. Such information is not yet available. It is hoped though that some further knowledge might be gained about the structure of the water molecule by methods outlined in the next few sections.

B. Theoretical Development of an Equation of State for an Imperfect Gas

The equation of state for an imperfect gas may be developed by utilizing the "Theorem of the Virial" first enunciated by Clausius.[14] It's derivation will not be given here since excellent derivations of this famous theorem of Clausius are given elsewhere.[32,128,131]

Goldstein[32] showed that the Virial Theorem of Clausius may be written in the following vector form,

$$\overline{T} = -\frac{1}{2} \overline{\sum_i \vec{F_i} \cdot \vec{r_i}} \tag{19}$$

where

$\overline{T}$ is the average kinetic energy

$\vec{F_i}$ is the force acting on the ith particle

$\vec{r_i}$ is a position vector

The expression on the right hand side of Equation (19), is known as the "virial" of the forces. The virial of the forces usually includes not only forces of constraint keeping the gas particles in the container but also the interaction forces between molecules.

It may be readily shown (see for example reference 39 and 88) that the virial of the forces of constraint is $(3/2)\,PV$. If the intermolecular forces are denoted by F'_i, Equation 19 becomes,

$$\vec{T} = \frac{3}{2}\,PV - \frac{1}{2}\,\overline{\sum_i \vec{F'_i} \cdot \vec{r_i}} \tag{20}$$

It may be shown from statistical mechanics that the average kinetic energy of translation for a system of N molecule is $(3/2)NkT$. Thus Equation (20) may be simplified to

$$PV - NkT = +\frac{1}{3} \overline{\sum_i F'_i \cdot \vec{r}} \qquad (21)$$

If the force F'_i depends only on coordinates and is derivable from a potential $\phi(r)$, considerable simplification results. Under these conditions it may be shown[88] that the equation of state becomes

$$PV - NkT = -\frac{1}{3} \sum_{i<j} r_{ij} \frac{\partial \phi}{\partial r_{ij}} \qquad (22)$$

where r_{ij} is the distance between the ith and j^{th} molecule $\partial \phi/\partial r_{ij}$ is the intermolecular force between the ith and j^{th} molecule. Making use of the concept of the radial distribution function (1) the equation of state is

$$PV - NkT = \frac{2\pi N^2}{3V} \int_0^\infty g(r) r^3 \frac{\partial \phi(r)}{\partial r} \, dr \qquad (23)$$

where $g(r) = e^{-\phi(r)/kT}$ is termed as the radial distribution function.

C. Molecular Size and the Potential Function

The parametric curve of Figure 1 is quite similar to the plot of the Lennard-Jones intermoleculer potential. Because of this similarity it was decided that an attempt should be made to obtain information about the average potential function of the water molecule and its size from P-V-T data.

The P-V-T data of Figure 1 and the data of Holser and Kennedy[44] were used to obtain this information. In addition the measurements of Tammann and Ruhenbeck[148] and Kiyama et al.[89] along the 752°F isotherm at high densities, were utilized. These latter data though not as precise as the former data, were used since there are no other measurements available which extend to high pressures.

The method used in this report to obtain information about the intermolecular potential and molecular parameters has a rational basis to it. It consisted of plotting experimental values of PV-RT against V with temperature as a parameter. A small scale reproduction of such a diagram is given in Figure 5. Upon examination of equation 21, it may be seen that the ordinate is equal to two thirds of the virial of the intermolecular forces. Thus along a given isotherm this quantity may be obtained as a function of specific volume.
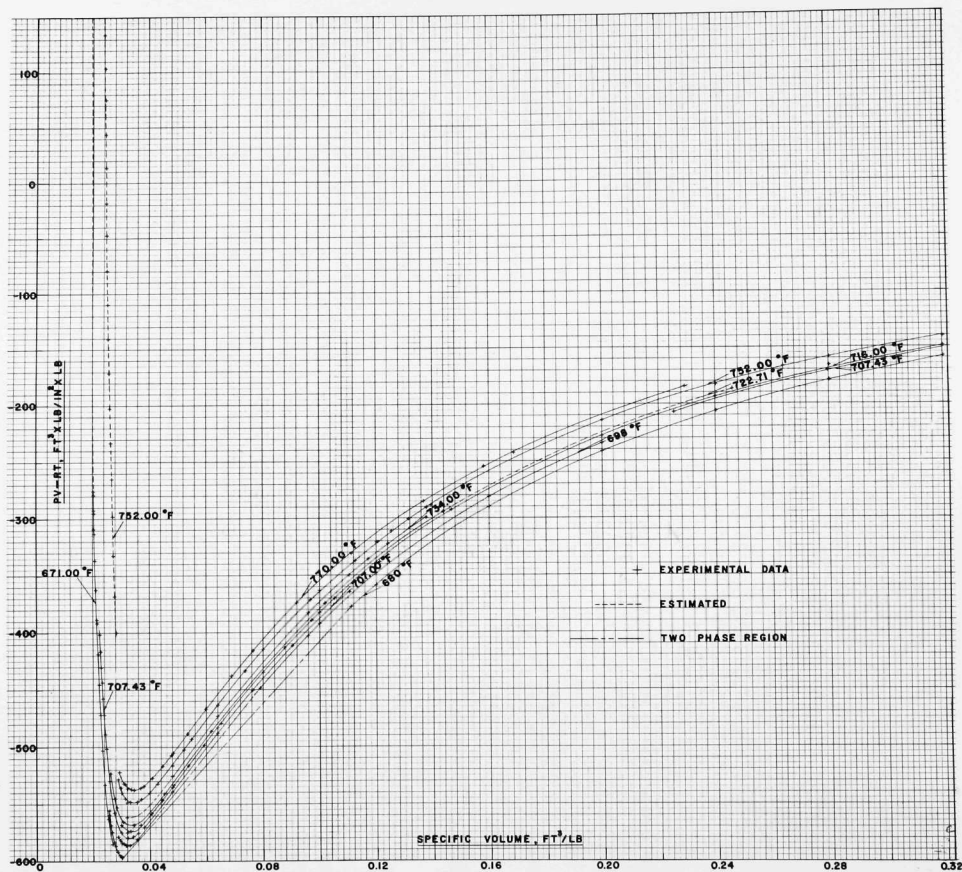
Fig. 5. Variation of PV-RT with Specific Volume along Isotherms

