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AN INVESTIGATION OF CERTAIN THERMODYNAMIC AND TRANSPORT PROPERTIES OF WATER AND WATER VAPOR IN THE CRITICAL REGION

by

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AN INVESTIGATION OF CERTAIN THERMODYNAMIC AND TRANSPORT PROPERTIES OF WATER AND WATER VAPOR IN THE CRITICAL REGION

E. S. Nowak and R. J. Grosh

ABSTRACT

An accurate knowledge of thermodynamic and transport properties of water in the critical region is required in order to analyze future power cycles, nuclear reactor configurations and other types of heat transfer apparatus. Preliminary investigations showed that this was not possible with presently existing tabulations Experimental data from volumetric viscosity and thermal conductivity studies were therefore selected and retabulated. Smoothings of this data are described and, for the first time, a tabulation at close intervals of pressure and temperature of the volumetric data is possible for steam in the critical region. A graphical presentation is given of volumetric data from 700° to 750°F

An important result of this study was that excellent agreement existed between the many P-V-T measurements for this substance even though some of the data was obtained many years ago Differences occurring between the tabulated data of various steam tables were found to arise from the use of inexact equations of state or interpolation techniques rather than from faulty primary data. New P-V-T data were derived in this study, from measurements of other investigators, by a graphical technique and it is estimated that it yielded pressure values accurate to some five parts in ten thousand except in the subcooled liquid region (for specific volumes below 0 040 ft^3/lb), where the uncertainty may be some twenty parts in ten thousand

Study of the existing thermal conductivity and viscosity data suggests the Russian work to be the most consistent. However, it appears that the empirical equations proposed for interpolation do not adequately represent the data in the critical region No attempt has been made to derive thermodynamic functions or to analyze the transport data.

NOMENCLATURE

A	Mechanical equivalent of heat
B_0	A function of temperature; see Eq. (7)
ΔB_s	A function of temperature; see Eq. (7)
C_p	Specific heat at constant pressure
C_{p_0}	Molecular specific heat at "zero pressure"
E	Maximum error in pressure measurement
f_p	Pressure factor; see Eq. (22)
h	Enthalpy per unit mass
h_{fg}	Enthalpy of vaporization
k	Thermal conductivity
k_0	Thermal conductivity at "zero pressure"
k_t	Thermal conductivity of water vapor at "zero pressure"
L	Length
M	Mass
P	Pressure
ρ_c	Critical Pressure
P_s	Saturation Pressure
Q	Heat input; also volume flow per unit time
q''	Heat flow per unit area per unit time
R	Gas constant
r	Radius
T,t	Temperature
T_c, t_c	Critical temperature
$V_{sp\alpha}$	Specific volume
V_{sp}	Specific volume computed from perfect gas law
v	Velocity; also specific volume of subcooled water
v_c	Critical volume
v_f	Specific volume of liquid at saturation
v_g	Specific volume of vapor at saturation
v_s	Specific volume of saturated water

x	A function of temperature; see Eq. (13)
y	A function of temperature; see Eqs. (7) and (16)
z	A function of temperature; see Eq. (16)
α	See Eqs. (8) and (24)
β	Coefficient of expansion; also see Eqs. (10) and (12)
γ	See Eq. (9)
Δ, δ	A function of pressure and temperature; see Eq. (19)
η	Dynamic viscosity
η_t	Dynamic viscosity of water vapor at "zero pressure"
τ	Shear stress

I. INTRODUCTION

A. General

Research is being conducted at the School of Mechanical Engineering, Purdue University, to study heat transfer in water over a range of temperatures and pressures. A study will be made of forced, free, and combined forced and free convection in the one and two-phase regions of water near the critical point.

Pressures considerably higher than the critical pressure are not of interest because in this region the water behaves as a constant-property gas for which relatively adequate information on heat transfer is available. At pressures considerably lower than the critical, water again behaves as a constant-property gas or liquid and adequate information on heat transfer is again available. In the vicinity of the critical point, water exists in states where extremely large and interesting property variations occur. Little heat transfer information exists for this condition and so research is of fundamental as well as practical importance. For instance, near the critical point small temperature differences give rise to exceedingly large free-convection forces; the resulting motion can be such as to produce free-convection heat transfer coefficients which approach or exceed those usually found in forced convection.

To adequately study the above phenomena and to obtain useful information, experiments will be carried out at pressures between 2700 and 4000 psia and at bulk temperatures up to 850°F. The information gathered from these experiments will be of greatest utility to the engineer if it is given in an equation involving such dimensionless groups as Nusselt number, Prandtl number, Reynolds number and Grashof number. With an empirical correlation of this type it will be possible to interpolate heat transfer rates within the range of pressures and temperatures at which the experiments were carried out. The success of this interpolation or any theoretical attempt to predict the results will depend on accurate and detailed information for the thermodynamic and transport properties of water, for instance, pressure-volume-temperature, enthalpy, specific heat at constant pressure, dynamic viscosity and thermal conductivity.

Near the critical point, which for water occurs at about 3210 psia and 705.5°F, the above properties vary quite markedly with pressure and temperature. Furthermore, different investigators have reported inconsistent values for the same property. Therefore, in order to appraise these differences and devise a consistent, but tentative, set of values for these properties, an analytical investigation of properties was carried out and is the subject of this thesis.

Because of the complexity of the topic this investigation was limited to pressure-volume-temperature, thermal conductivity and dynamic viscosity for water and water vapor near the critical point. The observations and conclusions of different investigators with regard to the critical point were noted. Specifically, this thesis gives information for pressure-volume-temperature from 2700 to 4000 psia, from 680° to about 800°F and specific volumes from 0.025 to 0.125 ft^3/lb. Data for the thermal conductivity and dynamic viscosity are given for pressures from 1 up to 4300 psia and for temperatures from 660° up to 850°F.

The starting point of this investigation was an investigation of the various national steam tables.[1-14] The book by Dorsey[15] and the survey paper by Liley[16] were excellent sources of reference in the early stage of this work.

The equations derived by various investigators were noted, provided that they were valid in the region of interest. The constants in these equations were converted from metric to British units since in this form they are of greatest use to the engineer.

B.   Definitions

To avoid confusion the thermodynamic and transport terms used in this thesis will now be defined.

Saturated Vapor. A vapor that is in thermodynamic equilibrium with its liquid is defined as a saturated vapor.

Saturated Liquid. A liquid in thermodynamic equilibrium with its vapor is defined as a saturated liquid.

Enthalpy of Vaporization. The enthalpy of vaporization is defined as the amount of heat required to change a unit mass of saturated liquid to saturated vapor under conditions of constant pressure.

The enthalpy of vaporization has been used as a criteria to determine the "critical point" of a pure substance. Calorimetric experiments have established the fact that the enthalpy of vaporization decreases as the temperature increases. The logical end point of this behavior is when the enthalpy of vaporization becomes zero.

Critical Point. The critical point is defined as that state of pressure and temperature when the enthalpy of vaporization is zero. At the critical point the meniscus separating the liquid phase from the vapor phase disappears and hence the distinction between phases disappears.

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Subcooled Liquid. A subcooled liquid is defined as a liquid subjected to a pressure greater than the saturation pressure for the temperature in question.

Superheated Vapor. A superheated vapor is defined as a vapor at a temperature which is higher than the saturation temperature for the pressure in question.

State Regions. A review of the state regions as defined by several authorities[17-20] will now be given. Figures 1 to 3 show the various regions on a pressure-volume diagram.

Figure 1 shows the various regions as defined by Dodge.[17] The term fluid was given to water substance when subjected to both a pressure and temperature greater than the critical pressure and temperature. His reason for defining the fluid region as such was that a liquid at a pressure greater than the critical pressure can change to a vapor, or vice versa, without any observable phase change. He concluded that a substance in this region can neither be called a gas nor a liquid.

The various regions defined by Sears[18] and also by Zemansky[19] are shown in Figure 2. Sears mentions that the boundary between the gaseous and vapor regions is unnecessary since the properties of a vapor differ in no respect from the properties of a gas.

The regions as defined by Young[20] are shown in Figure 3. He mentioned that it was difficult to classify a fluid whose temperature is very near the critical temperature and whose pressure is greater than the critical pressure. He made no attempt to quantitatively define this difficult region.

The regions as defined by Young[20] correspond to the regions used in this thesis. No attempt will be made to define quantitatively the region near the critical isotherm and at pressures greater than the critical pressure.

Specific Heat at Constant Pressure. The specific heat at constant pressure is defined by the following thermodynamic relation,

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p \quad ,$$

where C_p is specific heat at constant pressure and h is the enthalpy per unit mass of material.

DEFINITION OF STATE REGIONS GIVEN BY VARIOUS SOURCES SHOWN ON PRESSURE-VOLUME DIAGRAM

DODGE [17]
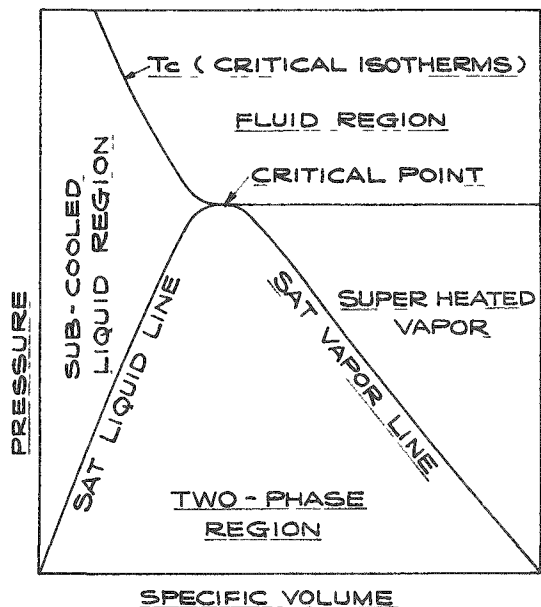
FIG. 1

SEARS [18] AND ZEMANSKY [19]
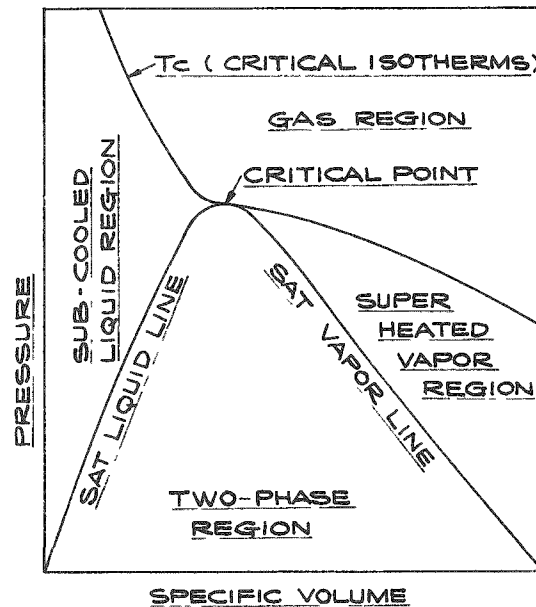
FIG. 2

YOUNG [20] AND IN THIS THESIS
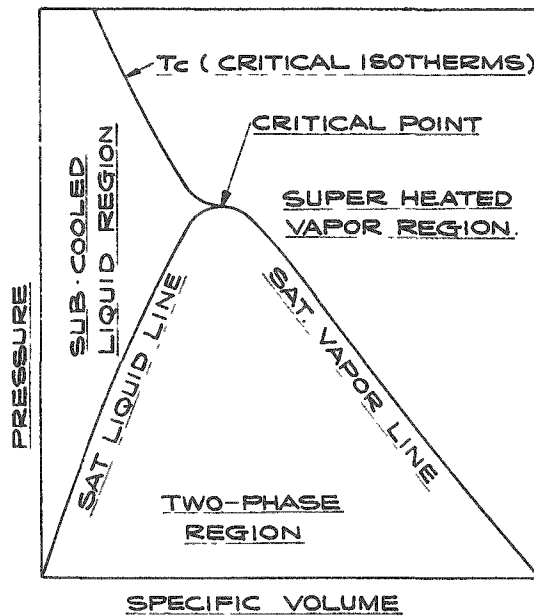
FIG. 3

Coefficient of Volume of Expansion. The coefficient of volume of expansion is defined by the following thermodynamic relation:

$$\beta = \frac{1}{V_{sp}} \cdot \left(\frac{\partial V_{sp}}{\partial T}\right)_p \quad ,$$

where β is the coefficient of volume expansion and V_{sp} is specific volume defined as volume per unit mass. The magnitude of β serves as a measure of the heat transfer by free convection. At the critical point β theoretically is infinite.

Thermal Conductivity. The thermal conductivity is defined by the Fourier-Biot law as

$$k = - q'' \Big/ \frac{\partial T}{\partial y} \quad ,$$

where k is the thermal conductivity, q" is the heat flow per unit area per unit time, and $\partial T / \partial y$ is the temperature gradient.

Dynamic Viscosity. Dynamic viscosity is defined by the following equation between the shear stress and the shearing strain,

$$\eta = \tau \Big/ \frac{\partial v}{\partial y}$$

where η is the dynamic viscosity, τ the shear stress (defined as force per unit area), $\frac{\partial v}{\partial y}$ the rate of shearing strain, and v is the velocity.

II. PRESSURE-VOLUME-TEMPERATURE ALONG THE SATURATION LINE

A. General

In 1921 the Steam Research Committee[21] of the American Society of Mechanical Engineers requested that precise measurements of the volumes of water and steam be undertaken to pressures and temperatures as high as experimental techniques would permit. Thus the Committee with the material aid of the steam power industries initiated an extensive steam research program. This research was carried out primarily at the Massachusetts Institute of Technology by the Keyes group and at the United States Bureau of Standards by the Osborne group. At the same time similar work was conducted in England, Germany and Czechoslovakia.

B. Saturation Pressure

Vapor Pressure Measurement. The saturation vapor pressure of water may be measured by a static method or by a dynamic method. The liquid and its vapor are stationary during the static measurement of vapor pressure, while both the liquid and vapor are moving continuously during the dynamic measurement. In both methods the saturation pressure is observed at the boundary between the liquid and vapor at a constant temperature in a suitable container.

Table 1 shows the extent of accurate measurements on the vapor pressure of saturated water. Egerton and Callendar[23] employed a dynamic method to measure the vapor pressure while Osborne et al.[24] and Smith et al.[25] employed the so-called static method. It is thought that Holborn and Baumann[22] measured vapor pressure by means of a static method.

TABLE 1

Summary of Vapor Pressure Measurements

No.	Author(s) and Date	Reference	Pressure Range		Temperature Range	
			psia	kg/cm^2	°F	°C
1	Holburn and Baumann, 1910	22	To 3200	To 225	To 707	To 375
2	Egerton and Callendar, 1932	23	120 to 3202	8.5 to 225	340 to 707	170 to 375
3	Osborne, Stimson et al., 1933	24	14.7 to 3200	1 to 225	212 to 705.4	100 to 374
4	Smith, Keyes et al., 1934	25	69 to 3206	4.8 to 225	300 to 705.4	150 to 374

Osborne and Meyers[26] reviewed the measurements of Callendar and Egerton,[23] Osborne et al.,[24] and Smith et al.[25] and found them in remarkably good accord. However, they observed noteworthy differences between the three sets of measurements in the critical region, and therefore concluded that more precise experimental measurements may be required to establish the true course of the saturation curve.

A comparison of the measurements of Egerton and Callendar,[23] Osborne et al.,[24] and Smith et al.[25] is given in Table 2. The bulk of the measurements agree with each other to well within four or five parts per 10,000, corresponding to about $1\frac{1}{2}$ psi at a pressure of 3000 psia.

Empirical Equations for Saturation Pressures. Table 3 gives some of the more recent empirical equations which have been proposed for the saturation pressure of water vapor.

Osborne, Stimson et al.[24] deduced Equation (1), Table 3, from their measurements on the saturation pressure of water vapor. The constants in the equation were evaluated by the method of least squares. They thought that except for the region near the critical point the values computed by Equation (1) do not differ from the truth by more than 3 parts in 10,000.

Smith, Keyes, and Gerry[25] found that Equation (2) gave an accurate representation of vapor pressure measurements for saturated water. They evaluated the constants by the method of least squares and used the values for saturation pressures in the International Critical Tables[27] in preference to their own for temperatures from 212° to 284°F (110° to 140°C). They found that their measurements were represented by Equation (2) in all cases to within 4 parts in 10,000 (see Table 2).

Osborne and Meyers[26] used the measurements for saturation pressures of the Physikalisch Technische Reichsanstalt (PTR),[28] Egerton and Callendar,[23] Osborne, Stimson et al.,[24] and Smith, Keyes, and Gerry,[25] to deduce Equation (3). The PTR data was used only up to about 390°F (200°C). Osborne and Meyers state that Equation (3) represents a fair appraisal of the existing data though it may require modification when more precise experimental evidence is available, establishing more definitely the true course of the pressure curve on approach to the critical region.

Saturation Pressures given in the Various Steam Tables. Equation (2) was used to compute the saturation pressures in the Keenan and Keyes steam tables from 112 to 705.40°F (30° to 374.11°C).

TABLE 2

Comparison of Saturation Pressure Measurements

Temperature, C	Mean Observed Saturation Pressure (Int. Atm.)			Observed Pressure (Osborne)-Observed Pressure (Smith)	Observed Pressure (Egerton)-Observed Pressure (Smith)	Observed Pressures-Calculated Pressures (Osborne et al.)	Observed Pressures-Calculated Pressures (Smith, Keyes and Gerry)
	Egerton and Callendar[23]	Osborne et al.[24]	Smith, Keyes and Gerry[25]				
100	--	--	--	--	--	--	--
110	--	1.414	--	--	--	+0.0005	-0.00005
120	--	1.9598	--	--	--	+0.0005	-0.00004
130	--	2.6658	--	--	--	0.0000	+0.00004
140	--	3.5661	--	--	--	-0.0003	+0.00007
150	--	4.6969	4.6967	0.0002	--	-0.0008	-0.00136
160	--	6.1098	6.1032	-0.0031	--	-0.0002	+0.00249
170	7.8246	7.6178	7.6174	+0.0004	+0.0072	-0.0007	-0.00062
180	9.9086	9.8958	9.8959	-0.0001	+0.0127	-0.0004	-0.00155
190	12.400	12.3887	12.3898	-0.0011	0.0102	+0.0006	+0.0001
200	15.355	15.3472	15.352	-0.0048	+0.003	+0.0004	-0.0034
210	18.835	18.8300	18.832	-0.0020	+0.003	+0.0004	+0.0006
220	22.903	22.8964	22.897	-0.0006	+0.006	-0.0005	-0.0013
230	27.621	27.6117	27.608	0.0037	-0.013	-0.0005	-0.0047
240	33.012	33.0416	33.011	-0.0024	+0.004	-0.0005	+0.0028
250	39.252	39.2566	39.256	+0.0006	-0.004	+0.0003	+0.0024
260	46.325	46.3286	46.332	-0.0066	+0.003	+0.0006	-0.0012
270	54.315	54.3333	54.321	+0.0093	+0.021	-0.0006	-0.0029
280	63.366	63.3556	63.345	0.0129	0.023	+0.0031	-0.0029
290	73.471	73.1779	73.461	+0.0169	+0.010	+0.0056	-0.0051
300	84.762	84.7969	84.776	-0.0209	+0.006	+0.0088	-0.0031
310	97.411	97.4062	97.389	+0.0172	+0.025	+0.0047	+0.0036
320	111.436	111.418	111.402	+0.016	+0.034	-0.002	+0.0086
330	126.946	126.960	126.939	-0.021	+0.007	-0.004	+0.0125
340	144.152	144.167	144.139	+0.028	+0.013	-0.001	+0.0112
350	163.224	163.205	163.164	+0.041	+0.064	+0.005	-0.0064
360	184.299	184.297	184.260	+0.037	+0.039	+0.007	-0.0144
370	207.839	207.771	207.737	+0.034	+0.102	-0.010	-0.0077
372	212.88	212.795	--	--	--	-0.013	--
374	218.018	217.995	--	--	--	+0.027	--
374.11	--	--	218.167	--	--	--	--

TABLE 3

Empirical Equations Proposed for the Saturation Pressure

Author(s) and Date	Ref.	Eq. No.	Temperature Range		Equation	Constants
			F	°C		
Osborne, Stimson et al., 1933	21	1	527 to 705.2	275 to 374	$T \log_{10} p = aT - b + cx^5 + dx^6 + ex^6$ where $x = 1.03571 \times 10^{-3} T - 1$	$a = 6.5903158$ $b = -3605.348$ $c = 197.17$ $d = -1094.8$ $e = -2518.2$
Smith, Keyes et al., 1933	25	2	212 to 705.1	100 to 371.11	$\log_{10} \dfrac{P_c}{P} = \dfrac{x}{T}\left[\dfrac{a + bx + cx + ex^4}{1 + dx}\right]$ where $x = t_c - t$	$P_c = 3206.2$ psia $t_c = 705.40$ F $a = 3.346313$ $b = 2.30063 \times 10^{-2}$ $c = 1.288663 \times 10^{-9}$ $d = 7.6636005 \times 10^{-5}$ $e = 6.2532777 \times 10^{-12}$
Osborne and Meyers, 1934	26	3	32 to 705.2	0 to 371	$\log_{10} p = A + \dfrac{B}{T} + \dfrac{C}{T}\left(10^{Dx^2} - 1\right) + \left(10^{Fy^{5/2}}\right)$ where $x = (T - K) 3.24$ $y = (705.40 - t) 1.8$	$K = 951,588$ $A = 6.5938507$ $B = -3609.2$ $C = 2.4964 \times 10^{-4}$ $D = 1.1965 \times 10^{-11}$ $E = -0.0044$ $F = -0.0057148$
1952 VTI Steam Tables (D. I. Timroth)	4	4	32 to 705.17	0 to 374.15	$\log_{10} p = 2.23112 + v_1 - (3.309 \times 10^{-4} T + 0.83985) v$ where $v_1 = 4.16294(1 - 828.29)(1 - 65.009)$ $v = \dfrac{1}{251.691}\left(x - \dfrac{x}{100}\right)\left[3.1969 - \left(x - \dfrac{x^2}{100}\right)\right]$ $z = x(3.197 - x)^2;$ $x = (T - 828.29) 180$ $0.1150 - 0.064x + \dfrac{0.7500}{(x - 1.2) + 1}$	
1955 Steam Tables of JSME	6	5	430 to 705.17	230 to 374.15	$\log_e \dfrac{3209.5}{P_s} \left[7.21379 + (z + 1) + \sum F^n \left(\dfrac{T - 869.69}{1.8}\right)^2\right]\left(\dfrac{1165.16}{T} - 1\right)$ where $n = 32$	$\alpha = 1.0071 \times 10^{-6}$ $\beta = 1.07289 \times 10^{-6}$ $\gamma = 6.04374 \times 10^{-10}$

*Units
p = pressure psia
t = temperature °F
T = absolute temperature °R = t + 159.69

Equation (3) was used to compute the values of vapor pressure from 212° to 705.5°F given in the following steam tables:

1934 Skeletal steam tables[10]

1939 Osborne et al. steam tables[12]

1951 and 1955 Russian (Vukalovich) tables[2,3]

1953 Faxen steam tables[7]

1955 Dzung and Rohrbach steam tables[9]

Equation (4) was used to compute the saturation pressures given in the 1952 Russian (Timroth) steam tables.[4] No reference was made to the measurements on which the formula was based. It is interesting to note that the values [26] computed by Equation (3) are identical to the values[4] computed by Equation (4) for saturation pressures from 212°F to the critical temperature (705.5°F).

