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AN ANALYSIS OF SPECIFIC HEAT DATA FOR WATER  
AND WATER VAPOR IN THE CRITICAL REGION

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## NOMENCLATURE

$P$	pressure, psia
$V$	specific volume, $\text{ft}^3/\text{lb}$
$T$	absolute temperature, $459.69 + t$ , $^{\circ}\text{R}$
$t$	temperature, $^{\circ}\text{F}$
$U$	internal energy per pound mass, $\text{B}/\text{lb}_m$
$h = U + PV/J$	enthalpy, $\text{B}/\text{lb}_m$
$J$	mechanical equivalent of heat, $778.29 \frac{\text{lb ft}}{\text{B}}$
$C_V \equiv (\partial U/\partial T)_V$ ,	specific heat at constant volume, $\text{B}/\text{lb}_m \text{ } ^{\circ}\text{R}$
$C_{V_0}$	specific heat at constant volume for zero pressure
$C_P \equiv (\partial h/\partial T)_P$ ,	instantaneous specific heat at constant pressure, $\text{B}/\text{lb}_m \text{ } ^{\circ}\text{R}$
$C_{P_0}$	instantaneous specific heat at zero pressure
$C_{P\text{mean}} \equiv (\Delta h/\Delta T)_P$	mean specific heat at constant pressure over the temperature interval, $\Delta T$ , $\text{B}/\text{lb}_m \text{ } ^{\circ}\text{R}$
$C_{P\text{max}}$	maximum value for the instantaneous specific heat on a given isobar or on a given isotherm
$\beta = (1/V) (\partial V/\partial T)_P$	coefficient of volume expansion, $^{\circ}\text{R}^{-1}$
$\beta_{\text{max}}$	maximum value of the volume expansion coefficient along either an isobar or an isotherm
$\mu \equiv (\partial T/\partial P)_h$	Joule Thompson Coefficient, $\frac{^{\circ}\text{R ft}^2}{\text{lb}}$

Abbreviations

P-V-T	pressure, specific volume and temperature
JSME	Japan Society of Mechanical Engineers
VDI	Verein Deutscher Ingenieure, Germany

VTI All Union Institute, Moscow  
 MPI Moscow Power Institute

Miscellaneous

$Q$ , rate of heat addition or removal, B/hr  
 $G$ , flow rate of fluid,  $\text{lb}_m/\text{hr}$   
 $Q' \equiv h$ , amount of heat addition or removal per unit mass,  $\text{B}/\text{lb}_m$

Subscripts

$c$  property at the critical point  
 $f$  property of saturated water  
 $g$  property of saturated water vapor  
 $fg$  change in property between saturated liquid state and saturated vapor state at constant temperature  
 $m$  mean condition  
 $s$  property along the liquid-vapor saturation  
 $1,2$  known conditions

AN ANALYSIS OF SPECIFIC HEAT DATA FOR WATER  
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ABSTRACT

A comprehensive review of the available data for the specific heat at constant pressure of water and water vapor is given for pressures from 14.22 to 4300 psia and temperatures from 680 to 800°F. In addition a description is given of the various experimental techniques employed by different investigators to carry out measurements of this property.

Deviations of up to twenty per cent are shown to be in existence between the measured values of specific heat of different investigators. The estimated apparent overall error in the specific heat measurements was found always to be within five per cent. In view of the actual deviation it would appear that the various estimates that have been made on the apparent overall error are somewhat optimistic. The authors of this report have attempted to show that excessive random and systematic errors may arise in the critical region when values obtained from mean specific heat measurements are considered as being identical to the instantaneous values of specific heat.

There are no specific heat formulations  $C_P = C_P(P, T)$ , in existence for that part of the critical region where the specific heat first increases with temperature, attains a maximum finite value, and then subsequently decreases with temperature. Consequently, the smoothed values of the specific heat at constant pressure of various steam tables were derived by graphical interpolation of different experimental data. Deviations between the various smoothed data for the specific heat at constant pressure approach and even exceed thirty per cent. This is especially true in the regions of maxima of various isobars. These large deviations are due, in part, to the error introduced by graphical interpolation and also to the previously mentioned deviations among the experimental data.