The striking feature of Figure 5 is that the variation of PV-RT versus V along an isotherm is similar to the variation given by any rational intermolecular potential function. The ordinate PV-RT in this case may be thought to be analogous to the potential energy function while the abscissa V is related to the average intermolecular separation. For a given isotherm the variation of PV-RT at very large densities is extremely large. This may be taken as a demonstration of very strong but finite repulsive forces. At low densities PV-RT asymptotically approaches zero. This behaviour may be attributed to forces of attraction. In the region of the critical specific volume the isotherms of PV-RT undergo inflection. This is caused by the interaction of repulsive and attractive forces.

The specific volume corresponding to the condition where the virial of the attractive forces is balanced by the virial of the repulsive forces at a temperature of 671°F is 0.0200 ft³/lb (0.381 V_c). It is interesting to note that the specific volume corresponding to the condition where the virials are balanced for a Van der Waals gas is $V = b = V_c/3$.

The molecular diameter of various substances may be estimated from a knowledge of the specific volume corresponding to the conditions where the virials are balanced. As an example Van der Waals computed the molecular diameter from the following equation,

$$\frac{2}{3} \frac{\pi \sigma^3 N}{M} = \frac{V_c}{3} \tag{24}$$

where σ is the molecular diameter

N is Avogadro's number

M is the molecular weight

That is the Van der Waals constant, b, may be shown to be four times the volume actually occupied by the molecules.

The following equation will be used to compute the diameter of the water molecule,

$$\frac{2}{3} \frac{\pi \sigma^3 N}{M} = 0.0200 \tag{25}$$

In actuality the void spaces may comprise a smaller percentage of the total specific volume. Nonetheless a value of 2.61 A° was computed for the diameter of the water molecule from Equation 25. This is in excellent

agreement with a value of 2.65 A° obtained by Rowlinson by analyzing the second virial coefficient data of Keyes et al.*

MacCormack and Schneider[108] by utilizing "approximate expressions" computed the molecular diameter of inert gas-type molecules from critical constants. Apparently the relation they used $[2\pi N\sigma^3/3M = 0.68 V_c]$ was based on the Lennard-Jones and Devonshire theory of gases.[103] They concluded, however that values computed for σ by means of the above in the case of carbon dioxide and sulfur hexafluoride are some twenty per cent smaller than that computed from the second virial coefficient. They stated that "in fact for both gases (carbon dioxide and sulfur hexafluoride) b derived from virial data is almost as large or larger than the critical specific volume."

Table 5 lists some of the estimates which have been made on the effective size of the water molecule. It may be seen that various estimates on the size ranged from between 2 to 6 A°.

Table 5

VARIOUS ESTIMATES OF THE DIAMETER OF THE WATER MOLECULE[†]

Basis	Diameter, A°
Viscosity data at 100°C and 1 atm	4.16
Van der Waals equation assuming	
$\quad$ b = $2\pi N\sigma^3/3$ M = $RT_c/8P_c$	2.88
assuming	
$\quad$ b = $2\pi N\sigma^3/3$ M = $RT_c/15P_c$	2.34
If in the liquid state the molecules were cubes and were closely packed at 4°C.	1.55
Bombardment of a water molecule with elections by E. Bruche showed that molecular diameter determination was influenced by the kinetic energy of the colliding electron	
$\quad$ Energy = 4 electron volts	4.48
$\quad$ Energy = 9 electron volts	4.78
$\quad$ Energy = 16 electron volts	4.60
$\quad$ Energy = 36 electron volts	3.66
Mokrouskin derived the diameter of the water molecule from a formula which related it to surface tension,	5.44
$\quad$ This work	2.61

[†]Table 5 is based on the table on pp. 43-45 in Dorsey.[20]

*According to Hirschfelder et al.[37] on page 214 Rowlinson obtained a value of 2.65 A° for the diameter of the water molecule from the second virial data of Keyes et al.[71]

The various estimates were based on viscosity data, equations of state and results obtained by electron bombardment of the water molecule. The value obtained for the diameter of the water molecule in this work, 2.61 A°, agrees favorably with those of Table 5.

The authors of this report recommend that the molecular diameter of other substances be computed from the specific volume corresponding to where the virial of the attractive forces is just balanced by the virial of the repulsive forces.

D. Summary

     1.   The molecular diameter of water was estimated as about 2.6 A° from the specific volume where the virial of the intermolecular forces became zero. This compares very favorably with other values which range from two to six Angstrom units.

     2.   Apparently the diameter of the water molecule increases with temperature. The available P-V-T data for temperatures near the critical temperature and at high densities is virtually non-existent and therefore the dependence could not be evaluated.

     3.   More research is recommended along both experimental and analytical lines.

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