Equation (5) was derived by Sugawaro[29] in 1945 and was used to compute the saturation pressures listed in the 1955 JSME steam tables.[6] It is thought that the values adopted for saturation pressure at the Third International Conference[10] were used to construct Equation (5).

C. The Specific Volume of Saturated Water and Water Vapor

Saturation Volume Measurements. The specific volume along the saturation line may be determined by a volume measurement with the water or the water vapor at or close to saturation conditions. To date the above type of volume measurement has not been employed extensively. Instead the specific volumes along the saturation line have been deduced from calorimetric measurements and also by the extrapolation of isometrics for subcooled liquid and superheated vapor to their respective saturation lines. The latter two methods form the basis for the values of specific volume for saturated water and vapor that are listed in the various national steam tables.

Table 4 lists the principal investigators and the methods used to deduce the specific volume of water and steam along the saturation line. The individual works will be discussed and a comparison of the results will be given in the last section of this chapter.

Callendar[13] conducted measurements on the enthalpy of steam in the critical region. A detailed discussion on his observation is given in Section VI of this thesis. Table 5 gives values for the specific volume of saturated steam which were derived by Callendar from his enthalpy measurements.

TABLE 4

Measurements of Specific Volume Along Saturation Line

No.	Investigator(s) & Date	Ref.	Type of Experiment	Temperature Range	
				°F	°C
1	Callendar (1929)	13	Calorimetric	400 to 717	210 to 380
2	Smith and Keyes (1934)	30	Extrapolation	86 to 680	30 to 360
3	Jakob and Fritz (1935)	31	Calorimetric	To 690	To 365
4	Keyes, Smith and Gerry (1936)	32	Extrapolation	To 704.1	To 373.40
5	Eck (1936)	33	Analytical	To 705.64	To 374.24
			Calorimetric	212 to 705.2	100 to 374
6	Osborne, Stimson and Ginnings (1937)	35	Direct Volume Measurement	At 696	At 370

TABLE 5

The Specific Volume of Saturated Steam
Derived by Callendar [13]

Temperature, °F	Pressure, psia	Specific Volume of Saturated Steam, ft^3/lb
680	2693	0.1124
690	2886	0.0936
700	3099	0.0731
705.2	3222	0.0607
707	3268	0.0560
710	3350	0.0539
716	3563	0.0453
717	3650	0.0413

Smith and Keyes[30] conducted pressure-volume-temperature measurements on subcooled water over a wide range of temperatures and pressures. They deduced saturation volumes by extrapolating their measured isotherms to the saturation line. They found that the following equation represented their saturation volumes from 86° to 680°F (30° to 360°C) with a high degree of precision:

$$v_s = \frac{v_c + a(t_c - t)^{\frac{1}{3}} + b(t_c - t) + c(t_c - t)^4}{1 + d(t_c - t)^{\frac{1}{3}} + e(t_c - t)} \quad , \qquad (6)$$

where

v_c = critical volume, 0.051219 ft^3/lb,

t_c = critical temperature, 705.40°F,

a = -4.149828 x 10^{-3},

b = -1.070894 x 10^{-5},

c = 1.14276 x 10^{-15},

d = 1.103567 x 10^{-1},

e = -2.192368 x 10^{-3}.

The "observed" and calculated volumes of Smith and Keyes are given in Table 6.

TABLE 6

"Observed" and Computed Saturation Volumes
of Smith and Keyes [30]

Temperature, °C	Specific Volume of Saturated Water, cm^3/g		Observed minus Calculated
	Observed	Calculated	
30	1.004445	1.004531	-0.000086
50	1.012116	1.012097	+0.000019
75	1.025810	1.025704	+0.000106
100	1.043437	1.043378	+0.000059
150	1.090505	1.090589	-0.000084
200	1.156329	1.156516	-0.000187
250	1.251487	1.251234	+0.000253
300	1.403733	1.403569	+0.000164
320	1.498757	1.499236	-0.000479
330	1.561779	1.561898	-0.000119
340	1.641273	1.640848	+0.000425
350	1.745006	1.746777	-0.001771
360	1.906541	1.906617	-0.000076

Jakob and Fritz,[31] by means of the Clapeyron equation derived specific volumes of saturated steam from their enthalpy of vaporization measurements. The Osborne and Meyers formula[26] Equation (3) was used to compute dP/dT. Table 7 gives their computed specific volumes of saturated steam in the critical region.

TABLE 7

Specific Volumes of Saturated Steam
Derived by Jakob and Fritz [31]

Temperature, °F	Pressure, psia *	Specific Volume of Saturated Steam, ft^3/lb
680	2708.4	0.1118
689	2876.1	0.0967
698	3053.5	0.0799
701.6	3127.4	0.0717

*Computed from Osborne and Meyers
Formula (Equation 3).

Keyes, Smith and Gerry [32] investigated the specific volume of steam to high pressures and temperatures. They deduced the following empirical equation from their "extrapolated" values of specific volume of saturated steam,

$$v_s = C(T_s/P_s) + B_o - \Delta B_s \tag{7}$$

where

$$C = 0.595708,$$

$$B_o = 0.03027 - \frac{76.166}{T_s} \cdot 10^{262020/T_s^2}$$

$$\Delta B_s = \left[(62.4283 + 8.74 \times 10^{-24} y^{10})(0.17119 + 0.032 y^{\frac{1}{3}} + 4.73 \times 10^{-4} y) \right]^{-1},$$

$$y = (705.40 - t_s)/1.8 .$$

The equation is valid for saturation temperatures less than 704.1°F (373.40°C).

Keyes, Smith and Gerry derived an equation of state for saturated and superheated steam from their volume measurements. The equation was valid for specific volumes greater than 0.16 ft^3/lb (10 cm^3/g). The values obtained by Keyes, Smith and Gerry along the saturated vapor line by extrapolation and computation are given in Table 8.

TABLE 8

Saturation Volumes of Steam Computed and
Extrapolated by Keyes, Smith and Gerry [32]

Temperature, °C	Saturation Specific Volumes of Steam, cm^3/g		
	Extrapolated	Equation of State	Equation (7)
191.90	150	150.25	150.25
195.26	140	140.11	140.11
211.98	100	100.32	100.33
213.33	97.5	97.727	97.738
227.30	75	75.112	75.118
250.00	50	50.043	50.061
263.05	40	40.004	40.018
280.19	30	30.019	30.028
304.64	20	20.017	20.018
312.70	17.5	17.484	17.486
321.56	15	15.023	15.028
332.03	12.5	12.477	12.474
343.89	10	9.959	9.978
357.11	7.5	7.537	7.502
364.05	6.25		6.253
370.53	5		4.975
373.40	4		4.127

Eck[33] balanced and grouped certain measurements[30,31] of specific volumes for saturated water and steam with those obtained by the Clapeyron equation. His derived values for saturated water and steam in the critical region are given in Table 9.

TABLE 9

Saturation Volumes Derived
by Eck[33]

Temperature, °F	Saturation Pressure,* psia	Saturation Specific Volumes, ft^3/lb	
		Liquid	Vapor
680	2708.4	0.03034	0.1115
689	2876.1	0.03226	0.09624
698	3053.5	0.03542	0.07936
701.6	3127.4	0.03760	0.07119
705.2	3203.4	0.04245	0.05815
705.64	–	0.04911	0.04911

*Computed from Osborne and Meyers
Formula Equation (3).

In 1930, Osborne et al.[34] proposed the following three calorimetric experiments to evaluate the thermodynamic properties of saturated water vapor;

(1) Observed the changes in pressure and temperature when heat is added to a fixed amount of water and water vapor.

(2) Measure amount of saturated water vapor formed and removed when heat is added to contents under conditions of constant temperature and pressure.

(3) Measure amount of saturated water removed when heat is added to the contents under conditions of constant temperature and pressure.

The experiment of the first type evaluates the enthalpy of saturated water with temperature $(\partial h/\partial T)$ while the experiment of the second type evaluates the enthalpy of vaporization. The third experiment yields a measured quantity which is complementary to the measured quantities obtained in the first two experiments. Osborne proposed that the heat capacity of the calorimeter be eliminated in an experiment of the first type by conducting two separate measurements over the same temperatures and pressures with different amounts of fluid contents in the calorimeters. The heat capacity of the calorimeter in the second and third types of experiments was not a factor, since these were to be conducted under "isothermal" conditions.

The three experiments proposed by Osborne were subsequently carried out by Osborne et al.[35] at the U. S. Bureau of Standards. The equations used and the formulations that were derived are given in Table 10.

Equations (8),(9) and (10) were derived from energy balances between measured quantities (α, γ, β) and the thermodynamic properties (h_{fg}, h_f, v_f and v_g). The Clapeyron equation was used to reduce Equations (9) and (10) to Equations (11) and (12). The specific volumes of saturated water and steam may be computed from Equations (11) and (12) provided that γ, β and dP/dT are known.

Table 11 gives the saturation volumes computed by Osborne et al.[35] from the equation listed in Table 10 and values of dP/dT computed from Equation (3). They conducted confirmatory specific volume measurements at 698°F (370°C) to secure evidence concerning the reliability of their calorimetric measurements. Seven measurements of superheated vapor and six of compressed liquid were all made within about 0.4°F of 698°F (0.2 of 370°C) and at a pressure corresponding to saturation at 698°F. By extrapolation, 0.0356 and 0.07889 ft^3/lb were obtained for the saturation volumes of water and steam, respectively. These values are in excellent agreement with the specific volumes derived from their calorimetric measurements (Table 11).

TABLE 10

Equations and Formulations Derived at U. S. Bureau of Standards
by Osborne[34] and Osborne et al.[35]

Investigator(s), and Date	Eq. No.	Equation or Formulation	Constants
Osborne, 1930	8	$$\frac{Q_B - Q_A}{M_b - M_A} = \left[h_f - \frac{v_f h_{fg}}{v_g - v_f} \right]_2^1 = \alpha$$ where Q_A = the net heat required to change the state of mass M_A from 1 to 2.	-
	9	$$h_{fg} + \frac{v_f h_{fg}}{v_g - v_f} = -\frac{Q}{M_2 - M_1} = \gamma$$ where Q is the amount of heat required to evaporate $M_1 - M_2$ lb of water.	
	10	$$\frac{v_f h_{fg}}{v_g - v_f} = \frac{Q}{M_2 - M_1} = \beta$$ where Q is the amount of heat required to evaporate a weight $M_1 - M_2$, of water.	
	11	$$\gamma = T v_g \frac{dP}{dT}$$	
Osborne, 1930	12	$$\beta = T v_f \frac{dP}{dT}$$	-
Osborne, Stimson and Ginnings, 1937	13	$$D = \tfrac{1}{2}(\gamma + \beta) = A + B x^{0.617}$$ where $x = (705.47 - t)/1.8$, valid in range from 626 to 705.47°F (330 to 274.15° C)	A = 230.08 B = 7.9176
	14	$$h_{fg} = \gamma - \beta = a\left(\frac{705.47 - t}{180}\right)^{0.404}$$ $$-b\left(\frac{590 - t}{180}\right)^{1.73} + c\left(\frac{329 - t}{180}\right)^{2.2}$$ valid in range from 212° F to the critical temperature (705.47° F or 374.15° C)	a = 681.632 b = 15.80381 c = 7.70637

Note: t = temperature, °F

h_{fg} – enthalpy of vaporization, Btu/lb

v_f = Specific volume of saturated water, ft³/lb

v_g = Specific volume of saturated water vapor, ft³/lb

It was concluded that the calorimetric measurements at 698°F (370°C) showed no evidence of error.

TABLE 11

Saturation Volumes of Water and Steam
Derived by Osborne et al.[35]

Temper- ature °F	Saturation Pressure, psia	Saturation Specific Volumes, ft³/lb	
		Liquid, v_f	Vapor, v_g
680	2708.4	.0303	.1112
689	2876.1	.0323	.0961
690.8	2910.7	.0328	.0929
692.6	2945.8	.0334	.0896
694.4	2981.2	.0340	.0862
696.2	3017.1	.0348	.0827
698.0	3053.5	.0356	.0790
699.8	3090.2	.0367	.0750
701.6	3127.4	.0381	.0705
703.4	3165.1	.0402	.0649
705.2	3203.4	.0449	.0556
705.47	3209.5	.0497	.0497

Osborne et al. also carried out special tests to determine the possibility of mixing of the liquid and vapor phases in their experiments, which would give erroneous results. The experiments showed freedom from this effect except at temperatures of 704.3°F and higher (about 1.2°F near the critical point). They concluded that it appeared that the calorimetric process could not be trusted beyond 704.3°F (373.5°C).

Basis for Saturation Volumes Listed in Various Steam Tables. The formulations derived by Osborne et al.[35] were used to compute the specific volumes of saturated water and steam that are given in the following tables:

1939, Osborne et al. tables[12]

1951 and 1955, Vukalovich tables[2,3]

1953, Faxen tables[7]

1955, Dzung and Rohrbach tables[9].

The values for the specific volume of saturated liquid up to 680°F (360°C) adopted at the Third International Conference were those computed from Equation (6). The specific volume values for steam similarly adopted at the Third International Conference up to 662°F (350°C) were those computed from the Keyes, Smith and Gerry equation of state.[32] The values adopted for saturation volumes in the critical region probably were based on the German and American measurements.[30,31]

Values for the saturation volumes of water listed in the 1955 JSME tables[6] were derived by a graphical interpolation of the values in the 1934 international skeletal tables.[10] Values listed for the saturation volumes of steam above 3000 psia (210 kg/cm^2) were those adopted at the Third International Conference.[10]

Values for the saturation volumes listed in the Combustion Engineering tables[11] were derived from the values given in the skeletal tables.

No basis was given for the saturation volumes of liquid and vapor which were listed in the 1956 VDI tables.[8]

The saturation volumes given in the 1939 Callendar steam tables[14] were derived from the following sources of information:

(a) the vapor pressure measurements of Egerton and Callendar,[23]

(b) the values of specific volume adopted at the Third International Conference[10] and

(c) the values of specific volume given in the 1931 Callendar steam tables.[36]

Values listed in the Keenan and Keyes steam tables[1] for the specific volume of saturated water from 680°F (360°C) to the critical point, and for saturated water vapor from 620°F (344°C) to the critical point are based on the following sources of information

(1) the Keyes vapor pressure equation,[25]

(2) the specific volumes for saturated water and water vapor adopted at the Third International Conference,[10] and

(3) the enthalpies for saturated water and water vapor of Osborne et al.[35]

The values given for the specific volume of saturated steam in the critical region in the 1952 and 1958 Timroth tables[4,5] were derived from the observed isometrics of Timroth. No reference was made of the experimental values used to derive the specific volume along the saturated liquid line.

D. Comparison of Derived Saturation Volumes

Osborne et al.[35] compared his derived values of specific volume for saturated steam with those derived by Keyes et al. He found good agreement between the values in the lower range of temperature but progressively increasing disagreement in the upper range of temperatures.

Keyes, Smith and Gerry[32] made a similar comparison. They considered the derived values of Osborne et al. the more reliable at 662°F (330°C) and higher temperatures.

Figure 4 gives the derived values for the specific volume of saturated steam in the critical region of Keys et al.[32] and of Osborne et al.[35]
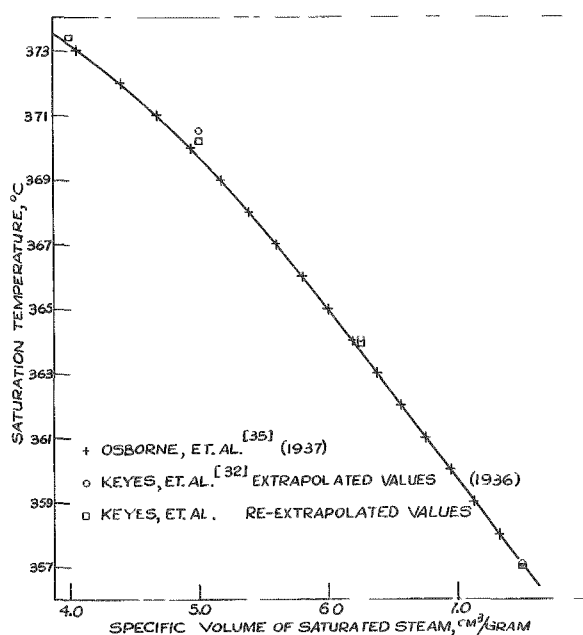
FIG 4 COMPARISON OF EXTRAPOLATED AND COMPUTED SATURATION VAPOR VOLUMES

The figure indicates fair agreement between the extrapolated and computed saturation volumes except for specific volumes at about 5.0 cm^3/gram. In view of this apparent disagreement and the precise nature of the calorimetric and volumetric experiments, the isometrics of Keyes et al.[32] were redrawn with a precision of a few parts in 10,000. The extrapolated values so obtained make the agreement even better between the volumetric and calorimetric experiments than the original extrapolation of Keyes et al. The agreement probably would have been still better if the pressure-volume-temperature measurements were made over smaller intervals of pressure and temperature and if the measurements were made closer to the saturation line.

The saturation values for pressure and specific volume in the vicinity of the critical point listed in the various national steam tables are given in Tables 12 to 18, and are shown graphically in Figure 5. The figure indicates good agreement among values listed for saturated liquid but significant differences among the values for saturated vapor.

Tables 19 and 20 list the differences between the values of the various steam tables and those in the 1934 skeletal tables.[10] For purposes of comparison the tolerances adopted at the Third International Conference[10] for specific volumes of saturated liquid and water vapor have been listed also in Tables 19 and 20.

TABLE 12

Saturation Pressures and Specific Volumes
from 1934 Skeletal Tables[10]

Temperature, °F	Saturation Pressure, psia		Saturation Specific Volumes, ft³/lb			
	Value	Tolerance, ±	Liquid	Tolerance, ±	Vapor	Tolerance, ±
680	2708.4	0.7	0.030541	0.000064	0.1115	0.0006
698	3053.5	0.7	0.03574	0.00034	0.08004	0.00160
699.8	3090.2	1.4	0.03679	0.00042	0.07626	0.00160
701.6	3127.4	1.6	0.03814	0.00054	0.07205	0.00176
703.4	3165.1	1.6	0.04008	0.00085	0.06700	0.00192
705.2	3203.4	1.6	0.0447	0.0024	0.05844	0.00192

TABLE 13

Saturation Pressures and Specific Volumes
from 1955 J.S.M.E. Tables [6]

Temperature, °F	Saturation Pressure, psia	Saturation Specific Volumes, ft³/lb	
		Liquid	Vapor
680	2709.1	0.03055	0.1111
689	2875.8	0.03253	0.09595
698	3053.5	0.03574	0.07993
699.8	3090.3	0.03679	0.07625
701.6	3127.5	0.03814	0.07208
703.4	3165.4	0.04008	0.06696
705.2	3203.7	0.04469	0.05847
705.47	3209.5	0.05094	0.05094

TABLE 14

Saturation Pressures and Specific Volumes from
Combustion Engineering Inc. Steam Tables[11]

Temperature, °F	Saturation Pressure, psia	Saturation Specific Volumes, ft³/lb	
		Liquid	Vapor
679.54	2700	0.0305	0.1123
680	2708.4	0.0305	0.1115
684.98	2800	0.0316	0.1032
685	2800.4	0.0316	0.1032
690	2895.0	0.0328	0.0945
690.26	2900	0.0329	0.0941
695	2992.7	0.0345	0.0856
695.37	3000	0.0346	0.0849
700	3094.1	0.0369	0.0758
700.29	3100	0.0372	0.0752
705	3199.1	0.0440	0.0597
705.04	3200	0.0443	0.0596
705.34	3206.2	0.0541	0.0541

TABLE 15

Saturation Pressures and Specific Volumes
from 1956 V.D.I. Steam Tables[8]

Temperature, °F	Saturation Pressure, psia	Saturation Specific Volumes, ft³/lb	
		Liquid	Vapor
680.0	2708.4	0.03055	0.1115
681.8	2741.1	0.03090	0.109
683.6	2774.3	0.03128	0.106
685.4	2807.8	0.03168	0.103
687.2	2841.8	0.0322	0.0998
689.0	2876.1	0.0325	0.0968
690.8	2910.7	0.0330	0.0937
692.6	2945.8	0.0335	0.0905
694.4	2981.2	0.0341	0.0871
696.2	3017.1	0.0349	0.0836
698.0	3053.5	0.0357	0.0798
699.8	3090.2	0.0368	0.0756
701.6	3127.4	0.0381	0.0710
703.4	3165.1	0.0400	0.0657
705.2	3203.4	0.0445	0.0573
705.47	3209.5	0.0509	0.0509

TABLE 16

Saturation Pressures and Specific Volumes
from 1939 Callendar Steam Tables [14]

Temperature, °F	Saturation Pressure, psia	Saturation Specific Volumes, ft³/lb	
		Sat. Liquid	Sat. Vapor
680	2708	0.0305	0.1115
685	2800	0.0316	0.1033
690	2895	0.0328	0.0953
695	2993	0.0345	0.0867
700	3094	0.0369	0.0761
701	3115	0.0376	0.0737
702	3136	0.0385	0.0710
703	3157	0.0396	0.0680
704	3178	0.0410	0.0645
705	3199	0.0438	0.0589

TABLE 17

Saturation Pressures and Specific Volumes from
Keenan and Keyes Steam Tables [1]

Temperature, °F	Saturation Pressure, psia	Saturation Specific Volumes, ft³/lb	
		Liquid	Vapor
679.55	2700	0.0305	0.1123
680.00	2708.1	0.0305	0.1115
684.99	2800	0.0315	0.1035
685.00	2800.2	0.0315	0.1034
690.00	2895.1	0.0328	0.0953
690.26	2900	0.0329	0.0947
695	2992.9	0.0344	0.0864
695.36	3000	0.0346	0.0858
700	3093.7	0.0369	0.0761
700.31	3100	0.0371	0.0753
702	3134.9	0.0385	0.0710
704	3176.7	0.0410	0.0645
705	3197.7	0.0438	0.0589
705.11	3200	0.0444	0.0580
705.4	3206.2	0.0503	0.0503

TABLE 18

Saturation Pressures and Specific Volumes
from 1952 Timroth Tables [4]