In this work values of the specific heat were derived in the critical region from P-V-T data. The deviations between the derived and measured values were generally between ten to twenty per cent. Near the critical point, at supercritical pressures, and in the region of maximum specific heats along various isobars, the deviations were larger. However, except for one point, even these deviations were entirely within forty per cent.

Finally it is shown that the pressure and temperature relation corresponding to the maximum values of specific heat along isobars is different to that corresponding to specific heat along isotherms. This is significant insofar as it was previously thought by other investigators that the locus of points on a pressure temperature diagram defining  $(\partial C_P / \partial P)_T = 0$  was identical to the locus of points defining  $(\partial C_P / \partial T)_P = 0$ . The authors are not certain of the physical significance of the region enclosed by the locus of points on a pressure temperature diagram defining  $(\partial C_P / \partial T)_P = 0$  and  $(\partial C_P / \partial P)_T = 0$ . It is quite possible that the region enclosed by the above two curves is the boundary between the liquid and vapor phases in the supercritical region.

THE HISTORY OF THE UNITED STATES

CHAPTER I

THE EARLY HISTORY OF THE UNITED STATES

THE DISCOVERY OF AMERICA

The discovery of America by Christopher Columbus in 1492 is one of the most important events in the history of the world. It opened up a new world of opportunity and led to the development of a new continent.

The early history of the United States is a story of exploration, discovery, and settlement. It begins with the arrival of the first Europeans in the Americas and continues through the years of colonial expansion and the struggle for independence.

The early years of the United States were marked by a period of rapid growth and expansion. The country grew from a small collection of colonies to a vast nation that stretched across a continent.

The early history of the United States is a story of a people who sought freedom and opportunity. It is a story of a nation that was born in struggle and grew through adversity.

The early history of the United States is a story of a people who were determined to create a new society. It is a story of a nation that was built on the principles of liberty and justice for all.

## CHAPTER I

### INTRODUCTION

#### A. General

Research is being conducted by the School of Mechanical Engineering, Purdue University, on the phenomena of heat transfer in water over a wide range of pressures and temperatures encompassing the critical point ( $P_c = 3208$  psia,  $V_c = .0525$  ft<sup>3</sup>/lb and  $t_c = 705.5^\circ\text{F}$ ). Comprehensive studies are being made of forced, free, and combined forced and free convection in the subcooled water and superheated water vapor regions. These studies are both experimental and theoretical so that intercomparisons of both will be possible.

The thermodynamic and transport properties of direct interest in heat transfer are pressure, volume and temperature data; coefficient of volume expansion; enthalpy; specific heat at constant pressure; dynamic viscosity; and thermal conductivity. Thus the success of heat transfer investigations will depend primarily on an accurate and detailed knowledge of the above properties in the critical region. Therefore in conjunction with the above heat transfer investigations, parallel studies are being conducted on the thermodynamic and transport properties of water and water vapor.

The subject of this report is the specific heat at constant pressure,  $C_p$ , of subcooled water and superheated water vapor. Because of the complexity of the topic, this study was limited to the region of pressures from 14.22 to 4300 psia and temperatures from 680 to 800°F. Heretofore such specific heat information has been widely scattered throughout the literature and much has also been in the form of unpublished reports of different investigators.

The starting point of this work began with a study of the smoothed values of various steam tables.<sup>(1-8)\*</sup> The text by Dorsey<sup>(9)</sup> and the survey report by Callendar<sup>(10)</sup> were excellent sources of information throughout the entire investigation.

This report is divided as follows: Chapter II gives a complete survey of available experimental data for the specific heat at constant pressure. Chapters III and IV review the various formulations and smoothed values proposed for the specific heat. Chapter V gives a description of the different methods and procedures used to derive values for the specific heat from P-V-T values. Chapter VI reviews the various attempts made to obtain a functional relation for pressure and temperature locating the maxima of specific heat along isobars and isotherms in the supercritical region.