Temperature, °F	Saturation Pressure, psia	Saturation Specific Volumes, ft³/lb	
		Liquid	Vapor
680	2708.4	0.03034	0.1112
681.8	2741.1	0.03069	0.1081
683.6	2774.4	0.03106	0.1051
685.4	2807.8	0.03146	0.1020
687.2	2841.8	0.03189	0.09915
689	2876.1	0.03236	0.09661
690.8	2910.7	0.03284	0.09290
692.6	2945.8	0.03332	0.08954
694.4	2981.2	0.03396	0.08618
696.2	3017.1	0.03476	0.08265
698	3053.5	0.03556	0.07897
699.8	3090.2	0.03667	0.07496
701.6	3127.4	0.03812	0.07048
703.4	3165.1	0.04021	0.06551
705.2	3203.4	0.04485	0.05782
705.5	3209.5	0.05286	0.05286
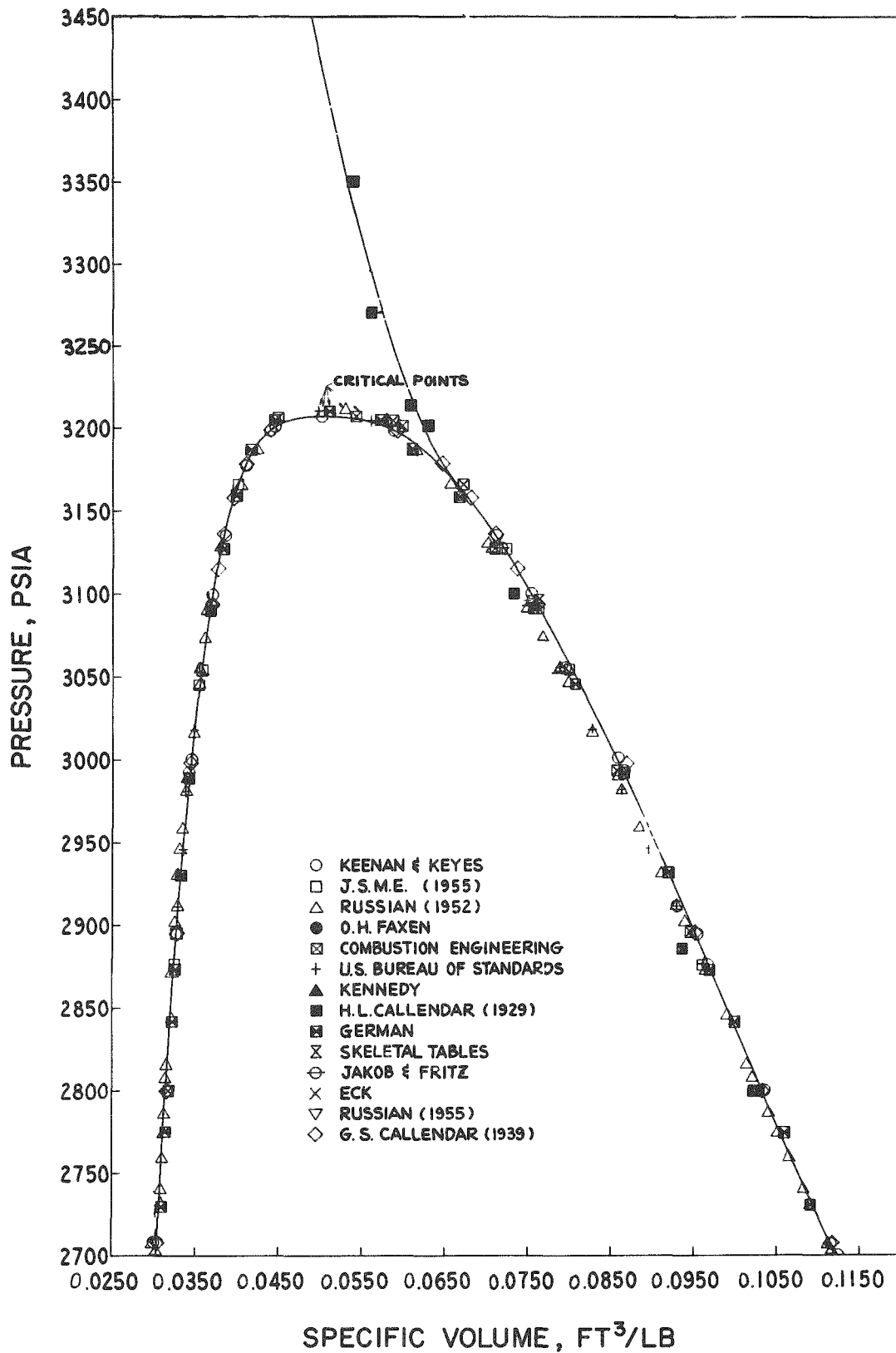
FIG. 5 PRESSURE – VOLUME DIAGRAM FOR
SATURATED WATER AND STEAM

TABLE 19

Differences between Specific Volumes Listed in 1934 Skeletal Tables and Those Given in Other Steam Tables--for Saturated Liquid (Difference in ft³/lb) x 10^5

Temperature, °F	Tolerance Adopted at 1934 Int. Steam Table Conf.(10) ±	Osborne et al.(35)	Eck(33)	1952 Timroth Tables(4)	1936 Keenan and Keyes(1)	1955 J.S.M.E. Tables(6)	1956 V.D.I Tables(8)	1940 Combustion Engineering Inc. Tables(14)	1939 Callendar Tables(14)
680	6.4	+24.1	20.1	+20.1	+4.1	-0.9	-0.9	+4.1	+4.1
698	34	+14	32	+18	--	0	+4	--	--
699.8	42	+9	--	*12	*-11	0	-1	*-11	*-11
701.6	54	+4	54	+2	--	0	+4	--	--
703.4	85	-12	--	-13	--	0	+8	--	--
705.2	240	-22	225	-15	**30	0	+20	--	--

TABLE 20

Differences between Specific Volumes Listed in 1934 Skeletal Tables and Those Given in Other Steam Tables--for Saturated Vapor (Difference in ft³/lb) x 10^4

Temperature, °F	Tolerance Adopted at 1934 Int. Steam Table Conf.(10) ±	Osborne et al.(35)	Callendar(13)	Jakob and Fritz(31)	Eck(33)	Keenan and Keyes(1)	1952 Timroth Tables(4)	1956 V.D.I Tables(8)	Combustion Engineering Inc. Tables(14)	1939 Callendar Tables(14)
680	6	+3	-9	-3	0	0	+3	0	0	0
698	16	+10.4	--	+1.4	+6.8	--	+10.7	+2.4	--	--
699.8	16	+12.6	*+31.6	--	--	*+1.6	+13	+6.6	*+4.6	*+1.6
701.6	17.6	+15.5	--	+3.5	+8.6	--	+15.7	+10.5	--	--
703.4	19.2	+22.1	--	--	--	--	+14.9	+13	--	--
705.2	19.2	+28.4	-22.6	--	+2.9	**+4.4	+6.2	+11.3	--	--

*Sp. Vol. at 700°F compared with that given at 699.8°F in 1934 Skeletal Tables.

**Sp. Vol. at 705.11°F compared with that given at 705.2°F in 1934 Skeletal Tables.

In some cases the differences listed exceed the tolerances adopted at the Third International Conference. Tables 19 and 20 indicate that there is a very good agreement up to about 701.6°F (372°C) between the saturation volumes derived by Osborne et al.[35] and those listed in the 1952 Timroth tables.[4] At the higher temperatures there is disagreement between these two sets of values. However it is interesting to note that Osborne et al. thought that his measurements were in error within one or two degrees of the critical point.

E. Summary

(1) Saturation pressures computed by the Osborne and Meyers formula are recommended for use, being based on at least three independent investigations.

(2) There is very good agreement up to 701.6°F (372°C) between the saturation specific volumes derived by Osborne et al.[35] from calorimetric measurements and those in the 1952 Timroth tables[4] derived from Timroth's isometrics[37] in the critical region.

(3) The values for specific volume of saturated liquid and vapor listed in the Timroth tables at temperatures of 701.6°F and higher are recommended for use because in this region they agree very well with the extrapolated values of Keyes et al.[32] (Figure 4).

III. PRESSURE-VOLUME-TEMPERATURE PROPERTIES
OF SUBCOOLED WATER

A. Measurements

The basic method of volume measurements on subcooled water consists of observing the pressure and temperature of a known amount of water in a closed container. Table 21 shows the extent of the investigations on the specific volume of subcooled water.

TABLE 21

Summary of Pressure-Volume-Temperature Measurements on Subcooled Water

Number	Author(s) Date	Reference	Pressure Range		Temperature Range	
			psia	kg cm²	°F	°C
1	Amagat, 1893	38	14 to 43,000	1 to 3000	32 to 390	0 to 198
2	Bridgman, 1913	39	14 to 170,000	1 to 12,000	-4 to 212	-20 to 100
3	Trautz Steyer, 1930	40	100 to 4300	50 to 500	32 to 698	0 to 370
4	Tammann and Ruhenbeck, 1932	43	14 to 36,500	1 to 2500	78 to 1200	20 to 650
5	Von Nieuwenburg Blumendal, 1932	44	2300 to 8500	160 to 600	662 to 845	350 to 480
6	Smith Keyes, 1931	30	60 to 5000	4 to 350	86 to 705 2	30 to 374
7	Kirillin et al , 1953	45	820 to 7000	57 to 410	570 to 704.8	298 30 to 373 78
8	Holser Kennedy, 1958	46	1470 to 20,000	103 to 1400	284 to 670	140 to 355

The measurements of Amagat[38] and Bridgman[39] are not of utility, since they only extended to temperatures of 390 and 212°F, respectively.

Trautz and Steyer [40] made measurements in the critical region. The following criticisms of the Trautz and Steyer work were made by Jakob:[41]

1. The apparatus was not properly insulated against heat loss.

2. The errors in the measurements of temperature amounted to more than the estimated 1°F (0.5°C).

3. Partial evaporation of water occurred at the walls of the container before the main body of water reached saturation temperature. Evaporation would have the tendency of making the specific volumes of water too high.

Jakob compared the measurements of Trautz and Steyer with the measurements of Keyes and Smith;[42] this is reproduced in Table 22. It was concluded that the results of Trautz and Steyer were in error by as much as some 4%.

TABLE 22

Specific Volume of Water (cm³/gram) measured by Keyes and Smith (K & Sm)[42] and by Trautz and Steyer (T & St)[40]

Pressure kg/cm²	Temperature, °C											
	150		250		310		330		350		360	
	K & Sm	T & St	K & Sm	T & St	K & Sm	T & St	K & Sm	T & St	K & Sm	T & St	K & Sm	T & St
50	1.087	1.087	1.250	1.257	--	--	--	--	--	--	--	--
100	1.084	1.083	1.241	1.247	--	--	--	--	--	--	--	--
150	1.081	1.078	1.233	1.233	1.422	1.44	1.542	1.57	--	--	--	--
200	1.078	1.073	1.226	1.221	--	--	--	--	1.671	1.72	--	--
250	1.075	1.069	1.219	1.208	--	--	--	--	1.604	1.64	1.706	1.77
300	1.072	1.064	1.212	1.196	--	--	--	--	1.560	1.570	--	--

The measurements of Tammann and Ruhenbeck[43] extended to high pressures and temperatures. Their results are not of utility since their measurements were conducted at intervals of 180°F (100°C) and no data fall in the region considered in this study.

Von Nieuwenburg and Blumendal[44] made measurements in the critical region. Their measurements on subcooled water as well as on superheated vapor are given in Section IV.

Smith and Keyes[30] measured the pressure and volume along a number of isotherms in the subcooled liquid region. Their measurements are given in Table 23.

Kirillin and Rumyanstev[45] made measurements on subcooled water which extended to pressures as high as 7000 psia (490 kg/cm²). These measurements along with measurements on superheated vapor are given in Section IV.

Holser and Kennedy[46] reported specific volume measurements on subcooled water and superheated vapor. The results for subcooled water so obtained were close to their earlier values,[47] which were not greatly in error for the liquid. Kennedy and Holser[48] did not extend their measurements to the immediate vicinity of the critical point, because their equipment was inferior to that used by the Keyes and Kirillin groups.

TABLE 23

Volume Measurements of Smith and Keyes[30]
in the Critical Region

Pressure, Int Atm	V observed cm³/g	V calculated, cm³/g
	360°C	
189 539	1 861906	1 861565
195 48?	1 833087	1 832380
195 7?6	1 831680	1 831050
225 559	1 739484	1 738823
285 127	1 640401	1 640329
514 920	1 607081	1 607606
344 715	1 579327	1 580244
	Av dev = 0 0310%	
	370°C	
213 493	2 075006	2 065802
225 567	1 956446	1 923102
237 565	1 889457	1 849800
249 162	1 841807	1 795978
261 070	1 801528	1 756528
	Av dev 1 858%	
	374°C	
219 566	2 37965	--
225 452	2 15915	--
2 7 318	2 01260	--
249 208	1 93430	--
261 108	1 87990	--
275 012	1 83798	--
278 ?6?	1 81737	--

B. Empirical Equations

Smith and Keyes[30] derived the following empirical equation from their specific volume measurements:

$$v = \frac{v_S + B(P - P_S) + D(P - P_S)^2 + E(P - P_S)^{\frac{1}{2}}}{1 + C(P - P_S)} \quad , \tag{15}$$

where

v = specific volume of subcooled water in ft^3/lb,

v_S = specific volume of saturated water in ft^3/lb,

P_S = saturation pressure in psia,

P = pressure of subcooled water in psia.

The coefficients in Equation (15) were represented by the following relations:

$$\log_{10} B = a + b(t_C + c(t_C - t) + d(t_C - t)^{\frac{3}{2}} \quad ,$$

where

t_c = critical temperature, 705.40°F

$b = -7.2306218 \times 10^{-2}$

$c = -0.71879605 \times 10^{-2}$

t = the temperature of subcooled liquid

$d = 2.4388820 \times 10^{-4}$;

a = -4.2551483

$$\log_{10} (-D) = a + b(t_c - t) \quad ,$$

where

a = -9.08717

$b = -1.6529204 \times 10^{-2}$;

$$\log_{10} (-1/E) = a + b(t_c - t)^{\frac{1}{2}}$$

where

a = 2.791848

$b = 2.980849 \times 10^{-1}$;

$$\log_{10} C = a + b(t_c - t)^{\frac{2}{3}} + c(t_c - t) + d(t_c - t)^{\frac{3}{2}} \quad ,$$

where

a = -2.7813352

$c = -3.8733567 \times 10^{-3}$

$b = -3.5717609 \times 10^{-2}$

$d = 1.8969266 \times 10^{-4}$.

Equation (15) was found to represent their measurements along any isotherm from 90° to 680°F (30° to 360°C) to about one part in 3450 (see Table 23).

The following equation for subcooled water was derived by Keenan[49] from the measurements of Amagat[38] and Smith and Keyes:[30]

$$v = 49.43 \times 10^{-3} - 13.1690 \times 10^{-3} z^{0.147166}$$

$$- 1.1166 \times 10^{-3} y^{-1.6}(P - 3211) + \Delta \quad , \tag{16}$$

where

$z = 705.4 - t \quad ,$

$y = 725 - t \quad$, and

Δ is a function of P and t to be treated graphically.

C. Values of Pressure-Volume-Temperature in Various Steam Tables

The values for subcooled water adopted at the Third International Conference[10] were those computed from Keenan's formulation Equation (16).

The values for subcooled water up to 680°F (360°C) listed in the Keenan and Keyes tables[1] were also computed from Equation (16). In the critical region values were derived from the specific volume measurements of Smith and Keyes[30] and the enthalpy measurements of Havlicek and Miskovsky.[50] A discussion of the method used to derive volume data in the critical region from enthalpy measurements is given in Section IV.

The values listed in the following steam tables were derived from the data adopted at the Third International Conference in conjuction with Keenan's formulation:[49]

1951 and 1955 Vukalovich steam tables[2,3]

1953 Faxen tables[7]

1955 J.S.M.E. tables.[6]

No mention was made of the basis for the values of the specific volumes for subcooled liquid in the 1952 Timroth tables,[4] but it appears to the authors that these were derived from the measurements of Timroth.[37] In the critical region the values in the 1956 V.D.I. tables[8] were taken from the 1952 Timroth tables.

The values for the specific volumes of subcooled water listed in the various steam tables are shown graphically in Figure 6. The good agreement between them is not surprising in view of the fact that all of the values, with the exception of those in the 1952 Timroth tables, are based on the volume measurements of Smith and Keyes or on the equation of Keenan, itself based on the Smith and Keyes data.

D. Summary

(1) With the exception of the 1952 Timroth tables,[4] and hence the 1956 V.D.I. tables, all other steam tables list values for subcooled water which are based on the volume measurements of Smith and Keyes.

(2) There is very good agreement between the values for subcooled water listed in the Keenan and Keyes tables[1] and those in the 1952 Timroth tables.[4]

4000

3950

3900

3850

3800

3750

3700

3650 ▲CRITICAL POINT

3600

3550

3500

3450

3400

3350

3300

3250

CRITICAL POINT

3200

3150

3100

3050

3000

PRESSURE, PSIA

2950

2900

2850

2800

2750

2700

	H L CALLENDAR	1929
	SKELETAL TABLES	1934
	JAKOB & FRITZ	1935
	ECK	1936
	KEENAN & KEYES	1936
	G S CALLENDAR & EGERTON	1939
	OSBORNE ET AL.	1939
	COMBUSTION ENGINEERING	1940
	TIMROTH	1952
	FAXEN	1953
	VUKALOVICH	1955
	J S M E	1955
	V D I	1956
▲	HOLSER & KENNEDY	1958

800°F
790°F
788°F
780°F
770°F
760°F
752°F
750°F
740°F
734°F
730°F
720°F
716°F
710°F
700°F
698°F

0 0250 0 0350 0 0450 0 0550 0 0650 0 0750 0 0850 0 0950 0 1050 0 1150

SPECIFIC VOLUME, FT³/LB

FIG 6 PRESSURE-VOLUME DIAGRAM FOR WATER

IV. PRESSURE-VOLUME-TEMPERATURE PROPERTIES OF SUPERHEATED WATER VAPOR

A. General

The common method of determining the specific volume of superheated vapor consists of observing the pressure and temperature of a known amount of water vapor in a closed container or piezometer. In very precise determinations many samples of freshly distilled water are used.

The specific volume of vapor may also be derived from enthalpy measurements. This method has not been used extensively but it merits attention, since accurate enthalpy measurements have been made in the critical region by various investigators.

B. Pressure-Volume-Temperature Measurements

The extent of measurements on the specific volume of superheated vapor is shown in Table 24.

TABLE 24

Summary of Pressure-Volume-Temperature-Measurements on Superheated Water Vapor

Number	Investigator(s) and Date	Reference Number	Pressure Range		Temperature Range	
			psia	kg cm²	°F	°C
1	Nieuwenburg and Blumendal, 1932	44	2300 to 8500	160 to 600	662 to 895	350 to 480
2	Keyes, Smith and Gerry, 1936	32	190 to 5400	14 to 380	383 to 860	195 to 460
3	Timroth and Vargaftik, 1950	51	1570 to 4260	110 to 300	662 to 1022	350 to 550
4	Kirillin et al., 1953 to 1956	45, 52, 53, 54	To 13500	To 950	To 1200	To 650

Nieuwenburg and Blumendal[44] made very extensive measurements on the specific volume of water vapor in the critical and supercritical regions. Unfortunately their measurements were not precise, since they estimated temperatures to be accurate to within 1.8°F (1°C), pressures to be accurate to within 57 psia (4 kg/cm²). The volume of the container was known only with an accuracy of 1%. Their measurements in the critical region are given in Table 25.

Keyes, Smith and Gerry[32] made very precise measurements on the specific volume of superheated water vapor. It was stated in a previous paper that the readings obtained with their resistance thermometers were consistent to about 0.02°F (0.01°C). Their measurements in the critical region are given in Table 26.

TABLE 25

Measured Isometrics of Nieuwenburg and Blumendal[44] for Water
and Water Vapor in the Critical Region

Specific Volume, ft³/lb	0.09707	0.08514	0.07569	0.06816	0.06207	0.0570	0.0527	0.0488
Temperature, °F	Pressures, psia							
701.6	3072	3129	3158	3101	3129	3115	3101	3101
712.4	3186	3257	3300	3271	3286	3314	3271	3300
721.4	3300	3385	3485	3428	3485	3513	3499	3513
731.3	3428	3527	3613	3613	3641	3684	3670	3727
743.0	3542	3669	3783	3769	3812	3883	3897	3968
753.8	3641	3798	3911	3911	4011	4096	4125	4253

Specific Volume, ft³/lb	0.0456	0.0428	0.0402	0.0381	0.0361	0.0342	0.0326	0.0311
Temperature, °F	Pressures, psia							
701.6	3122	3101	3101	3115	3143	3257	3385	3655
712.4	3328	3314	3342	3385	3442	3556	3727	4125
721.4	3556	3542	3627	3684	3755	3926	4111	4523
731.3	3798	3798	3897	3958	4068	4324	4537	4893
743.0	4039	4068	4238	4338	4466	4679	4893	5305
753.8	4352	4423	4523	4623	4779	5007	5277	5746

TABLE 26

Measured Isometrics of Keyes, Smith and Gerry[32]
for Water Vapor in the Critical Region

Specific Volume, cm³/g	2.0	3.0	4.0	5.0	6.25	7.5
Temperature °C	Pressure in int atm					
357.5	-	-	-	-	-	178.402
360.0	-	-	-	-	-	181.389
364.5	-	-	-	-	194.118	-
370.0	220.025	-	-	-	201.951	193.226
371.5	-	-	-	210.784	-	-
375.0	-	220.644	219.842	-	-	-
380.0	267.878	234.370	230.931	225.819	216.133	204.683
390.0	317.298	262.404	252.748	-	-	-
400.0	367.654	290.947	274.367	260.715	243.518	226.821
410.0	-	319.801	-	-	-	-
420.0	-	348.962	317.218	294.563	269.746	248.049
430.0	-	-	338.537	-	-	-
440.0	-	-	359.710	327.836	295.539	268.715
460.0	-	-	-	360.173	320.444	288.700

In 1950 Timroth and Vargaftik[51] described research on the properties of water and water vapor carried out at the All-Union Institute of Heat Engineering in Moscow (V.T.I.). Measurements of pressure, volume, and temperature on superheated water vapor extended to a pressure of 4260 psia (300 kg/cm²) and to a temperature of 1022°F (550°C). The error in the volume measurement amounted to about 0.3%. Figure 7 gives the measurements of the V.T.I. in the supercritical region for specific volumes from 2 to 5 cm³/g.

Kirillin et al. [45,52,53,54] made experimental investigations at the Moscow Power Institute (MEI) on the specific volume of water and water vapor at extremely high pressures and temperatures. The maximum error, E, in pressure measurement was estimated by

$$E(\text{psia}) = 0.05\% \ P + 0.7 \quad ,$$

where P is the pressure in psia. At 3500 psia the maximum error in pressure measurement would be about 2.3 psi (0.16 kg/cm²). They estimated that temperatures were accurate to within 0.09°F (0.05°C). The corresponding maximum error in volume measurement was in general about 0.2% and only exceeded this value in the region near the critical point.

The measurements of Kirillin et al. in the critical region are given in Table 27. Kirillin found that his measurements were in good accord with the data in the tables of Vukalovich[2] and of Timroth[4]. In particular, better agreement was obtained with the data in the tables of Vukalovich for pressures from 100 to 150 atmospheres; but in the pressure range from 200 to 300 atmospheres, and particularly in vicinity of the critical point better agreement was found with the data in the Timroth tables.

The values of pressure-volume-temperature in the Vukalovich tables were derived by an equation of state, proposed by Vukalovich. It is based on the values adopted at the Third International Conference,[10] which in turn were derived from the measurements of Keyes, Smith and Gerry.[32]

Figure 8 gives the isometrics measured at the V.T.I.[51] along with those measured by Keyes, Smith and Gerry. There is a discrepancy between the 19.85-cm³/g isometric of the V.T.I. and the 20-cm³/g isometric of Keyes, Smith and Gerry. In view of the good agreement found by Kirillin between his measurements and the data in Vukalovich tables for pressures from 100 to 150 kg/cm² it appears that the pressure-temperature measurements of the V.T.I. for the 19.85-cm³/g isometric are slightly in error.
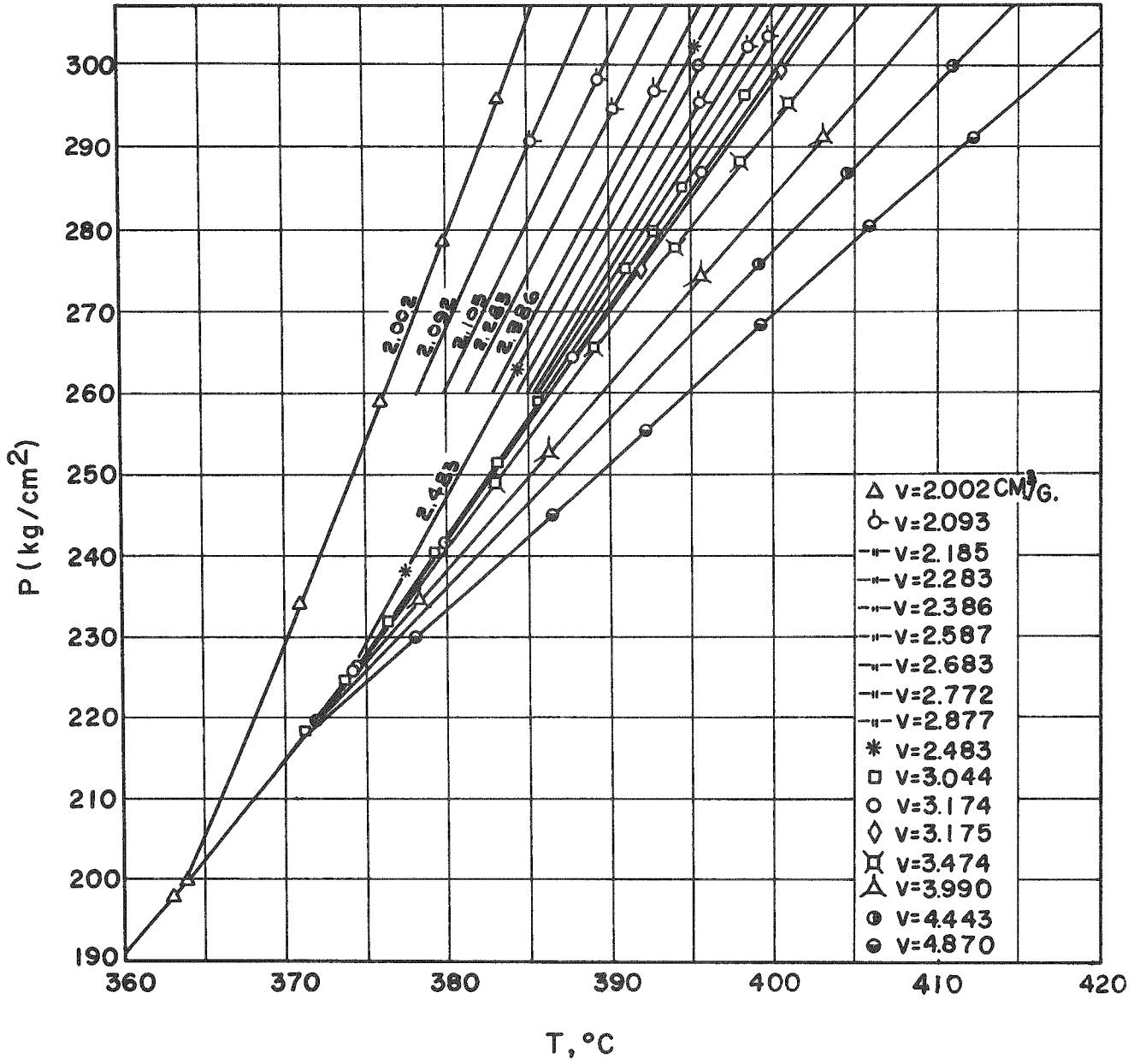
Figure 7. Isometrics of V.T.I. for Subcooled Water and Superheated Water Vapor in the Supercritical Region.

TABLE 27

Pressure-Volume-Temperature Measurements of Kirillin et al., [52-54]
on Subcooled Water and Superheated Water Vapor

t = 695.86		t = 695.88		t = 702.81		t = 703.72	
Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb
2392.4	0.18053	1892.14	0.26783	2212.3	0.2140	2190.3	0.2183
3009.8	0.048864	3011.24	0.04773	2979.2	0.1063	2668.7	0.1489
3142.9	0.032487	3011.52	0.041183	3141.7	0.07501	3144.8	0.07429
3533.7	0.029855	3341.50	0.03068	3154.7	0.03908	3183.2	0.03899
4239.7	0.027787	4545.51	0.02717	3231.7	0.03551	3221.6	0.03684
4923.0	0.026650	5443.86	0.02599	3390.4	0.03281	3298.7	0.03454
5592.1	0.025870	6697.80	0.02488	3595.2	0.03106	3600.2	0.031244
6276.8	0.025218	-	-	3983 7	0.02941	4388.5	0.02835
7009.6	0.024623	-	-	4455.2	0.02814	5596.3	0.02638

t = 704.80		t = 705.94	
Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb
2163.4	0.22362	2100.9	0.2351
2688.6	0.14703	2869.6	0.1254
2995.4	0.10681	3123 5	0.08890
3145.1	0.081894	3218.8	0.05371
3193.2	0.060360	3224.0	0.04325
3195.4	0.046998	3281.3	0.03662
3215.9	0.038872	3396.8	0.03383
3308.4	0.035056	3616.4	0.03160
3464.1	0.032593	-	-
3644.9	0.031173	-	-

t = 707.43		t = 708.94		t = 716.00		t = 721.94	
Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb
1153.4	0.5212	2024.4	0 25106	2778.5	0.14669	1153	0.5325
1527.5	0.3695	-	0.23723	3132.0	0.10534	1946.3	0.2744
1875.6	0.2798	2821.9	0.13449	3314.9	0.080387	2759.6	0.1539
2164.4	0.2254	3106.1	0 097707	3392.3	0.065075	3360.3	0.08629
3030.4	0.1065	3174.7	0.086888	3430.7	0.053617	3600.9	0.04549
3336.0	0.03606	3183.5	0.085439	3443.5	0.048550	3685.3	0.03931
3587.9	0.03224	3216.1	0.079770	3460.6	0.044509	3869.2	0.03495
5000.7	0.02754	3282.8	0.055166	3495.3	0.040643	4500.0	0.03055
6402.8	0.02581	3304.5	0.42759	3580.3	0.036924	5326.4	0.02830
7833	0.02472	3396.1	0.036024	3817.7	0.033177	6399.4	0.02669
8484	0.02432	3531.5	0.033557	4148.1	0.031092	7644	0.02550
9345	0.02388	3693.8	0.032051	4418.1	0.029922	8837	0.02467
10,080	0.02355	3701.6	0 031944	-	-	9854	0.02411
10,820	0.02324	4070.6	0.030042	-	-	10980	0.02358
11,520	0.02297	4396 3	0.029040	-	-	12265	0.02308
12,260	0.02273	4760.3	0.028135	-	-	13377	0.02271
13,070	0.02247	4954.9	0.027834	-	-	-	-
-	-	5392.9	0.027130	-	-	-	-
-	-	5788.5	0.026629	-	-	-	-
-	-	6257.0	0.026126	-	-	-	-
-	-	6568.8	0.025836	-	-	-	-

TABLE 27 (Continued)

t = 722.71		t = 730.40		t = 751.28, #1		t = 751.28, #2	
Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb
2103.1	0.2460	2273.9	0.22288	1144	0.5595	1421	0.4343
2849.5	0.1438	2710.1	0.16531	1836.1	0.3160	2021.7	0.2779
3235.1	0.1019	3053.8	0.12839	2578.1	0.1948	2684.4	0.1824
3530.1	0.06173	3247.1	0.10932	3773.8	0.08394	4213.7	0.05073
3612.9	0.04516	3419.3	0.091739	4314.1	0.04583	4959.6	0.03508
3948.3	0.03447	3587.0	0.072690	5362.9	0.03223	5705.4	0.03092
4529.4	0.03064	3653.7	0.064213	6686.0	0.02866	6367.2	0.02923
5326.9	0.02843	3724.5	0.054897	7648	0.02728	7206	0.02862
5738.7	0.02768	3793.7	0.047275	8504	0.02638	7975	0.02689
6891.9	0.02625	3833.3	0.044422	9376	0.02568	8826	0.02609
-	-	3985.0	0.038467	-	-	9678	0.02545
-	-	4165.0	0.035461	-	-	10578	0.02488
-	-	4304.7	0.034042	-	-	11309	0.02448
-	-	4674.0	0.031795	-	-	12034	0.02412
-	-	5067.5	0.030316	-	-	12632	0.02387
-	-	5820.2	0.028561	-	-	-	-
-	-	6595.7	0.027401	-	-	-	-
-	-	7332.9	0.026603	-	-	-	-

t = 751.48		t = 752.00		t = 770.00	
Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb	Pressure, psia	Specific Volume, ft^3/lb
1192	0.5337	1012	0.6576	2389.4	0.22924
1922.2	0.2975	2102.1	0.2640	2913.2	0.16867
2732.6	0.1772	3106.1	0.1394	3267.7	0.13690
3467.2	0.1091	3323.2	0.1206	3610.8	0.11117
-	0.1323	3619.4	0.09672	3898.6	0.091889
4889.9	0.03521	3910.2	0.0737	4121.8	0.077598
5260.4	0.03119	4175.8	0.05478	4273.6	0.068930
6584.7	0.02885	4211.0	0.05211	4435.9	0.059833
7763	0.02715	4433.9	0.04278	4571.4	0.053413
9195	0.02581	4545.1	0.04001	4710.9	0.048302
10727	0.02480	4876.5	0.03564	4849.8	0.044489
12187	0.02406	5244.0	0.03311	5024.8	0.040888
13553	0.02350	5619.0	0.03143	5357.4	0.036709
-	-	6014.9	0.03023	5816.1	0.033565
-	-	6335.0	0.02947	6492.3	0.030906
-	-	6715.6	0.02879	7184.1	0.029264
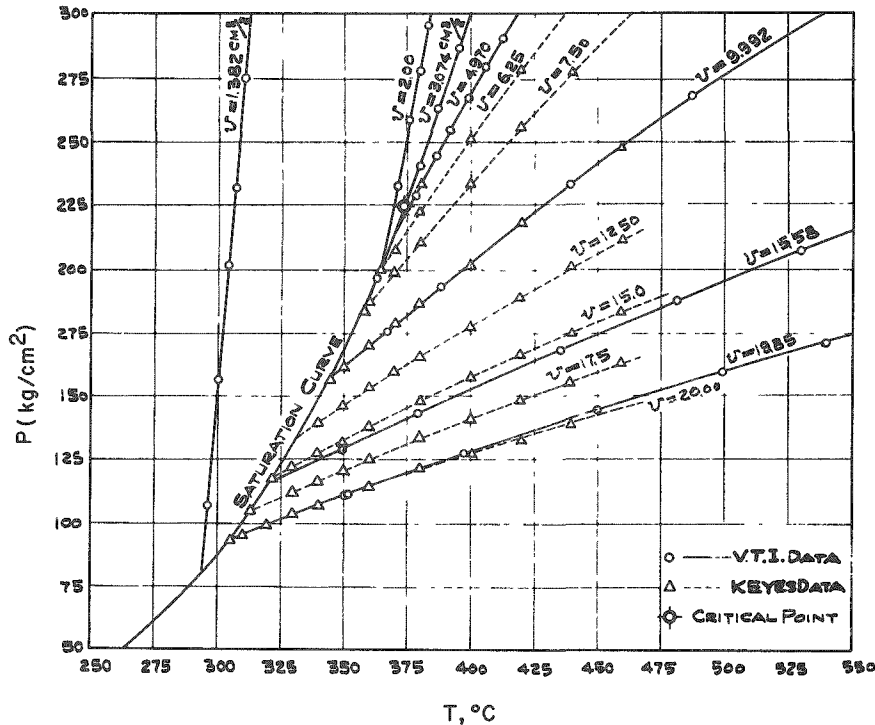
Figure 8. Isometrics of V.T.I.[51] and Keyes, et al.,[32] for Superheated Steam in the Critical Region.

C. Specific Volumes Derived from Enthalpy Measurements

In 1929 Callendar measured the enthalpy of superheated water vapor for pressures up to 4000 psia (280 kg/cm^2) and for temperatures up to about 750°F (400°C). His derived values are not of utility since they did not fall in the region under investigation.

In 1936 Havlicek and Miskovsky[50] reported measurements of enthalpy and specific heat for water vapor in the critical region. They derived pressure-volume-temperature data by starting with the following thermodynamic relation:

$$\left(\frac{\partial h}{\partial P}\right)_T = -\frac{T^2}{AP}\frac{\partial}{\partial T}\left(\frac{PV_{sp}}{T}\right)_P \tag{17}$$

where

h = enthalpy per unit mass of material,
P = pressure,
T = absolute temperature,
V_{sp} = volume per unit mass, and
A = mechanical equivalent of heat.

Havlicek and Miskovsky derived the following from Eq. (17) for changes in state that occur under constant pressure process:

$$\frac{V^*_{sp,1} - V_{sp,1}}{RT_1} - \frac{V^*_{sp,2} - V_{sp,2}}{RT_2} = -\frac{1}{AR} \int_{T_1}^{T_2} \frac{1}{T^2} \left(\frac{\partial h}{\partial P}\right)_T dT \quad , \quad (18)$$

where

V^*_{sp} = specific volume computed from perfect gas law
V_{sp} = actual specific volume
R = gas constant
1   is the known condition and
2   is the unknown condition to be evaluated.

The specific volume data in the critical region derived by Havlicek and Miskovsky from their enthalpy measurements by means of Eq. (18) are given in Table 28. In their calculations they assumed that the specific volume along the 752°F (400°C) isotherm were known. Specifically, Havlicek and Miskovsky chose values of specific volume along the 752°F isotherm which were interpolated from the 1932 Keyes data.[55] They imply that a functional relationship was developed for $(1/T^2)(\partial h/\partial P)_T$ from their enthalpy measurements. Unfortunately, this relationship was not given in their paper.

TABLE 28

Specific Volumes in the Critical Region Derived from
Enthalpy Measurements by Havlicek and Miskovsky [50]

Pressure, psia	2986.91	3129.15	3200	3271.38	3413.62
Temperature,°F	Specific Volume, ft³/lb				
698	0.09598	0.03298	0.03229	0.03165	0.03080
703.4	0.1056	–	0.03639	0.03414	0.03239
707	0.1106	0.09050	0.07638	0.03812	0.03420
712.4	0.1173	0.1006	0.09086	0.07897	0.04013
716	0.1212	0.1056	0.09715	0.08759	0.05909
719.6	0.1249	0.1100	0.1022	0.09380	0.07309
725.0	0.1300	0.1158	0.1085	0.1008	0.08408
734	0.1377	0.1242	0.1172	0.1104	0.09609
752	0.1509	0.1378	0.1316	0.1254	0.1126

Keenan and Keyes[1] used the following formula to compute the enthalpy of steam in the critical region:

$$h = 477 - \frac{859.5 \times 10^4}{P} + \frac{14,220\,t}{P} + \delta \tag{19}$$

where

    h is the enthalpy in BTU/lb,
    P is the pressure in psia,
    t is the temperature in °F, and
    δ is a graphically formulated function of P and t.

The enthalpies used in their formulation were essentially the measurements of Havlicek and Miskovsky. Values for specific volume in the critical region, i.e., less than 0.16 ft³/lb (10 cm³/g), were derived from the following relation:

$$\left(\frac{V_{sp}}{T}\right) = \int \left(\frac{h}{P}\right)_T \; d\left(\frac{1}{T}\right) \;\; , \tag{20}$$

where

    V_{sp} is the specific volume, and T the absolute temperature. The integrand was evaluated using Eq. (19).

D. Values of Pressure-Volume-Temperature in Various Steam Tables

The values adopted for specific volumes less than 0.16 ft³/lb (10 cm³/g) at the Third International Conference[10] were derived by interpolating the measurements of Keyes, Smith and Gerry.[32] Values for specific volumes greater than 0.16 ft³/lb were those obtained from the Keyes, Smith and Gerry equation of state.

It was stated previously that values in the 1951 Vukalovich tables were computed from an equation of state which was based on the values adopted at the Third International Conference. However, the values listed for water vapor in the supercritical region below 770°F (410°C) were derived by means of a combined analytical and graphical technique. Although no reference is made of the experimental values used for this purpose it appears that the measurements of Keyes, Smith and Gerry and Kirillin et al., were relied upon.

A combined analytical and graphical technique was used to obtain values listed for the specific volumes in the critical region in the 1952 Timroth tables.[4] It is thought that the observed isometrics of Timroth[37]

from 2 to about 7 cm^3/g were used for this purpose. It is interesting to note that two equations of state were given in the 1952 Timroth tables. The first equation describes the whole range of parameters covered by the tables with the exception of those near the saturation line and the critical region. The second equation describes the region near the saturation line as well as the supercritical region. Both equations were based on the specific heat determinations of German[56,57] and Russian[51] investigators.

The Faxen table values were computed by means of the equation of state suggested by Juza.[58] Juza derived the equation from calorimetric measurements made in Germany[56,57] England,[59] and Czechoslovakia[50], and from volume measurements made in the United States.[32] No mention was made by Faxen for the basis of the values for superheated vapor in the critical region.

The equation of state by Tanishita[60] was used to compute the values listed for superheated vapor in the 1955 J.S.M.E. tables.[6] In the critical region, values were derived by a graphical technique from the Third International Steam Table Conference[10] values.

The values listed in the 1956 V.D.I. tables[8] were taken from the 1952 Timroth tables.[4]

Values from the various steam tables are given in Tables 29 to 34. A graphical comparison is given in Figure 6. Solid lines were drawn through the Keenan and Keyes values[1] while broken lines were drawn through the 1952 Timroth values.[4]

The figure emphasizes the lack of smoothed values of specific volumes at sufficiently close intervals in the critical region. Furthermore, appreciable differences exist between the values given in the various steam tables for temperatures up to about 752°F (400°C).

E. Summary

(1) With the exception of the 1952 Timroth tables[4] the values given in the various steam tables were derived from the calorimetric experiments conducted in Germany,[56,57] England,[59] and Czechoslovakia[50] and volume measurements conducted in the United States.[32]

(2) Even though experimental measurements were made in the critical region, very little specific volume data for this region are given in the various steam tables.

(3) There are appreciable differences between the specific volume data given in the various tables for temperatures up to about 752°F (400°C) (see Figure 6).

(4) In the critical region the values of pressure-volume-temperature for superheated water vapor given in the various steam tables were derived by graphical methods.

TABLE 29

Pressure-Volume-Temperature for Subcooled Water and Superheated Vapor in the Critical Region from 1952 Timroth Tables[4]

Pressure, psia	2560	2631	2702	2774	2845	2987	3129
Temperature, °F	Specific Volume, ft³/lb						
662	-	-	-	-	-	-	-
680	0.1387	0.1264	0.1124	-	-	-	-
698	0.1585	0.1488	0.1390	0.1293	0.1193	0.0956	-
716	-	-	-	0.1474	0.1394	0.1227	0.1059
734	-	-	-	-	-	0.1386	0.1246
752	-	-	-	-	-	-	0.1373

Pressure, psia	3271	3414	3556	3648	3840	3983
Temperature, °F	Specific Volume, ft³/lb					
662	0.02600	0.02580	0.0256	0.02547	0.02532	0.02516
680	0.02771	0.02737	0.02707	0.02683	0.02659	0.02637
698	0.03165	0.03050	0.02976	0,02922	0.02875	0.02834
716	0.0873	0.0586	0.03812	0.03476	0.03300	0.03188
734	0.1105	0.0963	0.08201	0.06712	0.05126	0.04117
752	0.1249	0.1132	0.1017	0.09018	0.07897	0.06808
770	0.1365	0.1253	0.1147	0.1046	0.09547	0.08634
788	-	0.1355	0.1253	0.1160	0.1075	0.09915
806	-	-	0.1347	0.1257	0.1173	0.1094
824	-	-	-	0.1344	0.1259	0.1182
842	-	-	-	-	0.1338	0.1261

TABLE 30

Pressure-Volume-Temperature for Subcooled Water and Superheated Vapor
in the Critical Region from the 1951 Vukalovich Tables[2]

Pressure, psia	2560	2631	2702	2774	2845	2987	3129
Temperature, °F	Specific Volume, ft³/lb						
680	0.138	0.126	0.112	-	-	-	-
698	0.159	0.149	0.139	0.129	0.119	0.0956	-
716	-	0.1643	0.156	0.147	0.139	0.123	0.106
734	-	-	0.1688	0.1610	0.1534	0.139	0.125
752	-	-	-	0.1728	0.1655	0.152	0.138
770	-	-	-	-	0.1759	0.1621	0.149
788	-	-	-	-	-	0.1716	0.1589
806	-	-	-	-	-	-	0.1677

Pressure, psia	3271	3414	3556	3698	3840	3983
Temperature, °F	Specific Volume, ft³/lb					
662	0.02609	0.02590	0.02573	0.02557	0.02542	0.02526
680	0.02792	0.02758	0.02728	0.02704	0.02680	0.02657
698	0.03165	0.03066	0.02992	0.02938	0.02891	0.02850
716	0.0873	0.0593	0.0376	0.0348	0.0341	0.0324
734	0.111	0.0966	0.0822	0.0671	0.0556	0.0412
752	0.125	0.113	0.102	0.0905	0.0796	0.0687
770	0.137	0.126	0.115	0.105	0.0953	0.0859
788	0.147	0.136	0.126	0.116	0.107	0.0984
806	0.156	0.145	0.135	0.126	0.117	0.109
824	-	0.154	0.144	0.134	0.125	0.117
842	-	-	0.151	0.142	0.133	0.125

TABLE 31

Pressure-Volume-Temperature for Subcooled Water and Superheated Vapor
in the Critical Region According to Holser and Kennedy [46]

Pressure, psia	2900.8	3626.0
Temperature, °F	Specific Volume, ft³/lb	
680	0.02923	0.02718
716	0.1323	0.03611
752	0.1597	0.09701

TABLE 32

Pressure-Volume-Temperature for Subcooled Water and Superheated Vapor
in the Critical Region from 1953 Faxen Tables[7]

Pressure, psia	2765	2828	2901	3046	3191	3336	3481
Temperature, °F	Specific Volume, ft³/lb						
680	0.02984	0.02951	0.02918	0.02866	0.02822	0.02782	0.02745
698	0.1318	0.1217	0.1112	0.08778	0.03247	0.03133	0.03039
716	–	–	0.1325	0.1156	0.09803	0.07609	0.04434
734	–	–	–	0.1326	0.1184	0.1044	0.08938
752	–	–	–	–	0.1323	0.1200	0.1084
770	–	–	–	–	–	0.1320	0.1209
788	–	–	–	–	–	–	0.1317