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

At the end of each chapter, conclusions and recommendations are made. A considerable amount of time was devoted toward making this work as comprehensive as possible. An effort was made to obtain all papers and reports dealing with  $C_P$  data for water and water vapor which have been published during the past thirty-five years. Dorsey's text<sup>(9)</sup> was relied upon for the earlier experiments on the specific heat at constant pressure for water and water vapor. Even the earlier work was consulted in a few cases where it proved possible and convenient.

## B. Definitions

To avoid misunderstanding, this section will give certain definitions of terms which appear frequently in the text of this report. These definitions will be of help and useful in explaining certain discrepancies between various sets of specific heat data. Thus, this section will consider the significance and full meaning of enthalpy and specific heat at constant pressure.

### Enthalpy, h

In the past, enthalpy bore such names as heat content, total heat and thermal potential. It is defined as the sum of the internal energy and the pressure specific volume product, i. e.

$$h \equiv U + PV/J \quad (1)$$

The authors of various thermodynamic texts<sup>(11-14)</sup> show, from First Law consideration, that the heat added to a unit mass of a pure substance under constant pressure and during a non-flow process is equal to the change in enthalpy.

### Specific Heat at Constant Pressure, $C_P$

The instantaneous specific heat at constant pressure is defined as

$$C_P \equiv (\partial h / \partial T)_P \quad (2)$$

It may be interpreted analytically as being the value of the tangent at a given condition along a constant pressure curve of enthalpy versus temperature (isobaric curve). The instantaneous specific heat at constant pressure of water and water vapor is a function of both pressure and temperature, i.e.  $C_P = C_P(P, T)$ . Furthermore it has very large values in the critical region. For example, at the critical point  $C_P$  is infinite in value.

If accurate values of enthalpy were available at close intervals of temperature along an isobaric curve reliable values for the tangent (i.e. the specific heat) may be derived by a finite difference technique. It is usual to consider the quantity so derived as the mean specific heat over a temperature interval  $\Delta T$ . The mean specific heat is defined therefore as,

$$C_{P\text{mean}} \equiv (\Delta h / \Delta T)_P \quad (3)$$

Thus, it may be seen from Equations (2) and (3) that there is a fundamental difference between the mean and instantaneous specific heat. However, in the limit as  $\Delta T$  approaches zero  $(\Delta h / \Delta T)_P$  approaches  $(\partial h / \partial T)_P$ . Hence, if the limit exists, the mean specific heat becomes identical with the instantaneous specific heat.

It may be shown that the mean and instantaneous specific heat at constant pressure are related as follows,

$$C_{P\text{mean}} \equiv \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} C_P dT \quad (4)$$

It may be concluded from Equation (4) that the mean specific heat between  $T_2$  and  $T_1$  will only be identical to the instantaneous specific heat at a temperature of  $(T_2 + T_1)/2$  if the variation of the instantaneous specific heat at constant pressure with temperature is linear or fulfills very special conditions.

### C. Systematic Errors Introduced in Specific Heat Determinations

The continuous flow method has been used extensively to measure the specific heat at constant pressure. It consists of passing a predetermined amount of fluid through a constant area duct (calorimeter) at nearly constant pressure. The temperature change between the inlet and outlet of the calorimeter is measured along with the corresponding heat addition or removal to or from the fluid in the calorimeter.

A number of systematic errors are associated with such measurements. The systematic errors of most importance are caused by the kinetic energy of fluid flow, by the throttle effect due to friction and finally by the error resulting from the assumption of the equality between the mean and instantaneous specific heat. In a well designed experiment the first two mentioned errors are of secondary importance compared to the third error.

#### 1. Kinetic Energy Correction

The heat added during a nearly constant pressure flow process may only be assumed identical to the change in enthalpy of the fluid if the changes in the flow kinetic energy are small compared to the heat addition. The calorimeters which were used by various investigators appear to be designed in such a manner that the kinetic energy changes, which are marked in the critical region, are insignificant compared to the amount of heat added. Thus if kinetic energy changes are insignificant, the mean specific heat may be alternatively defined as

$$C_{P_{\text{mean}}} \equiv (Q/G\Delta T)_P \equiv (Q'/\Delta T)_P \quad (5)$$

## 2. Throttling Effect Due to Friction

The pressure loss due to the action of friction between the fluid and the walls of the calorimeter is known as the throttling effect. A small reduction in static temperature is associated with the above pressure loss. In most of the specific heat investigations described in this report, the throttle effect was taken into account even though it was very small.