Pressure, psia	3626	3771	3916
Temperature, °F	Specific Volume, ft³/lb		
680	0.02715	0.02686	0.02659
698	0.02967	0.02907	0.02862
716	0.03836	0.03511	0.03309
734	0.07496	0.06055	0.04998
752	0.09627	0.08441	0.07272
770	0.1105	0.1004	0.09066
788	0.1213	0.1118	0.1027

TABLE 33

Pressure-Volume-Temperature for Subcooled Water and Superheated Vapor
in the Critical Region from 1955 J.S.M.E. Tables [6]

Pressure, psia	2792	2845	2987	3129	3271	3414	3556	3698
Temperature, °F	Specific Volume, ft³/lb							
680	0.1123	0.0295	0.0288	0.0283	0.0279	0.0276	0.0273	0.0271
698	–	0.1189	0.0948	0.0338	0.0319	0.0307	0.0300	0.0294
716	–	–	0.1221	0.1062	0.0873	0.0601	0.0412	0.0360
734	–	–	–	0.1248	0.1107	0.0963	0.0820	0.0671
752	–	–	–	–	0.1253	0.1134	0.1020	0.0907
770	–	–	–	–	–	0.1257	0.1152	0.1051
788	–	–	–	–	–	–	0.1262	0.1166
806	–	–	–	–	–	–	–	0.1264

TABLE 34

Values of Pressure-Volume-Temperature for Subcooled Water and
Superheated Water Vapor from Keenan and Keyes Steam Tables[1]

Temperature, °F	680	690	700	705.4	710	720	730	740
Pressure, psia	Specific Volume, ft³/lb							
2700	0.1137	0.1299	0.1416	–	–	0.1592	–	0.1732
2800	–	0.1141	0.1281	–	0.1387	0.1475	0.1533	0.1622
2900	–	–	0.1143	–	0.1266	0.1362	0.1444	0.1617
3000	0.0288	0.0311	0.0984	–	0.1142	0.1251	0.1339	0.1416
3100	–	–	–	–	0.1012	0.1140	0.1238	0.1320
3200	–	–	–	–	0.0852	0.1027	0.1138	0.1226
3206.2	0.0281	0.0298	0.0334	0.0503	0.0843	0.1020	0.1132	0.1220
3300	–	0.0293	0.0320	–	0.0545	0.0905	0.1037	0.1134
3400	–	0.0290	0.0312	–	0.0363	0.0773	0.0935	0.1042
3500	0.0274	0.0287	0.0306	0.0322	0.0342	0.0557	0.0823	0.0952
3600	–	0.0285	0.0301	–	0.0329	0.0410	0.0701	0.0860
3700	–	0.0282	0.0297	–	0.0320	0.0371	0.0557	0.0764
3800	–	0.0279	0.0293	–	0.0313	0.0349	0.0450	0.0664
3900	–	0.0277	0.0290	–	0.0308	0.0337	0.0400	0.0558
4000	0.0265	0.0275	0.0287	0.0295	0.0303	0.0328	0.0373	0.0478

Temperature, °F	750	760	770	780	790	800	820	840
Pressure, psia	Specific Volume, ft³/lb							
2700	–	0.1853	–	0.1960	–	0.2059	0.2150	0.2235
2800	0.1686	0.1745	0.1801	0.1854	0.1904	0.1953	0.2043	0.2128
2900	0.1583	0.1644	0.1701	0.1754	0.1805	0.1853	0.1944	0.2028
3000	0.1485	0.1548	0.1606	0.1660	0.1711	0.1760	0.1851	0.1935
3100	0.1391	0.1456	0.1516	0.1571	0.1623	0.1672	0.1763	0.1847
3200	0.1301	0.1369	0.1430	0.1486	0.1539	0.1589	0.1681	0.1765
3206.2	0.1295	0.1363	0.1424	0.1480	0.1533	0.1583	0.1676	0.1760
3300	0.1215	0.1285	0.1348	0.1406	0.1459	0.1510	0.1602	0.1687
3400	0.1129	0.1204	0.1270	0.1329	0.1384	0.1435	0.1529	0.1613
3500	0.1047	0.1126	0.1195	0.1256	0.1312	0.1364	0.1458	0.1543
3600	0.0965	0.1049	0.1121	0.1185	0.1243	0.1296	0.1392	0.1477
3700	0.0885	0.0975	0.1051	0.1117	0.1177	0.1231	0.1328	0.1414
3800	0.0804	0.0903	0.0983	0.1052	0.1113	0.1169	0.1268	0.1354
3900	0.0721	0.0832	0.0917	0.0989	0.1052	0.1109	0.1210	0.1297
4000	0.0638	0.0761	0.0852	0.0927	0.0993	0.1052	0.1155	0.1243

V. RECOMMENDED VALUES OF PRESSURE-VOLUME-TEMPERATURE FOR WATER AND WATER VAPOR IN THE CRITICAL REGION

A. General

In Sections III and IV it was concluded that there were a lack of smoothed data at sufficiently close intervals in the critical region. Furthermore, it was shown in Figure 6, a graphical representation of previous smoothed data, that there were appreciable differences in the data. In view of this an attempt has been made in this thesis to derive data from the various measurements cited and compiled in Sections III and IV.

The water molecule possess a permanent dipole. As a consequence, the behavior of water is very complicated, especially in the critical region. In view of this, graphical techniques have been used in this thesis to derive new P-V-T values in the critical region.

One reason for the lack of smoothed data is that properties in the critical region change rapidly, making it difficult to maintain precision in analysis. Figure 6 indicates that there are marked changes in the slopes of isotherms up to about 730°F. From only a pressure-volume plot it would indeed by very difficult to interpolate accurately between the experimental results of various investigators.

The graphical method used in this thesis to interpolate between measurements consisted of plotting the product of pressure and specific volume (PV_{sp}) against the specific volume (V_{sp}) with temperature as a parameter. A horizontal line would result if PV_{sp} were plotted against V_{sp} at constant temperature for a gas obeying the perfect gas law. For water vapor a plot of this type would yield slightly curved inclined lines. The analysis with results obtained for water and water vapor will now be discussed.

B. Derived Data for Pressure-Volume-Temperature

The experimental measurements of specific volume by Keyes et al.,[32] Kirillin et al.,[53,54] and values obtained from calorimetric measurements by Havlicek and Miskovsky[50] and Osborne et al.,[35] were used to derive new data. These values were plotted accurately to a few parts in ten thousand and smooth curves were drawn through the points, as shown in Figure 9. It was thought by the writers that the experimental values chosen were the most consistent.

At 716°F one may note the excellent agreement between the values of Keyes et al., Havlicek and Miskovsky, and Kirillin et al., and the corresponding smooth curve. Figure 9 illustrates the care taken to make the
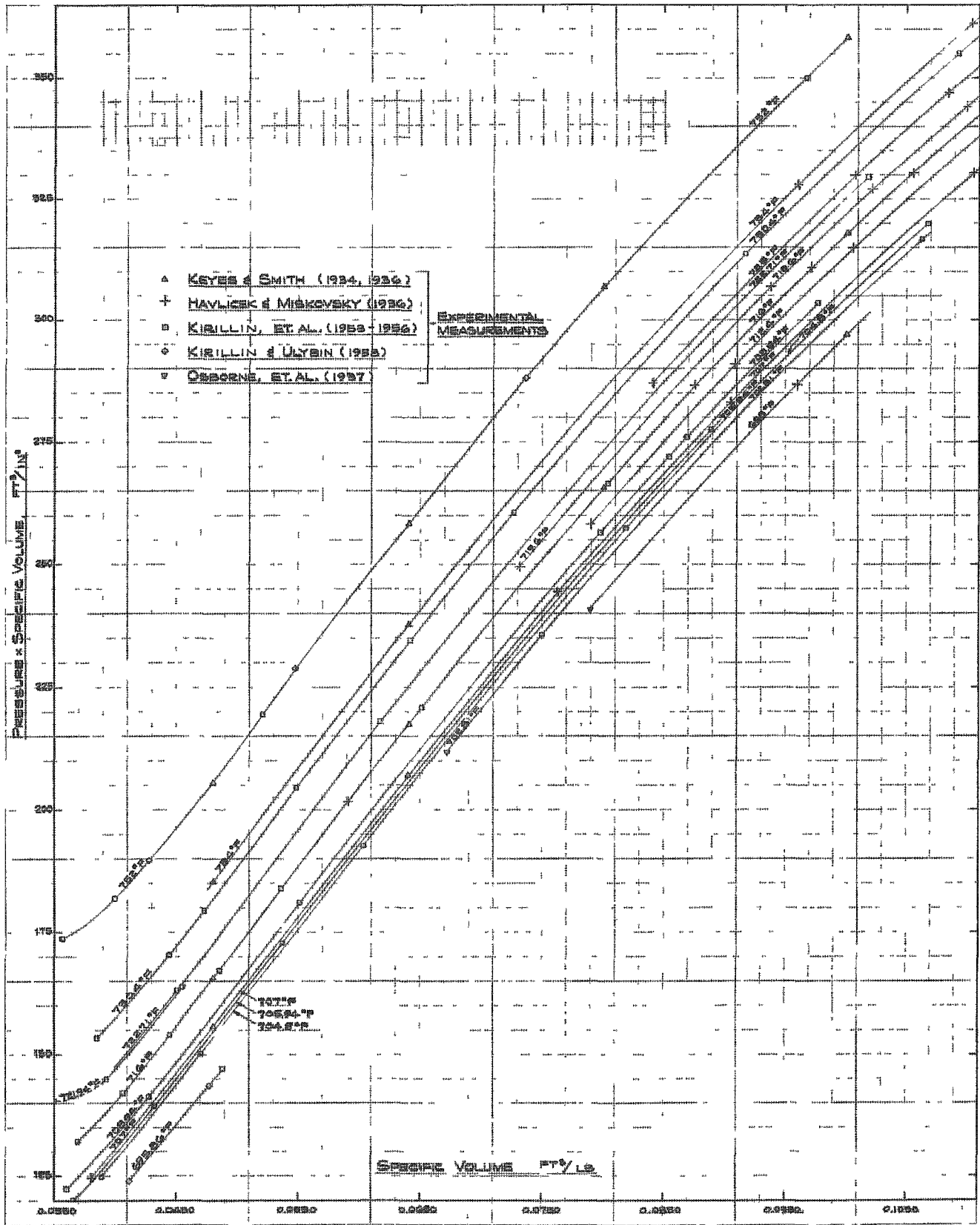
58

FIG. 9   PV$_{SP}$–V$_{SP}$ ISOTHERMS IN THE CRITICAL REGION

lines pass through all of the experimental values. It may be concluded that there is excellent agreement between all the measurements shown in Figure 9. This is noteworthy since the measurements of Keyes et al., and of Havlicek and Miskovsky were conducted some twenty years ago.

In Section IV appreciable differences were noted between the data given in the various steam tables for the specific volume of steam in the critical region. In view of the good agreement between the various sets of experimental measurements as illustrated by Figure 9 the reason for previous inconsistencies is due to the choice of different "smoothing" methods and not errors in experimental measurements, as has been suggested by Timroth and Vargaftik[51] and by other investigators from time to time.

Values of the product of pressure and volume (PV_{sp}) were read from the isotherms shown in Figure 9. The calculated pressures and specific volumes obtained from the $PV_{sp} - V_{sp}$ isotherms are shown in Figure 10. Smooth curves were drawn through those values. One may note the excellent agreement between the various experimental measurements and our smoothed curves. The enlargement of Figure 10 gives an indication of the relative accuracy by which computed values represent the various experimental measurements

Pressures computed from Figure 9 were next plotted against temperature for constant specific volume, and some of these are shown in Figure 11 to illustrate the temperature dependence. For the range of pressures and temperatures shown it is interesting to note that for specific volumes between 0.045 and 0.060 ft^3/lb the isometrics are linear. For specific volumes outside this range the isometrics are nonlinear. A similar conclusion regarding the linearity of isometrics in the critical region was made by Timroth[39] in 1950 and by Kirillin[52] in 1955.

Figure 11 indicates the very good agreement between the data obtained from the various experimental isotherms of different investigators. The values of Kirillin for the temperature of 730.4°F and for specific volumes between 0.040 and 0 051 ft^3/lb are evidently in error, since they are not consistent with computed pressures obtained from the other isotherms of Figure 9. For the range shown in Figure 10 it was concluded that Kirillin's determinations of pressure between 3750 and 3950 psia are too high by as much as 30 psi along the 730.4°F isotherm.

Values read from Figure 11 for temperatures from 702 to 752°F were plotted on a pressure-volume diagram shown in Figure 12. It was possible to draw smooth curves through all of these values. In general, it is estimated that the deviation in pressure from the smoothed curve
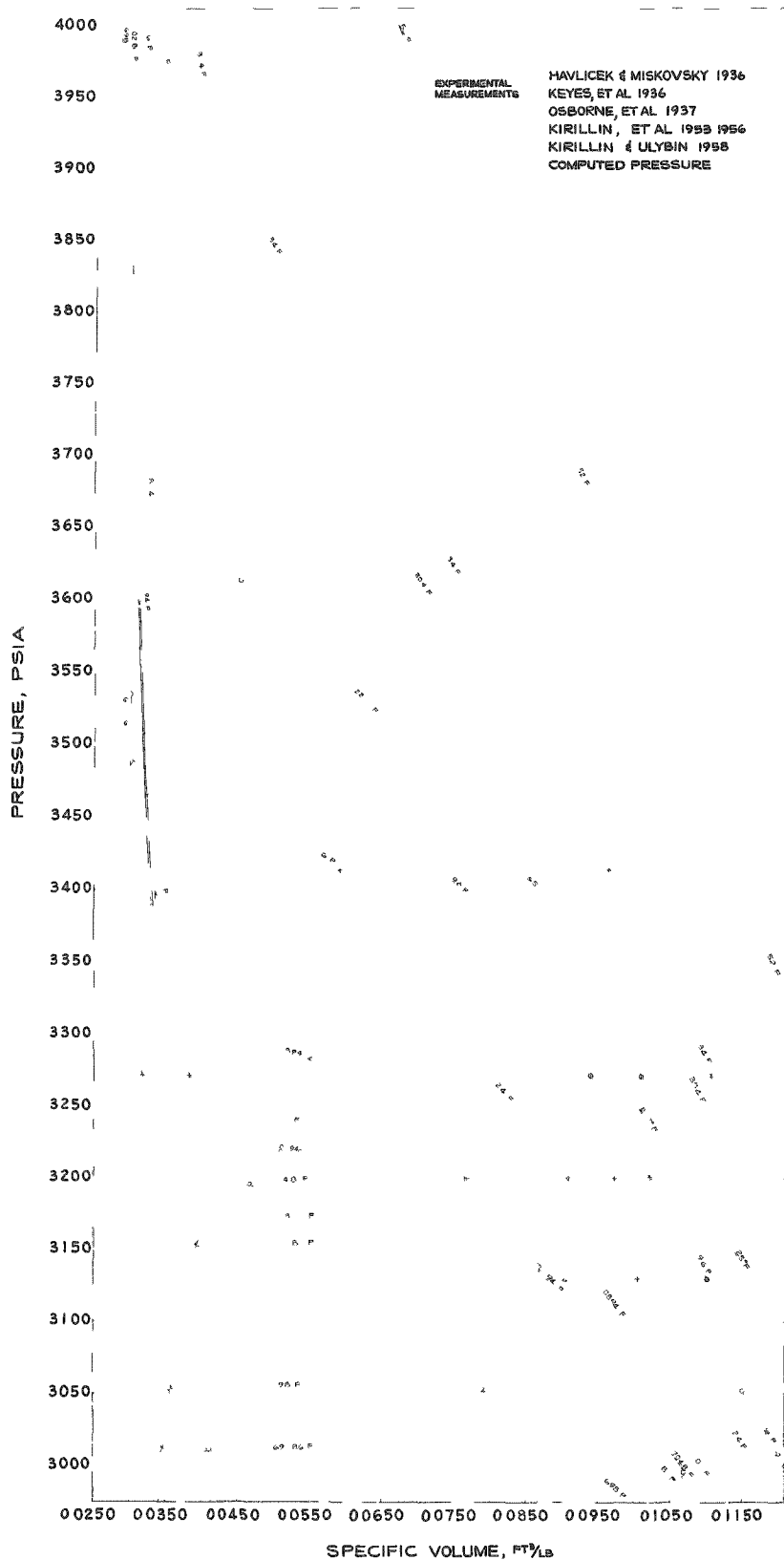
FIG 10   ISOTHERMS IN THE CRITICAL REGION
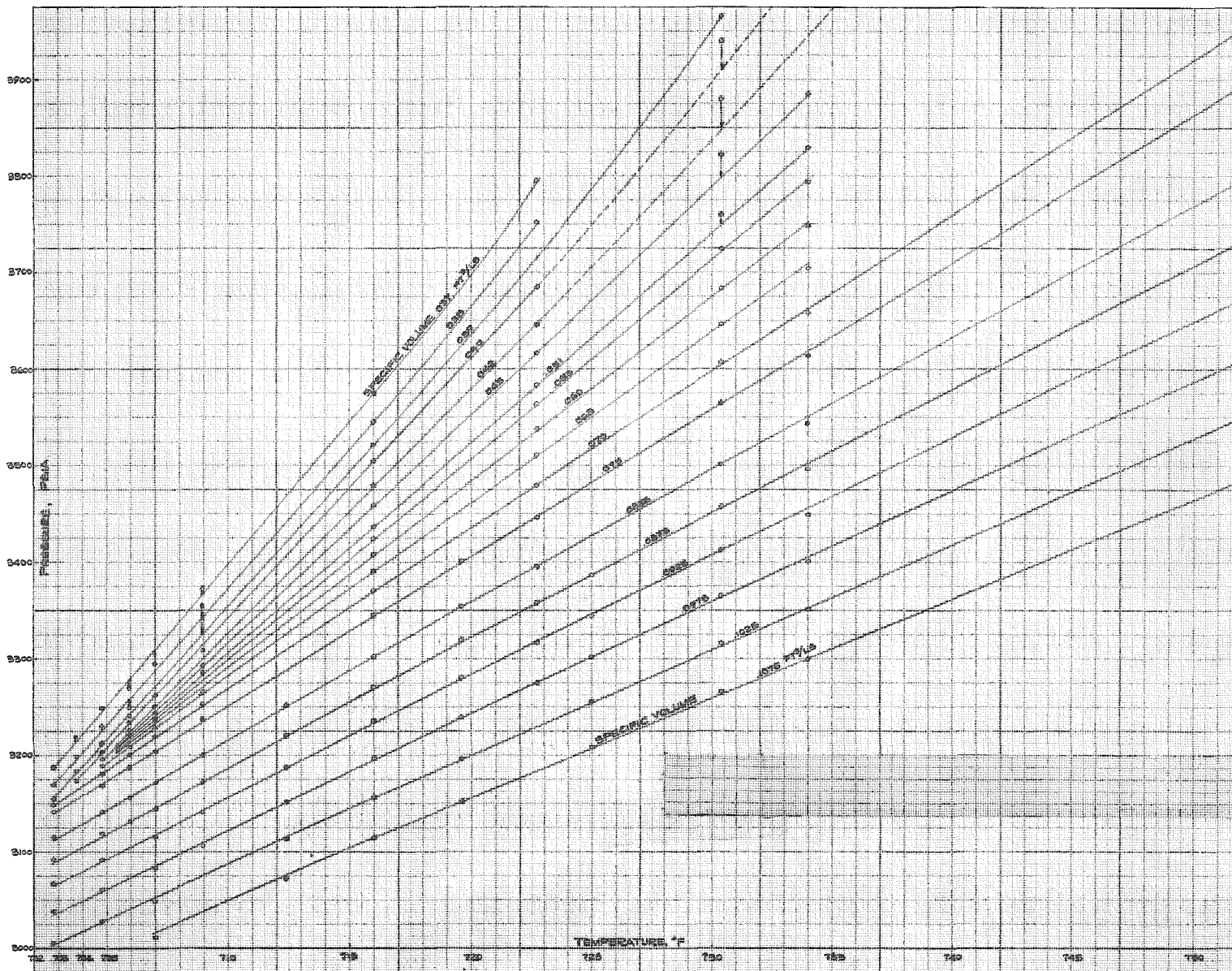
FIG. II ISOMETRICS IN THE CRITICAL REGION BASED ON GRAPHICALLY SMOOTHED DATA
OF VARIOUS INVESTIGATORS

PRESSURE, PSIA

SPECIFIC VOLUME, FT³/LB

CRITICAL POINT
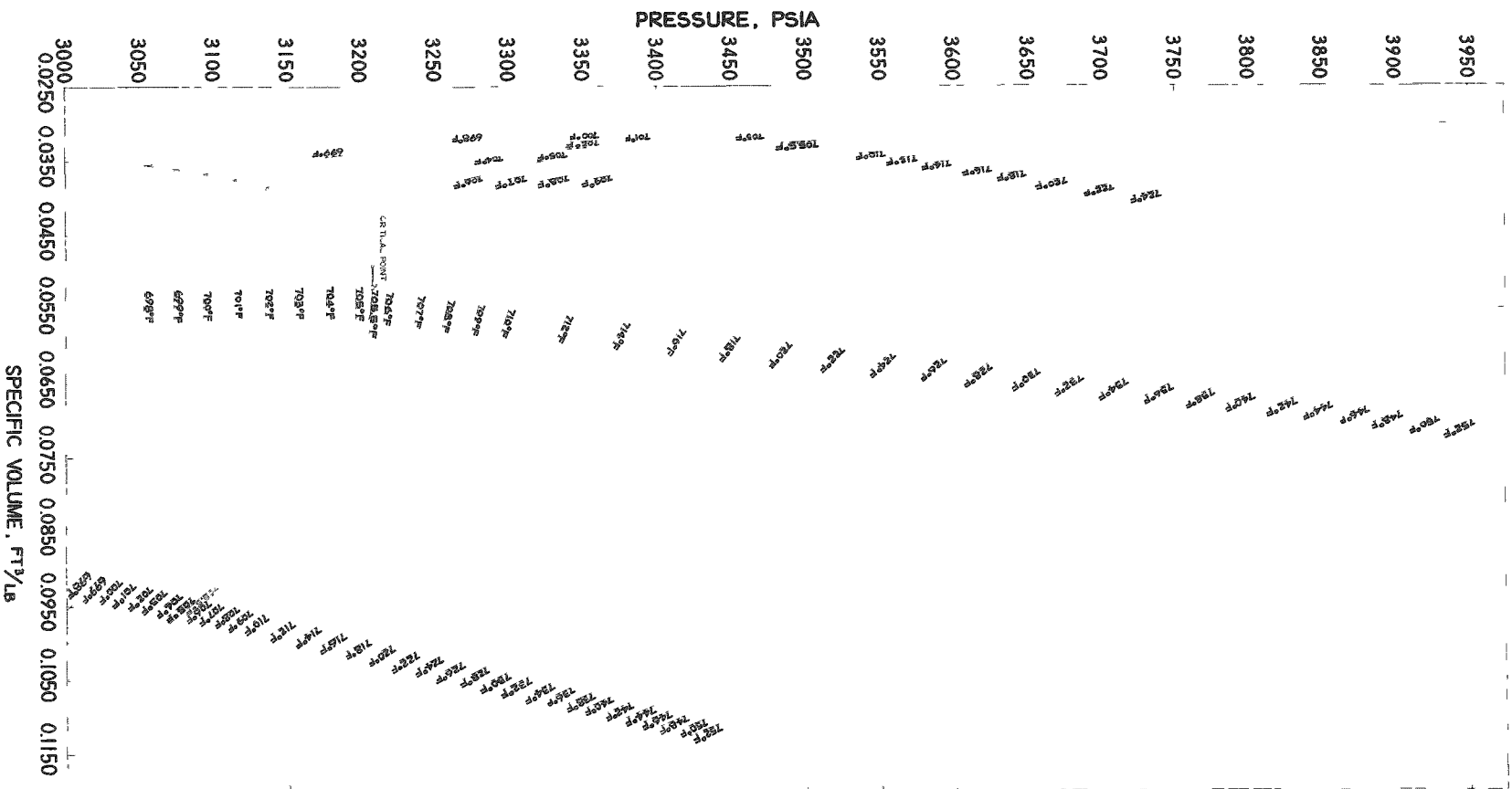
FIG. 12 SMOOTHED P-Vsp ISOTHERMS IN THE CRITICAL REGION FOR WATER AND WATER VAPOR

amounted to about 5 parts in ten thousand; however, in the subcooled liquid regions and for specific volumes less than 0.040 ft³/lb the uncertainty in pressure may be some 20 parts in ten thousand.

A discussion on the critical data for water derived from Figures 11 and 12 is given in the next section.

C. Summary

(1)   There is excellent agreement between the experimental values of pressure-volume-temperature of Keyes et al.,[32] Havlicek and Miskovsky,[50] and Kirillin et al.[52] for temperatures between 696 and 752°F, for pressures between 3000 and 4000 psia and for specific volumes between 0.03 and 0.12 ft³/lb.

(2)   The experimental determination of pressure along the 730.4°F isotherm made by Kirillin appear to be too high by as much as 30 psi for pressures from about 3750 to 3950 psia.

(3)   For the first time a graphical tabulation at close intervals of pressure-volume-temperature has been made possible for water vapor in the critical region by utilizing graphical techniques and the measurements of Keyes et al.,[32] Havlicek and Miskovsky,[50] Osborne et al.,[35] and Kirillin et al.[52-54]

(4)   The discrepancies between the pressure-volume-temperature data of various steam tables are due to the use of inexact interpolation techniques or of inaccurate equations of state and not due to errors in the measurements.

VI. THE CRITICAL POINT

A. General Studies

Many of the early investigations of critical phenomena in the last century were reviewed by Preston [61] The phenomena was first observed by la Tour in 1822. His apparatus consisted of a bent sealed tube. A sample of water was contained in one arm while air to indicate the pressure was contained in another arm. Mercury which separated the air and water, transmitted the pressure from the water in one arm to the air in the other arm. A value of 688°F (362°C) was obtained for the critical temperature of water. One of the reasons given for the low value is that a foreign substance was added to water to retard the leaching attack on the glass. The effect of mercury was not taken into account.

In 1881 Cailletet and Hautefeuille, and Hannay conducted investigations with carbon dioxide Cailletet and Hautefeuille concluded from their experiments that there existed two phases above the critical point, while Hannay concluded that only one phase existed Preston[61] was of the opinion that none of these experiments proved or disproved the simultaneous existence of two phases above the critical point. Preston stated that all of the measurements made up to that time showed that, as the critical temperature and pressure were approached, the density of the liquid approached the density of the vapor

Several noteworthy experiments on the critical point were subsequently carried out with precision and care H. L. Callendar[62] measured the pressure-volume-temperature relations of saturated water in the vicinity of the critical point. His experiments showed that the density of "saturated water" was about twice that of "saturated vapor" at the temperature where the meniscus disappeared, i.e , at 705.2°F (374°C). He further observed that the density of the vapor became equal to the density of the liquid at 717°F (380 5°C) and 3650 psia (257 kg/cm^2), which is considerably different from the modern day values of 705.5°F (374.15°C) and 3210 psia (225.65 kg/cm^2)

From his volume experiments Callendar postulated that the region between 705 2° and 717°F was unstable He considered that the water vapor in his experiments was very pure, containing air in the proportion of only 1 part out of 10^9 by volume. Callendar was of the opinion that an appreciable amount of impurity in the water vapor would obliterate the unstable region.

In 1929 H. L. Callendar[13] reported on calorimetric experiments which were conducted to investigate the effect of air and other impurities on the equilibrium between water vapor and water in the critical region. Specifically, he made enthalpy measurements in the "unstable" region

along the 709.6°F and 711.5°F isotherms with water vapor containing about 3 parts in 10^5 by weight of air. He stated that during "condensation" in the unstable region the pressure did not remain constant but increased uniformly. It should be pointed out, however, that trends in the measured isotherms would be identical to that for air-free water vapor in the region now accepted as supercritical.

Unfortunately, Callendar made no mention of measurements of enthalpy on air-free water vapor in the "unstable" region. It appears to the writer that he made the conjecture that the isotherms from 705.2° to 717°F (374° to 380°C) for pure water vapor would have a vertical flat segment between the two "saturation lines" on a enthalpy pressure diagram. Therefore, it is to be concluded that Callendar's conjecture is not valid, since he was not wholly justified in attributing the measured uniform increase of pressure in the unstable region solely to air in the water vapor.

Callendar estimated that his temperature measurements were accurate to about 0.01°C (0.018°F) and that his pressure measurements were accurate to about 0.02%. If these estimates are correct, the accuracy is excellent even when compared to modern standards of measurements. However, it appears that, since the measured values of enthalpy made by Callendar are not consistent with those in the Keenan and Keyes tables,[1] the air may have been contained in the water vapor in a larger proportion than estimated.

Similar conclusions regarding Callendar's work had been made some thirty years ago. Jakob[63] reviewed the work of Callendar and concluded that "Callendar stands absolutely on his own feet - that is to say, he personally measured practically all of the properties in question and also worked them out theoretically." However, Jakob recorded the following objections of Davis and Keenan[64] to the deductions made by Callendar:

> It may be mentioned that the group of Callendar's points.. ..constitute the only experimental basis yet adduced for his startling suggestion that two miscible phases persist at temperatures above what is commonly regarded as the critical point. It seems to us that this group of points while valuable is not characterized by a high enough precision to enable anyone to distinguish by means of them, between an isothermal with a flat segment $[(\partial P/\partial v)_T = 0]$ and the very slightly curved isothermal $[(\partial P/\partial v)_T < 0]$ which the accepted theory would predict in this region. Furthermore, the apparent existence of true latent heat in accordance with the Callendar suggestion and the existence of very large specific heats in this region as required by classical critical point theory, would be from the experimental point of view, two pictures so nearly identical in every observable respect as to be indistinguishable. Indeed we doubt if any possible measurements of either

specific volumes or latent total heats and of pressure along any isothermal in this region would be expected to distinguish between these two theories. We therefore see no reason for abandoning the traditional point of view as to what happens at the critical point.

Experiments subsequently carried out by Havlicek and Miskovsky,[50] G. S. Callendar and Egerton,[23] and Koch[65] showed that only one phase existed above the critical point.

It was mentioned in Section 1 that most properties of water and water vapor change rapidly in the immediate vicinity of the critical point. Rossini[66] and Hirschfelder, Curtiss and Bird[67] give accounts of investigations on the critical point. These investigations showed that certain properties change very rapidly with a few hundredths of a degree of the critical point. For instance, Wentorf[68] measured the pressure and volume along isothermals in the critical region of carbon dioxide at temperature intervals of 0.02°C. His measurements indicate that within a few hundredths of a degree of the critical point the specific volume along the saturation line changes by about 10%.

B. Critical Data for Water

The methods and results of various investigations conducted in the past twenty years to evaluate the critical constants for water will now be reviewed. Table 35 summarizes values for the critical constants of water.

TABLE 35

Critical Data for Water as Obtained by Various Investigators

No.	Investigator(s) and Date	Reference	Pressure		Specific Volume		Temperature	
			psia	kg/cm²	ft³/lb	cm³/g	°F	°C
1	Havlicek and Miskovsky, 1936	50	Between 3200 and 3225	Between 225 and 227	-	-	706	374.5
2	Smith, Keyes and Gerry, 1936	32	3206.2	225.41	0.0512	3.1975	Between 705.4 and 705.6	Between 374.11 and 374.21
3	Keenan and Keyes, 1936	1	3206.2	225.41	0.0504	3.15	705.4	374.11
4	Osborne, et al., 1937	35	3209.5	225.65	0.05	3.1	705.5	374.15
5	Timroth, 1952	4	3209.5	225.65	0.0529	3.3	705.5	374.15
6	Kirillin, 1955	52	3209.5	225.65	0.0529	3.3	705.5	374.15
7	This Report, 1959	-	3208	225.54	0.0525	3.28	705.5	374.15

Havlicek and Miskovsky[50] concluded from their measurements of enthalpy and specific heat that the critical pressure lies between 3200 and 3225 psia (225 and 227 kg/cm^2). They found that the enthalpy of vaporization was zero for temperatures greater than 706°F (374.5°C).

Smith, Keyes and Gerry[32] derived values for the critical constants of water by graphically observing the trends in the isotherms in the critical region. No basis is given for the somewhat lower value listed for the critical volume in the Keenan and Keyes steam tables.[1]

The method used by Osborne et al.[35] to derive the critical constants of water was not given. However, it appears that the constants were evaluated from their saturation pressure[24] and calorimetric[35] measurements.

Timroth[4] and Kirillin et al.[52] used identical methods to derive the critical volume for water from their pressure-volume-temperature measurements. The method used by them is based on the fact that the change of saturation pressure with temperature, $(dP/dT)_{P_c, T_c}$, is identical to $(\partial P/\partial T)_{V crit}$. They assumed that the isometrics in the critical region were linear over a limited range of pressures and temperatures and thus were able to evaluate the relationship between the slopes of the isometrics and the specific volume. Both Timroth and Kirillin obtained a value of 0 0528 ft^2/lb for the critical volume of water. A value of 21.3 psia/°R for $(dP/dT)_{P_c, T_c}$ was used by Kirillin et al. and by Timroth. This was obtained by the differentiation and evaluation of Eq (4) at the critical point. Both used values for T_c and P_c which were identical to those derived by Osborne et al.[35]

It was stated in the previous section that the isometrics shown in Figure 11 ranging from 0 045 to 0 060 ft^2/lb were linear. Since the values for the critical volume derived by other investigators fall somewhere between 0.045 and 0.060 ft^3/lb, it may be concluded that the critical isometric is linear for the range of pressures and temperatures of Figure 11. The value obtained for $(dP_s/dT)_{P_c, T_c}$ from the Osborne and Meyers Formula (Eq. 3) is 21.5 psia/°R. Therefore in this report the value of 21.4 psia/°R was taken for $(dP_s/dT)_{P_c, T_c}$

The following equation was derived for the critical isometric by assuming values of 3207.85 psia and 705 5°F for the critical pressure and temperature, respectively:

$$P = 3207.85 + 21 \ 4 \ (t - 705.5) \ , \tag{21}$$

where P is the pressure in psia and t is the temperature in °F. A value

of 0.0525 ± 0.0005 ft^3/lb was derived for the critical volume of water from Eq. (21) in conjunction with Figure 12.

The pressure at 0.0525 ft^3/lb along the 705.5°F isotherm of Figure 12 is 3208 psia. The close correspondence between the values of critical pressure read from Figure 12 and that obtained by taking the mean of the values listed in the Keenan and Keyes tables[1] and in the Timroth tables[4] is noteworthy. It is also very noteworthy to find good agreement between the value listed for the critical volume in the Timroth tables and the value derived in this report. The difference between these two values are within the error of calculation and experiment.

C. Summary

(1) Callendar's postulate of the existence of a small unstable region above the critical point cannot be accepted at this time for the following reasons:

(a) The measurements of Callendar probably were not as precise as were estimated in his paper.

(b) There was a systematic variation of air content in the water vapor between his volume measurements and the enthalpy measurements.

(c) Subsequent calorimetric and volumetric experiments of seemingly equal or better accuracy show no evidence of an unstable region above the critical point.

(2) Values of 0.0525 ft^3/lb and 3208 psia derived for the critical volume and pressure, respectively, were obtained by an analysis of previous measurements in the critical region.

VII. THERMAL CONDUCTIVITY OF SUBCOOLED WATER
AND SUPERHEATED VAPOR

The thermal conductivity of water and water vapor at moderate temperatures and pressures has been measured by several investigators. Two methods have generally been used, that of the hot wire, and that of coaxial cylinders. In the first method an electric filament is centered in the tube containing the sample of water. In the second method water is contained in the annulus formed by two coaxial cylinders.

A. Thermal Conductivity of Subcooled Water

The most comprehensive set of measurements of thermal conductivity were made by the German investigators Schmidt and Sellschopp[69] and by the Russian investigators Timroth and Vargaftik.[70] In 1932, Schmidt and Sellschopp measured the thermal conductivity of water by the coaxial cylinder technique up to a temperature of about 520°F (270°C) and a pressure of 1070 psia (75 kg/cm^2). Special care was taken to run all experiments at conditions where convection effects were negligible. The end heat losses were evaluated by means of the Schwartz-Christoffel equation. Calculations also indicated that the errors resulting from eccentricity were negligible amounting to some 0.5%.

The measurements of Schmidt and Sellschopp[69] are given in Table 36. They estimate that their measurements are accurate to about ±1½%. They concluded that the thermal conductivity along the saturation line reaches a maximum at a temperature of about 266°F (130°C), and at 570°F (300°C) the value corresponds to the value at 32°F (0°C).

In 1940 Timroth and Vargaftik measured the thermal conductivity of subcooled water up to a temperature of 628°F (331°C) and to a pressure of about 5670 psia (400 kg/cm^2). The hot wire method of measuring the thermal conductivity was employed by these investigators.

TABLE 36

Thermal Conductivity of Subcooled Water as Measured by Schmidt and Sellschopp[69]

Temperature, °F	Pressure, psia	Thermal Conductivity, B hr^{-1} F^{-1} ft^{-1}
47.84	14.22	0.3313
64.58	14.22	0.3427
104.72	14.22	0.3655
162.50	14.22	0.3843
167.00	420.91	0.3850
185.90	405.27	0.3890
194.00	106.65	0.3931
195.44	277.29	0.3931
204.44	345.32	0.3910
216.68	281.56	0.3957
221.72	210.46	0.3971
222.62	382.52	0.3944
237.38	359.77	0.3937
251.96	322.79	0.3957
269.42	339.86	0.3957
288.32	314.26	0.3951
310.82	270.18	0.3924
316.22	403.85	0.3957
331.70	318.53	0.3897
335.30	166.37	0.3917
381.74	423.76	0.3877
386.24	487.75	0.3877
469.58	597.24	0.3655
516.56	1077.88	0.3467

A calculation indicated that the end heat loss amounted to about 1%.

Timroth and Vargaftik state that the heated wire was not exactly centered in the quartz tube. Special experiments were conducted on air and water at low temperatures in an effort to evaluate the error due to end heat loss and eccentricity. Air and water were chosen because their respective conductivities are accurately known at low temperatures. The special experiments showed that as the thermal conductivity changes from 0.27 to 0.40 B $hr^{-1}F^{-1}ft^{-1}$ (0.4 to 0.6 kcal $hr^{-1}C^{-1}m^{-1}$), which corresponded to their range of thermal conductivity determinations; the combined error due to end heat loss amounted to about $\frac{1}{2}$%. This correction was applied to all of their measured values.

The result of Timroth and Vargaftik are given in Table 37. They found good agreement between their measurements and those of Schmidt and Sellschopp.

TABLE 37

Thermal Conductivity of Subcooled Water as Measured by Timroth and Vargaftik[70]

Temperature, °C	Pressure, kg/cm²	Thermal Conductivity, kcal hr^{-1} C^{-1} m^{-1}
27.8	1	0.534
29.3	400	0.561
38.4	1	0.543
39.6	300	0.558
41.2	1	0.545
47.8	1	0.557
142	10	0.588
141.3	400	0.614
127.5	33	0.587
152.5	37	0.593
152.5	300	0.607
215.4	58	0.557
215.1	400	0.594
321.3	400	0.481
322.3	300	0.451
331.0	166	0.402

Several noteworthy experiments have been conducted on water at temperatures below 212°F (100°C). Jakob[71] in 1920 measured the conductivity of water between 32° and 176°F (0° to 80°C) and at a pressure of 14.2 psia (1 kg/cm²). In these experiments the water was contained between two parallel plates, one of which was heated. Timroth and Vargaftik found that the measurements of Jakob were in good agreement with their own. Bridgman[72] measured the variation of conductivity with pressure at temperatures of 86° and 167°F (30° and 75°C) with water flowing continuously through an annulus formed by two coaxial cylinders. Bridgman found that for pressure up to 1000 atmospheres the conductivity increased by about 1%.

Timroth and Vargaftik found that the very small effect of pressure on thermal conductivity as measured by Bridgman was also borne out in their experiments. However, the values of Bridgman at one atmosphere are about 5% lower than the values of Timroth and Vargaftik.

Timroth and Vargaftik[70] derived values of thermal conductivity from their own results and those of Schmidt and Sellschopp[69] and Jakob.[71]

The values for the thermal conductivity of subcooled water in the critical region are given in Table 38. These values are identical to those in the Vukalovich steam tables[2,3] and the 1952 Timroth tables [4]

TABLE 38

Thermal Conductivity of Saturated and Subcooled Water
Derived by Timroth and Vargaftik[70]

Pressure, psia		2845	4267
Temperature, °F	Saturation Pressure	Thermal Conductivity, B hr^{-1} F^{-1} ft^{-1}	
662	0.231	0.241	0.265
680	0.206	0.211	0.245
698	0.169	--	0.219

Thermal conductivity values in the 1958 Timroth tables[5] are given in Table 39. There are significant differences between the values in the 1952 and 1958 Timroth tables, as can be seen in Figure 13. No mention was made of the basis of the thermal conductivity values in the latter steam tables.

TABLE 39

Thermal Conductivity of Saturated and Subcooled Water
of 1958 Timroth Steam Tables[5]

Pressure, psia		2845	4267
Temperature, °F	Saturation Pressure	Thermal Conductivity, B hr^{-1} F^{-1} ft^{-1}	
662	0.249	0.261	0.282
680	0.228	0.238	0.268
698	0.195	--	0.253

B. Thermal Conductivity of Superheated Water Vapor

Measurements

The most extensive thermal conductivity measurements on water vapor were made by Vargaftik and Timroth. In 1937 Vargaftik[73] used the hot wire method to measure the thermal conductivity of water vapor up to a temperature of about 890°F (475°C) and a pressure of about 720 psia (29 kg/cm^2). Care was taken to center the wire inside the glass tube accurately. Photographs under a microscope showed that the deviation of the filament from the axis of the glass tube was quite inconsiderable.
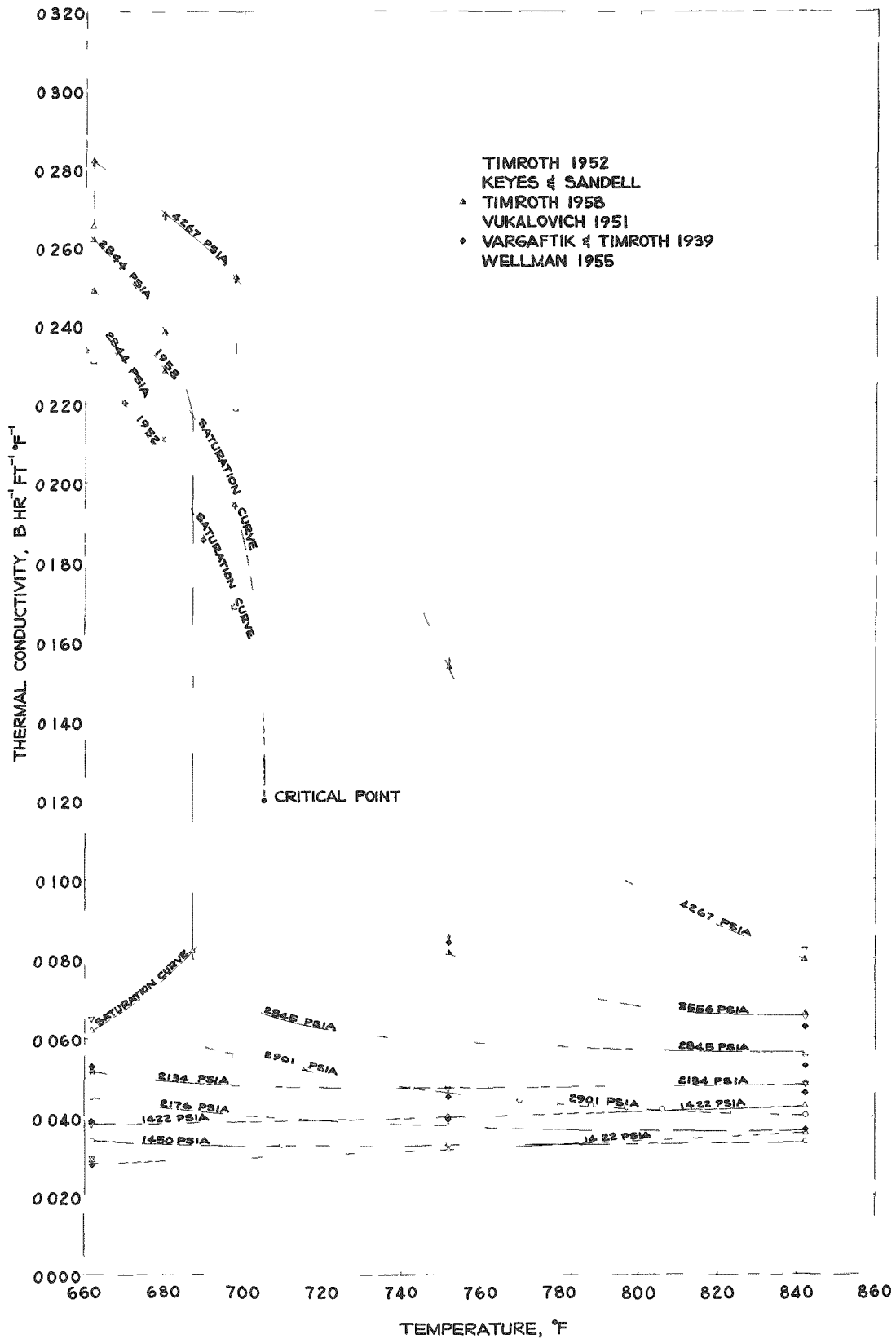
FIG. 13 THE THERMAL CONDUCTIVITY OF WATER AND
WATER VAPOR IN THE CRITICAL REGION

Vargaftik stated that each measurement was carried out with currents of different magnitude to establish whether convective heat transfer was eliminated. No mention was made of the size of terminal or end heat losses. The measured values of Vargaftik at 14.2 psia (1 kg/cm^2) are given in Table 40, while the results of his measurements at higher pressures are given in Table 41. Special measurements on air were carried out before and after the tests at 1 atmosphere to evaluate any distortion caused by high temperatures. These showed a systematic divergence of thermal conductivity of about 1.3%. Vargaftik therefore reduced the measured values of conductivity by 1.3%.