## 3. Instantaneous and Mean Values of Specific Heat

The variation of enthalpy with temperature along a given isobar in the supercritical region is very marked. It will be recalled that the specific heat at constant pressure at a temperature  $T$  is in reality equal to the magnitude of the tangent of such an isobaric enthalpy temperature curve at the same temperature,  $T$ . Thus, in the critical region significant errors conceivably could arise if values for  $(\Delta h/\Delta T)_P$  are assumed identical to the values for the instantaneous specific heat. This error will be termed throughout this report as a systematic error. It should be pointed out that it is not possible to eliminate this error completely from an experimental investigation. However, it may be reduced to minimum values by reducing the increment  $\Delta T$ . If this is done precise measurements must be made of both  $\Delta h$  and  $\Delta T$  which is extremely difficult in the critical region.

Large random errors may result in the critical region if the mean temperature is uncertain by even  $0.1^\circ\text{C}$ . This represents about the limit with which temperatures are measured in very carefully controlled P-V-T experiments. These factors are probably the cause of the excessive deviations between various sets of data.

## CHAPTER II

## MEASUREMENTS OF THE SPECIFIC HEAT AT CONSTANT PRESSURE

A. General

It was mentioned in Chapter I that several methods may be used to obtain values for the specific heat at constant pressure. The direct method will be the term used here to designate the continuous flow calorimetric method of determining specific heat. Most of the investigations described in this report were carried out by the direct method. However, several indirect methods such as the graphical differentiation of enthalpy and P-V-T data have been used to derive values for the specific heat.

According to Jakob<sup>(15,16)</sup> one of the first direct measurements of the specific heat of superheated water vapor were those by Knoblauch at the Munich Technical Institute. The investigations were first begun around 1900 and ended in 1935. The apparent error in these measured values of specific heat may still be estimated at about five per cent. This compares quite favorably with the magnitude of the probable error that has been estimated in more recent measurements of specific heat.

At the turn of this century, Barnes<sup>(17)</sup> conducted painstaking direct specific heat measurements on subcooled water at a pressure of one atmosphere from 32 to 212°F (0 to 100°C). The error in his experiments was small and it may still be estimated at being around one part in a thousand. This even compares very favorably with more recent specific heat investigations at the National Bureau of Standards.

B. Measurements for Superheated Water Vapor

Table 1 shows the extent of direct and indirect measurements of the specific heat at constant pressure of superheated water vapor. A considerable amount of overlapping of the ranges occurs. However, these measurements when considered as a single unified body of data are invaluable in obtaining the variation of specific heat with temperature and pressure in the critical region.

The care taken during the course of the investigations of Knoblauch and Koch<sup>(18)</sup> at the Munich Technical Institute is noteworthy. For example even the very small throttle effect was evaluated very accurately from the results of special throttling experiments. An error of only two tenths of one per cent would have been introduced if the effect were ignored. During the specific heat investigations of Knoblauch and Koch the weight rate of flow of the water vapor ranged between 22 to 37 lb/hr (10 to 17 kg/hr). The heat addition to the superheated water vapor was generally between 160 and 700 B/hr (40 to 175 kcal/hr).