TABLE 40

Thermal Conductivity of Superheated Water Vapor at
14.22 psia as Measured by Vargaftik[73]

Temperature, °F	Thermal Conductivity, B hr^{-1}F^{-1}ft^{-1}	Temperature, °F	Thermal Conductivity, B hr^{-1}F^{-1}ft^{-1}
156 2	0.01243	562.5	0.0246
164.7	0.01271	607.1	0.0262
210.9	0.01393	628.7	0.0269
220.1	0.01427	635.0	0.0271
287.8	0.01592	637.7	0.0272
297.3	0.01634	678.2	0.0285
392.7	0.01891	736.7	0.0324
402.6	0.01913	765.5	0.0316
478.0	0.02166	475.4	0.0322
487.6	0.02197	890.1	0.0383
551.8	0.0244		

TABLE 41

Thermal Conductivity of Superheated Water Vapor at
Moderate Pressures and Temperatures as
Measured by Vargaftik[73]

Temperature, °F	Pressure, psia	Thermal Conductivity, B hr^{-1}F^{-1}ft^{-1}
482.5	71.1	0.0226
508.5	213.4	0.0250
517.1	298.7	0.0265
529.0	71.1	0.0228
554.4	213.4	0.0259
560.3	284.5	0.0269
598.6	71.1	0.0262
620.8	213.4	0.0275
633.2	312.9	0.0294
630.7	398.3	0.0299
651.2	71.1	0.0278
670.1	213.4	0.0289
662.5	312.9	0.0302
668.5	398.3	0.0305

Jakob[74] states that Moser[75] carried out measurements of thermal conductivity on water vapor at a low pressure and at temperatures of 115° and 212°F (46° and 100°C) by the hot wire method. The value of 0.0137 B hr^{-1}F^{-1}ft^{-1} measured by Moser at 212°F is in very good agreement with the measured values of Vargaftik[73] (see Table 40).

In 1935 Milverton[76] measured the pressure dependence of the thermal conductivity of water vapor between temperatures of 183° and 205°F (84° and 96°C)

and between pressures of 2.4 and 14.2 in. Hg (6 and 36 cm Hg). Vargaftik states that the exaggerated pressure dependence found by Milverton was caused by the neglect of the "temperature jump" at the filament.

In 1939 Vargaftik and Timroth[77] extended their measurements of the thermal conductivity on water vapor to a pressure of 4300 psia (300 kg/cm^2) and to a temperature of 1020°F. Again care was taken to operate at conditions which would exclude convection effects. To prevent end heat losses measurements were carried out with two tubes of identical diameter but different lengths under identical conditions. At low pressures the "temperature jump" between the wire and the vapor was included in corrections applied.

Timroth and Vargaftik corrected their measurements for radiation on the basis of previous measurements[78] of the coefficient of thermal conductivity. The correction for radiation introduced by them was 2%. The results of measurements of Timroth and Vargaftik on the thermal conductivity of steam are given in Table 42. They estimate that the maximum error in their measurements did not exceed 3%.

In 1950 Keyes and Sandell[79] published new experimental data for the thermal conductivity of steam, obtained using the coaxial cylinder method. Their results generally were lower than the Timroth and Vargaftik[77] results of 1940. The empirical equation for conductivity deduced by Keyes and Sandell gives values which are lower than the older Timroth and Vargaftik data by about 30% at 1110°F along the 1-atmosphere line.

TABLE 42

Thermal Conductivity of Superheated Water Vapor at High Pressures
and Temperatures as Measured by Vargaftik and Timroth[77]

Temperature, °F	Pressure, psia	Thermal Conductivity B hr^{-1} F^{-1} ft^{-1}	Temperature, °F	Pressure, psia	Thermal Conductivity, B hr^{-1} F^{-1} ft^{-1}
492.8	284.47	0.0257	820.0	3555.85	0.06749
546.3	284.47	0.0255	813.6	4267.02	0.09093
590.0	284.47	0.0277	884.8	14.22	0.0393
662.4	284.47	0.0293	759.4	853.40	0.0367
631.6	568.94	0.0294	745.2	1422.34	0.0402
615.6	853.40	0.0316	974.7	284.47	0.0488
566.1	853.40	0.0338	970.2	853.40	0.0502
576.5	568.94	0.0294	966.7	1422.34	0.0517
765.5	284.47	0.0336	958.6	2133.51	0.0524
756.0	568.94	0.0341	834.6	2133.51	0.0454
723.0	1422.34	0.0387	814.1	2844.68	0.0541
705.2	2133.51	0.0475	798.3	3555.85	0.07065
882.7	284.47	0.0409	792.1	4267.02	0.09818
875.3	568.94	0.0414	851.2	4267.02	0.08018
865.8	1422.34	0.0446	875.7	3555.85	0.0591
852.4	2133.51	0.0457	750.7	2844.68	0.0572
839.5	2844.68	0.0531			

Vargaftik and Smirnova[80] carried out measurements at 14.2 psia (1 kg/cm²) in order to clarify the reason for the discrepancy between the above two sets of measurements. Both methods, the coaxial cylinder method and the heated filament method, were used. At the fifth international conference on the properties of steam Vargaftik[81] stated that their coaxial cylinder apparatus was similar to the one used by Keyes except for one improvement. The apparatus used by Keys and Sandell did not have guard heaters, while the coaxial cylinder apparatus of Vargaftik and Smirnova had guard heaters which minimized end heat losses.

Special experiments were conducted by Vargaftik and Smirnova to evaluate the amount of end heat loss. These showed that for an unbalance in temperature of 1.8°F (1°C) between the guard heaters and the heated filament the error in measurement of thermal conductivity amounted to about 1%. Special care was taken to conduct measurements with an unbalance of only 0.2°F (0.1°C).

The thermal conductivities of water vapor and nitrogen at one atmosphere measured by Vargaftik and Smirnova[80] by means of a coaxial cylinder apparatus and a hot wire apparatus are given in Tables 43 and 44. They found very good agreement among the thermal conductivity measurements by the two methods. Furthermore, their newest measurements were found to be in very good agreement with their older measurements conducted in 1937 and 1940.

The apparatus used by Keyes and Sandell did not have guard heaters and hence their measurements were conducted on a comparative basis, using nitrogen as a standard. The thermal conductivity data used by Keyes and Sandell for calibration purposes were the "lowered values" of Wilner and Borelius.[82] Wilner and Borelius conducted experiments in an apparatus where up to 75% of the total heat flow could have been charged to radiation.

TABLE 43

Thermal Conductivity of Water Vapor at 14.22 psia as Measured by Vargaftik and Smirnova[80] with a Coaxial Cylinder Apparatus

Temperature, °F			Temperature Difference, °F	Total Heat Transfer Through Water Vapor	Heat Transfer by Radiation	Heat Transfer by Conduction	Thermal Conductivity, B hr^{-1}F^{-1}ft^{-1}
Internal Cylinder	External Cylinder	Water Vapor					
469.11	425.14	447.1	43.97	27.0	0.2	26.8	0.0213
604.49	568.76	586.6	35.73	26.8	0.3	26.5	0.0260
755.65	727.18	741.2	28.47	26.6	0.4	26.2	0.0324
841.5	814.75	828.0	26.40	26.5	0.5	25.8	0.0344

TABLE 44

Thermal Conductivity of Water Vapor and Nitrogen at 14.22 psia as Measured by
Vargaftik and Smirnova[80] with a Hot Wire Apparatus

Temperature, °F	Thermal Conductivity of Water Vapor, B hr^{-1}F^{-1}ft^{-1}	Temperature, °F	Thermal Conductivity of Nitrogen, B hr^{-1}F^{-1}ft^{-1}
350.4	0.0185	126.3	0.0163
549.5	0.0246	354.4	0.0210
674.2	0.0281	527.2	0.0242
850.8	0.0349	839.8	0.0293
940.6	0.0380	990.1	0.0324

Vargaftik and Smirnova concluded that the "lowered value" data on the thermal conductivity for nitrogen used by Keyes and Sandell to calibrate their apparatus led to their lower values on the thermal conductivity of water vapor. Keyes in 1952 published new data for nitrogen,[83] which has been reported[81] to be in good agreement with the measured values of Timroth and Vargaftik. Vargaftik and Smirnova made the criticism that since a relative method was used to determine the thermal conductivity of nitrogen, Keyes should have recomputed his data on water vapor, making use of new data on nitrogen.

Vargaftik and Smirnova state that measurements[84,85] of thermal conductivity on water vapor have been carried out at a pressure of 14.22 psia (1 kg/cm^2) and up to temperatures of about 1650°F (900°C). According to Vargaftik[86] these measurements give a more accurate relationship between the thermal conductivity and the temperature.

Compilation

Tables 45 to 48 give thermal conductivity values for superheated water vapor derived by Vargaftik and Timroth,[77] Vukalovich,[2] Timroth,[4] and Timroth et al.[5] These tables have been computed from empirical equations derived from the measurements of Vargaftik[73] and of Vargaftik and Timroth.[77]

The following equation was derived by Vukalovich from the measurements of Timroth and Vargaftik:[73,77]

$$k = k_t f_p \quad , \tag{22}$$

where k is the thermal conductivity of water vapor in B hr^{-1}F^{-1}ft^{-1}, k_t is the thermal conductivity of water vapor at "zero pressure," and f_p is a multiplier to account for the effect of pressure on the thermal conductivity:

$$f_p = \frac{1 + \dfrac{5.2167 \times 10^{-4}}{p V_{sp}^2}}{\left(1 - \dfrac{6.246 \times 10^{-5}}{V_{sp}}\right)^2} \quad .$$

TABLE 45

Thermal Conductivity of Superheated Water Vapor at High Pressures and Temperatures Derived by Vargaftik and Timroth[77]

Pressure, psia	14.22	284.5	0.0306	0.0324	2134	2134	2845	3556
Temperature °F	Thermal Conductivity, B hr^{-1}F^{-1}ft^{-1}							
662	0.0279	0.0293	0.0306	0.0324	0.0383	0.0524	--	--
752	0.0314	0.0329	0.0341	0.0361	0.0394	0.0450	0.0571	0.0839
842	0.0368	0.0379	0.0392	0.0406	0.0430	0.0457	0.0526	0.0625

TABLE 46

Thermal Conductivity of Superheated Water Vapor at High Pressures and Temperatures from 1951 Vukalovich Steam Tables[2]

Pressure, psia		14.22	284.5	568.9	853.4	1138	1422	2134	2845	3556	4267
Temperature, °F	Saturation Pres,	Thermal Conductivity, B hr^{-1}F^{-1}ft^{-1}									
662	0.0647	0.0296	0.0308	0.0321	0.0336	0.0355	0.0381	0.0506	--	--	--
752	--	0.0330	0.0340	0.0353	0.0367	0.0382	0.0401	0.0465	0.0554	0.0893	--
842	--	0.0365	0.0375	0.0387	0.0401	0.0413	0.0430	0.0478	0.0546	0.0647	0.0821

TABLE 47

Thermal Conductivity of Steam at High Pressures and Temperatures from 1952 Timroth Tables[4]

Pressure, psia		14.22	284.5	568.9	853.4	1138	1422	2134	2845	3556	4267
Temperature, °F	Saturation Pres,	Thermal Conductivity, B hr^{-1}F^{-1}ft^{-1}									
662	0.0618	0.0288	0.0298	0.0314	0.0333	0.0357	0.0388	0.0513	--	--	--
752	--	0.0323	0.0332	0.0345	0.0361	0.0381	0.0404	0.0478	0.0594	0.0820	0.159
842	--	0.0358	0.0367	0.0379	0.0393	0.0410	0.0428	0.0486	0.0561	0.0661	0.0800

TABLE 48

Thermal Conductivity of Steam at High Pressures and Temperatures from 1958 Timroth Tables[5]

Pressure, psia		1422	284.5	568.9	853.4	1138	1422	2134	2845	3556	4267
Temperature, °F	Saturation Pres,	Thermal Conductivity, B hr^{-1}F^{-1}ft^{-1}									
662	0.0618	0.0289	0.0298	0.0314	0.0333	0.0358	0.0388	0.0513	--	--	--
752	--	0.0323	0.0332	0.0345	0.0361	0.0382	0.0404	0.0478	0.0594	0.0813	0.154
842	--	0.0358	0.0367	0.0379	0.0393	0.0410	0.0428	0.0486	0.0561	0.0661	0.0800

Further

$$k_t = 32.153\, \eta_t\, (400\, C_{p_o} - 1500) \quad ,$$

where η_t is the dynamic viscosity of water vapor in lb sec/ft^2 at "zero pressure" and C_{p_o} is the molecular specific heat in BTU/lb mole °F at "zero pressure."

The following equation was derived by Vargaftik[4,5] from the measurements of Timroth and Vargaftik:[73,77]

$$k = k_t + \frac{A}{(V_{sp})^{1.25}} \quad , \tag{23}$$

where k is the thermal conductivity in B hr^{-1}F^{-1}ft^{-1}, k_t is the thermal conductivity at 14.22 psia, V_{sp} is the specific volume in ft^3/lb,

$$k_t = 1.093 \times 10^{-6} T^{1.45} \quad ,$$

with T the absolute temperature in °R, and A = 28.58 x 10^{-4}.

The following equation was derived by Keyes and Sandell from their thermal conductivity measurements:[79]

$$k = k_0 + C(e^{\alpha P/T^4} - 1) \quad , \tag{24}$$

where k is the thermal conductivity in B hr^{-1}F^{-1}ft^{-1}, k_0 is the thermal conductivity at "zero pressure:"

$$k_0 = \frac{2.79 \times 10^{-3} T^{3/2} \times 10^{21.6/T}}{(T \times 10^{21.6/T}) + 3127} \quad ,$$

T is the absolute temperature in °R,

$$C = 2.65 \times 10^{-3} \quad ,$$

$$\alpha = 1.54 \quad ,$$

and p is the pressure in psia.

Figure 13 gives a comparison between the various values derived from thermal conductivity measurements. The figure indicates that the tie in between the liquid and vapor phases in the critical region is very unsatisfactory. More values are required in the critical region to adequately describe the change of thermal conductivity with temperature at a constant pressure.

C. <u>Summary</u>

(1) In view of the most thorough investigation of Vargaftik and Smirnova,[80] the various Russian values for the thermal conductivity of steam are to be preferred.

(2) Three empirical equations[2,4,77] have been derived from the measurements of Vargaftik[73] and of Vargaftik and Timroth.[77] All three equations give appreciably different values for the thermal conductivity in the critical region.

(3) The empirical equations in Ref. 4 and 77 fail to represent the measured values of thermal conductivity in the critical region.

(4) New measurements of thermal conductivity are required in the immediate vicinity of the critical point to accurately describe the functional relation of thermal conductivity with temperature and pressure.

VIII. DYNAMIC VISCOSITY

A. General

The viscosity of water and water vapor has been measured for the most part by the capillary method. The following relation, derived by Hagen and Poiseuille, is used to calculate the viscosity from observations of flow rate and pressure difference in a capillary tube:

$$Q = \frac{\Delta P}{L} \frac{\pi r^4}{8\eta} \quad , \tag{25}$$

where Q is the volume flow per unit time, ΔP is the pressure difference, L is the length of the capillary, r is the radius of the capillary, and η is the viscosity. This relation is valid only for laminar flow through a tube. For turbulent flow the pressure difference ceases to be proportional to the first power of the mean velocity (and the volume rate of flow) and becomes approximately proportional to the square of the mean velocity.

Some measurements on the viscosity of water and water vapor differ significantly from all of the other studies. These differences may be attributed to incorrect theories used to compute the viscosity from the experimental observations.

It is known that most of the formulations proposed for the viscosity of water vapor do not represent accurately available experimental data in the critical region. The differences between experimental and computed values in this region may amount to as much as 10%, which is usually greater than the experimental inaccuracies. In a preliminary survey, significant differences were found between computed values listed in various steam tables. This does not necessarily indicate that there is discord among the various sets of measurements. Instances will be cited in this section where three different formulations were derived from the same experimental data, giving appreciably different values in the critical region.

The experimental values obtained by various investigators have been reproduced, since more "accurate" values will likely be obtained if recourse is made to them instead of the formulations.

B. Measurements

A summary of the extent of the measurements and of the methods used in some of the more recent investigations on the viscosity of steam is given in Table 49. Comparison with the measurements made by other investigators will be given in a later section.

TABLE 49

Viscosity Measurements of Subcooled Water and Super Heated Water Vapor

Investigator(s) and Date	Reference	Method Used	Pressure Range		Temperature Range	
			psia	kg/cm²	°F	°C
Schugajew, 1934	87	Rankine Viscometer	14.2 to 1320	1 to 93	212 to 752	100 to 400
Schugajew and Sorokin, 1939	88	Rankine Viscometer	To 4000	To 280	564 to 753	295 to 400.5
Sigwart, 1936	89	Capillary Tube	150 to 3840	10.5 to 270	243 to 720	117 to 383
Timroth, 1940	90	Capillary Tube	1400 to 4200	100 to 300	66 to 1120	189 to 601.5
Bonilla et al, 1950	91	Capillary Tube	At 14.7	At 1.03	847 to 2197	453 to 1201.5
Bonilla et al, 1956	92	Capillary Tube	At 14.7	At 1.03	437 to 2610	225 to 1450
Georgia Institute of Technology, 1955 to 1958	94	Aldus-type Viscometer	67.6 to 4525	4.8 to 318	435 to 866	223 to 463
University of Glasgow, 1955	95	Rankine Viscometer	2845 to 14,000	200 to 1000	200 to 1000	377 to 540

In 1934, Schugajew[87] investigated the viscosity of superheated water vapor with a Rankine viscosmeter for pressures to 93 atmospheres and temperatures to 752°F (400°C). He concluded that:

(a) the viscosity increases linearly with temperature from 212° to 752°F at one atmosphere, and

(b) the effect of pressure on viscosity was small, and for pressures from 14.2 to 1320 psia did not exceed 6%.

In 1939 Schugajew and Sorokin[88] made further measurements of viscosity in the critical region. They estimated that the accuracy of their viscosity determinations was about ± 6%. Their viscosity results are given in Table 50. They found that the small effect of pressure observed by Schugajew was in accordance with their newer measurements.

In 1936 Sigwart[89] made extensive measurements of the viscosity of water and water vapor in the critical region; he estimated that the error in absolute pressure determination was about $\frac{1}{2}$ atmosphere and the error in temperature measurement was about $\frac{1}{2}$% Sigwart thought that the total error in his experiments was approximately 3% The viscosity data of Sigwart is given in Tables 51 and 52 for subcooled water and superheated water vapor respectively

In 1940 Timroth[90] reported viscosity measurements for water and water vapor at high temperatures and pressure. He estimated that temperatures were measured with an accuracy of 0.04°F (0.025°C) and controlled

TABLE 50

Viscosity of Superheated Water Vapor as Measured by Schugajew [88]

Specific Volume, in.^{3}/kg	Temperature, °C	Dynamic Viscosity, 10^{-5} poise	Specific Volume, in.^{3}/kg	Temperature, °C	Dynamic Viscosity, 10^{-5} poise
Saturation specific volumes	371	43.49	0.009	399	30.82
	361	31.30		375	29.42
	331.5	23.49		361	26.69
	329	23.98		352	26.15
	295	19.94			
	288	19.93	0.012	400.5	29.12
				391	26.96
0.0045	381	37.14		376.6	28.22
	380	37.16		369	26.69
	377.5	41.44		351.5	25.28
	373	41.09		342	24.32
	372.6	42.44			
			0.018	396	24.30
0.006	395	33.25		391	25.46
	383	31.60		384.5	23.82
	374	31.04		383.5	23.78
				369	23.13
0.0072	395	30.73		368	22.93
	385	29.71		358	24.09
	372	29.88		332.5	21.38
	361	28.48		330.5	21.69
				326	21.48

TABLE 51

Viscosity of Subcooled Water as Measured by Sigwart [89]

Temperature, °F	Pressure psia	Dynamic Viscosity, 10^{-6} lb sec ft^{-2}	Temperature, °F	Pressure psia	Dynamic Viscosity, 10^{-6} lb sec ft^{-2}
242.4	149	5.131	590.0	2090	1.98
247.5	164	5.018	616.5	2320	1.86
306.7	327	3.799	661.6	2770	1.58
306.9	178	3.769	665.4	2539	1.50
310.6	191	3.705	682.3	3020	1.37
351.1	412	3.304	683.6	2990	1.32
361.4	260	3.138	698.0	3230	1.20
428.9	462	2.591	698.7	3430	1.27
470.5	1220	2.349	698.9	3240	1.19
488.9	856	2.294	700.5	3600	1.31
532.4	1320	2.143			

TABLE 52

Viscosity of Superheated Water Vapor as Measured by Sigwart [89]

Temperature, °F	Pressure psia	Dynamic Viscosity 10^{-6} lb sec ft^{-2}	Temperature, °F	Pressure psia	Dynamic Viscosity 10^{-6} lb sec ft^{-2}
530.2	363	0.404	684	398	0.473
528.4	505	0.406	683.6	782	0.477
529.7	697	0.401	683.4	1170	0.488
529.2	839	0.404	682.9	1600	0.498
529.2	846	0.414	684	1850	0.494
573.1	391	0.420	683.4	2130	0.494
573.4	633	0.416	683.2	2296	0.502
571.6	861	0.430	683.6	2400	0.506
573.8	1040	0.432	683.2	2510	0.522
572	1145	0.440	683.6	2550	0.528
571.6	1150	0.426	684	2620	0.543
572.0	1210	0.430	707.7	548	0.481
571.6	1220	0.438	707.4	1050	0.504
573.8	1220	0.436	708.1	1370	0.510
617.7	711	0.451	708.1	1373	0.516
617.0	1050	0.461	707.7	1740	0.522
617.2	1370	0.473	708.4	2120	0.531
617.2	1520	0.465	707.7	2480	0.545
617.9	1710	0.463	708.4	2570	0.541
			708.8	2610	0.535
664	384	0.463	707.3	2790	0.549
663.6	676	0.471	707.0	2970	0.557
663.6	782	0.471	708.1	3100	0.588
663.6	1500	0.483	720.9	1780	0.512
662.9	1810	0.486	720.9	2176	0.524
663.6	1810	0.485	720.5	2550	0.531
663.1	2055	0.488	720.9	2890	0.547
663.6	2310	0.502	720.9	3210	0.600
			721.2	3340	0.623
			720.5	2300	0.805
			720.5	3840	1.25
			721.2	3840	1.26

to 1.8°F (1°C), and that viscosity measurements were accurate to about 3%. Timroth's viscosity determinations are given in Table 53.

In 1951 and 1956, Bonilla et al.,[91,92] measured the viscosity of superheated water vapor at one atmosphere and over a range of temperatures. Their latest measurements[92] below 1290°F (700°C) are several per cent higher than their original measurements.[91] Tables 54 and 55 give the results of both investigations.

In 1959, Thomas and Jackson[93] measured the viscosity of superheated water vapor with an annular-type viscometer. Their results[94] in the critical region are given in Table 56. They stated that the average deviation of the data from the equation developed for low densities was 1.88% and that the maximum deviation was about 6%. Thomas and Jackson made

TABLE 53

Viscosity of Subcooled Water and Superheated Water Vapor as Measured by Timroth[90]

Temperature, °F	Pressure, psia	Dynamic Viscosity, 10^{-6} lb sec ft^{-2}	Temperature, °F	Pressure, psia	Dynamic Viscosity, 10^{-6} lb sec ft^{-2}
66.0	1422.3	21.38	834.8	4331.0	0.707
144.5	2854.6	9.56	840.2	3541.6	0.625
149.0	2844.7	9.32	847.4	2826.2	0.604
272.1	2915.8	4.59	847.4	2150.6	0.588
272.1	1365.4	4.55	847.4	1318.5	0.569
396.7	5049.3	3.05	932.0	4281.2	0.696
396.7	1422.3	2.91	929.3	3534.5	0.655
456.8	4964.0	2.54	933.8	2837.6	0.651
455.0	2790.6	2.50	933.8	2147.7	0.637
505.4	5020.8	2.36	940.1	1436.6	0.610
501.8	1422.3	2.21	977.9	1372.6	0.703
569.3	4006.6	2.07	979.2	3541.6	0.694
569.3	1422.3	1.92	979.7	2863.2	0.668
627.8	1329.8	.461	982.4	4309.7	0.713
636.8	4978.2	1.85	982.9	4338.1	0.715
635.0	2851.8	1.71	989.6	2069.5	0.645
649.4	5049.3	1.76	987.1	1493.4	0.637
649.4	2858.9	1.63	984.2	4373.7	0.723
675.9	5156	1.68	987.8	3541.6	0.696
675.9	3570.1	1.57	987.8	2823.3	0.670
675.0	2887.3	1.49	986.0	2126.4	0.643
685.4	4267.0	1.54	984.2	1493.4	0.633
684.9	2972.7	1.38	1112.9	4217.2	0.784
696.2	2126.4	0.522			
694.4	2126.4	0.518			
696.2	2873.0	0.582			
710.6	1413.8	0.508			
719.6	3612.7	1.01		Measurements Along Saturation Line	
725.9	4992.4	1.51			
723.2	4281.2	1.32	588.2	1422.3	0.494
716.0	3570.1	1.11	645.8	2133.5	0.547
747.5	1450.8	0.514	687.2	2830.5	0.647
750.2	2901.6	0.563	694.8	2986.9	0.674
748.4	4267.0	0.989	703.4	3097.9	0.697
749.3	3548.7	0.653	705.2	3203.1	0.850
752.0	2076.6	0.533			

TABLE 54

Viscosity of Superheated Water Vapor at One Atmosphere Measured by Bonilla, Brooks and Walker[91]

Temperature, °F	Dynamic Viscosity 10^{-6} x lb sec ft^{-2}
847.89	0.5042
1117.7	0.6358
1387.6	0.7816
1654.0	0.8799
1924.6	0.9831
2194.7	1.070

TABLE 55

Viscosity of Superheated Water Vapor at One Atmosphere Measured by Bonilla, Wang and Weiner[92]

Temperature, °F	Dynamic Viscosity, 10^{-6} x lb sec ft^{-2}
618	0.42950
672	0.45323
759	0.49226
769	0.49611
845	0.53119
938	0.47370
958	0.58456
1090	0.63646
1122	0.65991
1212	0.69726
1245	0.71946

TABLE 56

Thomas and Jackson's Viscosity Data [94]
at High Pressures and Temperatures

Temperature, °F	Pressure, psia	Viscosity x 10^5, Poise
729.7	2985	24.44
728.2	3040	24.41
730.3	3025	24.02
714.0	3205	27.32
788.2	3265	25.37
722.3	3565	44.55
741.5	4020	37.31
841.6	4070	33.59
697.5	4035	86.50
727.1	3315	26.73
730.5	3350	26.83
732.5	3420	28.27
718.0	3500	45.07
722.0	3520	39.85
739.3	3715	33.23
752.0	4115	44.13
866	4250	31.29
745	4290	43.50
771.3	4415	37.75
761.5	1525	50.09

no mention of the deviation of the data from the equation developed by them for high densities, i.e., in the critical region.

It is interesting to note that Schugajew[87] concluded that the effect of pressure on viscosity was small and is less than 6% for pressures to 1320 psia. However, he stated that precise measurements were needed to evaluate the small but very definite pressure dependence. Hence it appears to the writer that the measurements of Jackson and Thomas for pressures below 1550 psia are accurate to about 6%.

In 1958, investigations were conducted at the University of Glasgow[95] in which temperatures were determined accurately to about 1.8° F (1°C). The viscosity data from these investigations are given in Table 57 and it was estimated that the maximum error in measurement was not greater than 2%.

C. Comparisons

The remarks and comparisons made by different investigators will now be noted. It is quite significant that consistency was found between the measurements of Sigwart,[89] Schugajew and Sorokin,[88] and Timroth.[90]

TABLE 57

Viscosity Data Obtained at
University of Glasgow [95]

Temperature, °C	Pressure, kg/cm²	Kinematic Viscosity, 10^{-3} cm³/sec
377	300	1.2
378	300	1.226
380	500	1.231
380	700	1.242
428.5	200	3.346
428	300	1.827
427	400	1.352
430	600	1.22
430.5	1000	1.237
542	200	5.42
538	300	3.50
539.6	300	3.51
540	500	2.01
541	500	2.01
540	700	1.59

These three investigators used essentially the same method (capillary method) to measure the viscosity of subcooled water and superheated water vapor.

At a pressure of one atmosphere Schugajew[87] found good agreement between his measurements and those of Speyerer,[96] Smith,[97] and of Braune and Linke.[98] He also found that the large pressure dependence found by Speyerer was not borne out by his measurements.

Sigwart found that the pressure dependence and viscosity values for superheated water vapor reported by Schugajew[87] corresponded approximately with his own results. He[89] attempted to explain the differences between his measurements and those of Speyerer by correcting the data of Speyerer for "end effects." Sigwart found that the corrected data of Speyerer corresponded very well with accepted values at one atmosphere and showed no appreciable pressure dependence.

Timroth[90] found no serious discord between his measurements and those of Schugajew,[87] Schugajew et al.,[88] and of Sigwart. The large pressure dependence found by Hawkins, Solberg and Potter [100] was not borne out in the above investigations. Hawkins, Solberg and Potter observed the rate of fall of a body in a medium of superheated water vapor. According to Timroth and Vargaftik,[99] Schugajew criticized this work and recalculated the data of Hawkins et al., taking into account eddy effects. It was reported that there was satisfactory agreement between the recalculated data and the measurements of Schugajew.

Thomas and Jackson[93] found an even smaller pressure effect than that found by Timroth.[90]

In general, the measurements of the University of Glasgow[95] were found to be in good agreement with those of Timroth. However, at about 4200 psia (300 kg/cm²) and 800°F (430°C), the University of Glasgow value of viscosity was about 6% lower than that of Timroth. It was thought[95] that incipient turbulence in the experiments of Timroth at this condition was the cause of the discrepancy.

A review of existing viscosity data of water vapor and subcooled water was made by Kestin and Moszynski[101] in 1959. They concluded that the data of Timroth[90,102] were probably most consistent, since it showed the smallest scatter except at 1110°F (600° C).

D. Empirical Equations

There have been a vast number of empirical equations proposed for the viscosity of water vapor   However, in view of the comparisons and conclusions reached by Schugajew,[87] Schugajew and Sorokin,[88] Sigwart,[89] Timroth,[90] Timroth and Vargaftik,[99] and finally by Kestin and Moszynski,[101] it appears that the primary data obtained by Speyerer,[96] Schiller,[102] Hawkins, Solberg and Potter,[100] and Thomas and Jackson[94] are in error. Therefore, only the empirical equations derived from the Russian and German (Sigwart) experimental values will be noted in this section.

The early Russian formulations were all based on the concept that water vapor behaved as a van der Waals gas. Using this equation of state, Schirokov[103] derived the following theoretical dependence of viscosity on pressure:

$$\eta_P = a \ (P + \frac{a}{v^2}) \ \frac{v^2}{v - b} \qquad , \tag{26}$$

where a is the coefficient accounting for existence of mutual attractions between molecules of a gas, and b is the covolume.   Equation (26) reduced to

$$\eta_P = a \ RT \left(\frac{v}{v - b}\right)^2 \qquad , \tag{27}$$

where R is the gas constant.

The equation indicates that the viscosity is a function of both pressure and temperature, and at very low pressures the viscosity is a function of only the temperature   Equation (27) also indicates that for constant volume the viscosity is proportional to temperature. Equation (27) may be rewritten in the following form:

$$\eta_P = \eta_t \left(\frac{v}{v - b}\right)^2 \quad , \tag{29}$$

where η_t is the viscosity at low pressures, and $[v/(v - b)]^2$ may be thought of as a multiplier to take into account the effect of pressure.

Schugajew and Sorokin[88] utilized Eq. (29) in setting up tables of viscosity for superheated water vapor. They proposed the following Sutherland equation for the viscosity at 14.22 psia (1 kg/cm²):

$$\eta_t = \eta_0 (T/T_0) [1 + (C/T_0)]/[1 + (C/T)] \quad , \tag{30}$$

where $\eta_0 = 0.189 \times 10^{-6}$ lb sec ft⁻² ,
$\quad$ C = 986°R ,
$\quad$ T₀ = 492°F .

Schugajew proposed a value of 0.01481 ft³/lb for the covolume, which was based on known values of viscosity for water and water vapor at 39°F (4°C). The viscosities of superheated water vapor as derived by Schugajew and Sorokin from Eqs. (29) and (30), are given in Table 58.

TABLE 58

Viscosity of Superheated Water Vapor Derived by Schugajew and Sorokin [88]

Pressure, lb/in.²	Saturation Temperature, °F	Saturated Water Vapor	Temperature (°F)				
			680	716	752	788	824
			Viscosity x 10⁶, lb sec ft⁻²				
14.22	210.4	0.268	0.463	0.477	0.492	0.504	0.518
1422	589.1	0.473	0.502	0.514	0.526	0.541	0.553
2845	687.6	0.651	-	0.600	0.594	0.598	0.606
3556	-	-	-	-	-	0.649	0.645

Timroth and Vargaftik[99] considered that the extrapolation made by Sigwart[89] was quite unreliable. They proceeded with Sigwart's measurements and were able as a result to propose a value of 0.00977 ft³/lb for the covolume appearing in Eq. (29). The viscosity of superheated steam derived by Timroth and Vargaftik from the results of Sigwart and Eq. (29) are given in Table 59. They did not mention the basis for the viscosity values at 14.2 psia (1 kg/cm²).

Timroth[90] proposed a mean value of 0.0120 ft³/lb for the covolume appearing in Eq. (29), on the basis of his experimental results. The viscosity values of superheated water vapor derived by Timroth from his measurements and Eq. (29) are given in Table 60. No basis was given for

TABLE 59

Viscosity of Superheated Water Vapor
Derived by Timroth and Vargaftik(99)
from the Results of Sigwart(89)

Temperature, °F	Pressure, psia	Viscosity, lb sec ft^{-2} x 10^{-6}
662	14.22	0.457
662	284	0.461
662	569	0.465
662	853	0.469
662	1422	0.480
662	2134	0.506
752	14.22	0.492
752	284	0.496
752	569	0.500
752	853	0.504
752	1422	0.510
752	2134	0.531
752	2845	0.551
842	14.22	0.527
842	284	0.531
842	569	0.535
842	853	0.539
842	1422	0.545
842	2134	0.561
842	2845	0.580

TABLE 60

Viscosity of Superheated Water Vapor and Subcooled Water
Derived by Timroth (90)

Pressure, psia	14.22	284.5	568.9	853.4	1139	1422	2134	2845	3556	4267
Temperature, °F	Viscosity x 10^8 lb sec ft^{-2}									
662	45.06	45.47	46.08	46.70	47.31	48.13	51.41	155.7	159.8	168.0
680	45.88	46.29	46.90	47.52	48.13	48.95	51.61	141.3	151.6	157.7
698	46.70	47.11	47.72	48.34	48.95	49.57	52.23	58.37	137.2	147.5
716	47.52	47.93	48.54	49.16	49.77	50.39	52.84	56.94	110.6	135.2
734	48.34	48.75	49.36	50.00	50.59	51.21	53.46	57.14	68.61	116.7
752	49.16	49.57	50.18	50.80	51.41	52.02	54.07	57.14	63.29	92.17
770	49.98	50.39	51.00	51.61	52.23	52.84	54.69	57.55	61.65	78.86
788	50.80	51.41	51.82	54.43	53.05	53.46	55.50	58.17	62.06	72.71
806	51.82	52.43	52.84	53.25	53.87	54.48	56.33	58.99	62.47	68.82
824	52.64	53.05	53.66	54.07	54.69	55.30	57.14	59.60	62.67	66.57
842	53.46	53.87	54.48	54.89	55.51	56.12	57.96	60.22	63.08	65.95

TABLE 61

Viscosity of Saturated Water and Water Vapor
Derived by Timroth [90]

Temperature, °F	Pressure, psia	Viscosity x 10^6 lb sec ft^{-2}	
		Saturated Water	Saturated Water Vapor
608	1637	1.78	0.512
626	1866	1.70	0.533
644	2119	1.62	0.557
662	2398	1.52	0.582
680	2708	1.39	0.623
698	3054	1.19	0.684

the viscosity values at 14.22 psia (1 kg/cm^2); however, the values assumed were close to those of Braune and Linke.[98] Timroth stated that Eq. (29) is not valid at high pressures and for the region near the saturation line. The viscosity of water and water vapor along the saturation line derived graphically by Timroth is given in Table 61.

Vukalovich[2] used relations of the form given by Eqs. (29) and (30) to derive viscosity data for water vapor. The following coefficients of Eqs. (29) and (30) were evaluated from the experimental data of Timroth,[90] Schugajew et al.,[88] and also of Sigwart,[89]

$$b = 18.7 \times 10^{-6} (t - 248)$$
$$\eta_0 = 0.171 \times 10^{-6} \text{ lb sec ft}^{-2}$$
$$C = 1730,$$

t being the temperature in °F. In evaluating these constants Vukalovich gave preference to the experimental data of Timroth. Values of dynamic viscosity of superheated vapor and subcooled liquid derived by Vukalovich are given in Table 62, while saturation values are given in Table 63.

TABLE 62

Viscosity of Superheated Water Vapor and Subcooled Water
Derived by Vukalovich [2]

Pressure, psia	14.22	1422	2133	2844	3556	4267
Temperature, °F	Viscosity x 10^6, lb sec ft^{-2}					
662	0.458	0.477	0.496	1.54	1.60	1.68
680	0.466	0.486	0.503	1.41	1.51	1.58
698	0.474	0.494	0.511	0.581	1.37	1.47
716	0.483	0.503	0.519	0.569	1.11	1.35
734	0.491	0.511	0.527	0.553	0.695	1.17
752	0.499	0.520	0.536	0.559	0.655	0.941
770	0.507	0.529	0.544	0.567	0.634	0.799
788	0.515	0.537	0.553	0.574	0.607	0.757
806	0.523	0.546	0.562	0.582	0.613	0.717
824	0.531	0.555	0.570	0.591	0.619	0.696
842	0.539	0.563	0.579	0.599	0.626	0.696

TABLE 63

Viscosity of Saturated Water and Water Vapor
of Vukalovich Steam Tables [2]

Temperature, °F	Dynamic Viscosity x 10^6, lb sec ft^{-2}	
	Saturated Water	Saturated Water Vapor
662	1.52	0.577
680	1.39	0.621
698	1.19	0.707

The following empirical equation derived by Vargaftik from the experimental data of Timroth was used to compute viscosity values for superheated vapor in the 1952 and 1958 Timroth tables: [4,5]

$$\eta_P = \eta/t + (B/v^m) \quad , \tag{31}$$

where η is the viscosity in lb sec ft^{-2} at a pressure P, η/t is the viscosity at temperature t°F at 14.22 psia, and v is the specific volume in ft^3/lb,

$$B = 1.77 \times 10^{-10}$$
$$m = 1.48 \quad .$$

Values of viscosity from the 1952 and 1958 Timroth tables are given in Tables 64 and 65.

TABLE 64

Viscosity for Subcooled Liquid and Superheated Water Vapor
from 1952 Timroth Tables [4]

Pressure, psia	14.22	1422	2134	2845	3556	4267
Temperature, °F	Viscosity x 10^6, lb sec ft^{-2}					
662	0.461	0.485	0.522	1.61	1.68	1.73
680	0.471	0.494	0.524	1.47	1.59	1.66
698	0.479	0.500	0.520	0.604	1.45	1.57
716	0.487	0.508	0.535	0.589	1.16	1.44
734	0.498	0.516	0.541	0.581	0.715	1.26
752	0.506	0.526	0.547	0.584	0.664	0.967
770	0.516	0.535	0.553	0.586	0.647	0.799
788	0.524	0.543	0.559	0.590	0.639	0.735
806	0.535	0.551	0.567	0.594	0.637	0.711
824	0.543	0.559	0.576	0.600	0.637	0.696
842	0.553	0.567	0.584	0.606	0.639	0.690

TABLE 65

Viscosity for Subcooled Liquid
and Superheated Water Vapor
from 1958 Timroth Tables[5]

Pressure, psia	2845	3556	4267
Temperature, °F	Viscosity $\times 10^8$, lb sec ft^{-2}		
662	156.5	161.4	165.7
680	144.2	151.6	157.3
698	60.42	138.9	147.5
716	58.78	113.9	136.2
734	58.37	71.48	119.6
752	58.37	66.32	94.22
770	58.58	64.72	79.88
788	58.99	63.90	73.53
806	59.40	63.70	71.07
824	60.01	63.70	69.64
842	60.63	63.90	69.02

A graphical representation of the various smoothed data is given in Figure 14. Solid lines were drawn through the derived values of the 1958 Timroth tables.[5] The data in the 1952[4] and 1958 Timroth tables are identical for pressures below 2845 psia and at higher pressures are somewhat different. This is surprising in view of the fact that Eq. (31) was used to compute the values of viscosity for superheated vapor in both these tables.

A dotted line was drawn through saturation values of viscosity from the 1952 Timroth tables. The values derived by Sigwart,[89] Schugajew et al.,[88] Timroth,[90] Jakob,[104] and Vukalovich[2] differ appreciably from the 1952 Timroth steam table values.[4] No basis is given for the viscosity values listed by Jakob.

A broken line was drawn through values obtained from a formulation[7] based on the data of Hawkins, Solberg and Potter.[100] Figure 14 indicates the magnitude of the exaggerated pressure dependence found by these investigators and the very much smaller pressure dependence found by Sigwart at the various Russian investigators.

The derived values of viscosity listed in the tables of Timroth[4,5,90] and of Vukalovich[2] are essentially based on the same measurements.[90] It was mentioned previously that there were appreciable differences between these derived values. It can be seen that in the vicinity of the critical point these differences may amount to as much as 10%.

Time did not allow the writer to smooth the combined measurements of Sigwart,[89] Schugajew and Sorokin,[88] and Timroth. Therefore, for the time being it is recommended that values of viscosity from the 1958 Timroth tables be used until the above appraisal becomes available.

E. Summary

(1) There is good agreement between the measurements of Schugajew,[87] Schugajew et al.,[88] Sigwart,[89] and Timroth.[90]
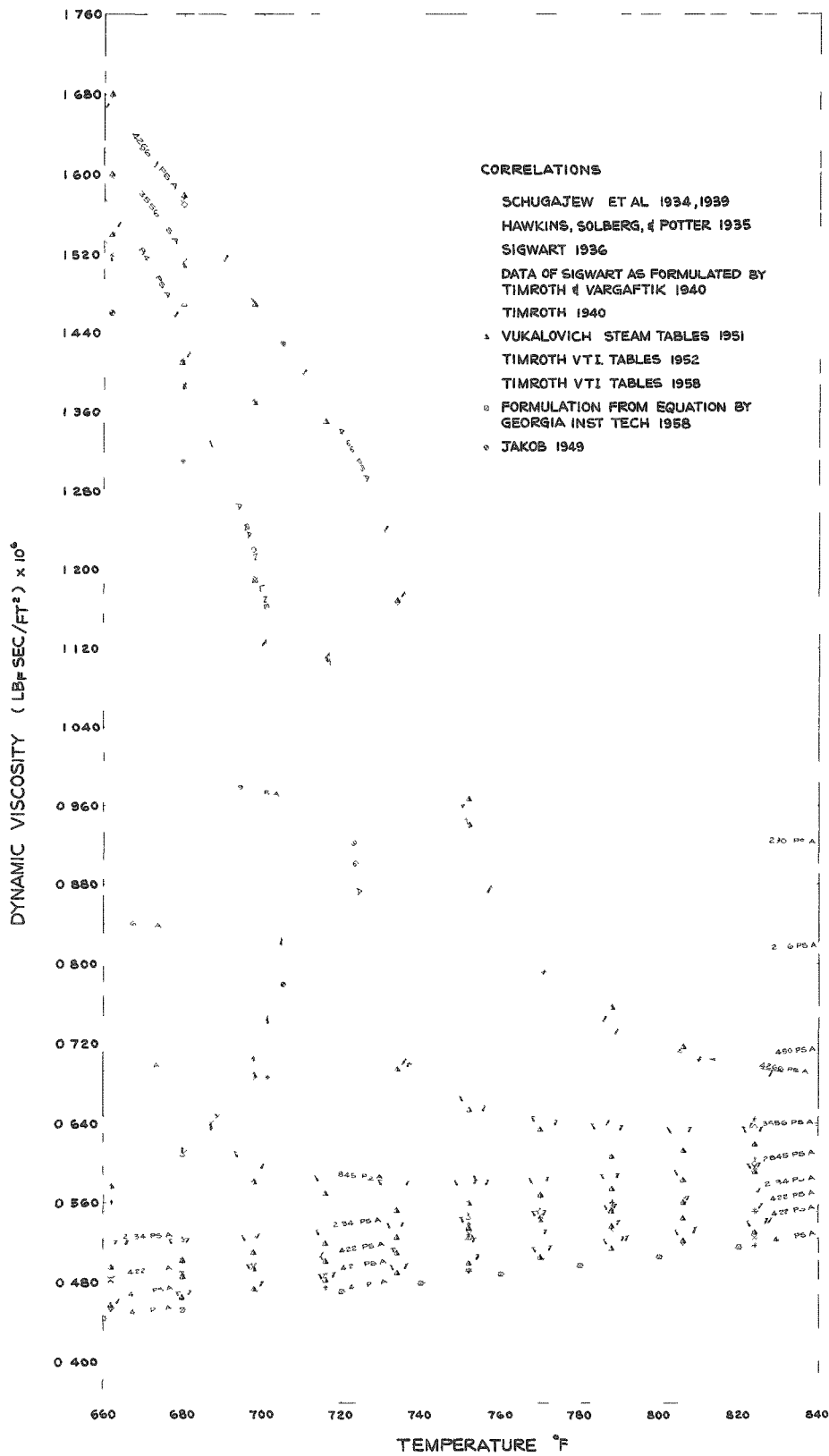
FIG 14 DYNAMIC VISCOSITY OF WATER AND WATER VAPOR
IN THE CRITICAL REGION

(2) Figure 14 indicated that the values obtained from the different formulations do not represent adequately the experimental values of viscosity in the critical region.

(3) It is recommended that a detailed analysis be made of measurements of viscosity in the critical region. Better values will be obtained if the measurements of Schugajew, et al.,[88] Sigwart,[89] and Timroth[90] are reappraised.

(4) The exaggerated pressure dependence found by Schiller, by Speyerer, and by Hawkins, Solberg and Potter were caused by systematic errors which were not taken into account.

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