Table 1

EXTENT OF  $C_p$  MEASUREMENT ON SUPERHEATED WATER VAPOR

Investigator(s)	Type of Experiment	Temperature Range		Pressure Range	
		$^{\circ}\text{C}$	$^{\circ}\text{F}$	$\text{kg}/\text{cm}^2$	psia
Knoblauch and Koch, 1929 Reference 18	Direct	250 to 500	482 to 932	20 to 120	260 to 1700
Trautz and Steyer, 1931 Reference 19	Indirect	350 to 500	662 to 932	150 to 300	2135 to 4270
Koch, 1932 Reference 22	Indirect	377 to 381	710 to 718	240 isobar	3410 psia isobar
Koch, 1932 Reference 23	Direct	to 450	to 832	120 to 200	1700 to 2840
Havlicek and Miskovsky, 1936 Reference 24	Direct	320 to 450	610 to 850	100 to 400	1420 to 5680
Timrot, 1950 Reference 25	Direct	350 to 480	662 to 896	200 to 300	2840 to 4270
Sirota and Timrot, 1956 Reference 27	Direct	200 to 375	392 to 707	20 to 120	285 to 1700
Sirota, A. M. 1958, Reference 28	Direct	300 to 550	572 to 1022	20 to 150	285 to 2135
Sirota and Maltzev, 1959 Reference 29	Direct	300 to 500	572 to 932	300 to 500	4270 to 7110
Sheindlin, 1954 Reference 31	Direct	194 to 660	381 to 1190	300 to 500	4270 to 7110
Russkazov and Sheindlin, 1957 Reference 32	Direct	280 to 685	535 to 1265	300 to 500	4270 to 7110
Vukalovich, Sheindlin and Russkazov, 1958 Reference 33	Direct	300 to 700	572 to 1290	500 to 700	7110 to 9950

The corresponding increase in temperature of the water vapor at the calorimeter inlet and outlet was between 4 and 25 $^{\circ}\text{F}$  (2 to 14 $^{\circ}\text{C}$ ). Since no error analysis was given by Knoblauch and Koch, an estimate on the error cannot be given for their measurements. However, because of the care taken, the error is probably of the order of several per cent.

Trautz and Steyer<sup>(19)</sup> derived values for the specific heat from their P-V-T measurements by means of the following relation,

$$\mu_{C_P} = \left\{ \frac{\partial h}{\partial P} \right\}_T = \frac{T^2}{J} \left[ \frac{\partial(V/T)}{\partial T} \right]_P \quad (6)$$

Even though their derived values do not compare favorably with recent direct measurements it should be emphasized that their pioneer values were a valuable contribution at the time. They gave an insight into the general variation of specific heat at constant pressure with temperature and pressure in the critical region. Their values showed that  $C_P$  along a given isobar in the supercritical region first increases with temperature, attains a finite maximum value and then subsequently decreases with temperature.

In 1928 Callendar<sup>(20,21)</sup> concluded from his thermodynamic property investigations on water that above the critical point (3210 psia, 705.2°F) there was an unstable two phase region, which extended up to 3650 psia and about 717°F. He considered that even though the meniscus had disappeared at the critical point (3210 psia, 705.2°F) the latent heat of vaporization would only become zero at 3650 psia and 717°F. Furthermore his experiments indicated that even a minute air content (0.003% by volume) influenced the variation of enthalpy with temperature of pressure in the critical region. Callendar considered that the true variation of enthalpy would remain unaffected only when the air content in the superheated water vapor was less than 0.001% by volume.

In 1932 Koch<sup>(22)</sup> carefully measured the variation of enthalpy difference with temperature along the 3410 psia (240 kg/cm<sup>2</sup>) isobar. These investigations were carried out with water vapor having air contents which varied from less than 0.001% to 0.003% by volume. Koch's measurements conclusively showed that such air contents did not influence the variation of enthalpy with temperature along the 240 kg/cm<sup>2</sup> isobar. There was no observable difference between the measurements of enthalpy difference with water vapor having air contents of between 0.001% and 0.003% by volume respectively. Koch concluded that above the critical point (3210 psia, 705.2°F), there is only a stable one phase region. He also stated that in Callendar's investigations the water vapor probably contained much larger air contents than 0.003% by volume. A comparison between the variation of enthalpy with temperature as measured by Koch and that conjectured by Callendar is given in Figure 1.\*

In 1932 Koch<sup>(23)</sup> also reported on specific heat investigations conducted at the Munich Technical Institute. A weight rate of water vapor flow of about 14 lb/hr (6.2 kg/hr) was used throughout the entire course of the investigations. He estimated that the flow rate did not fluctuate by more than one-half per cent during any specific heat test.

\*Koch<sup>(22)</sup> did not present his results in tabular form therefore Figure 1 was reproduced from his small scale diagram.

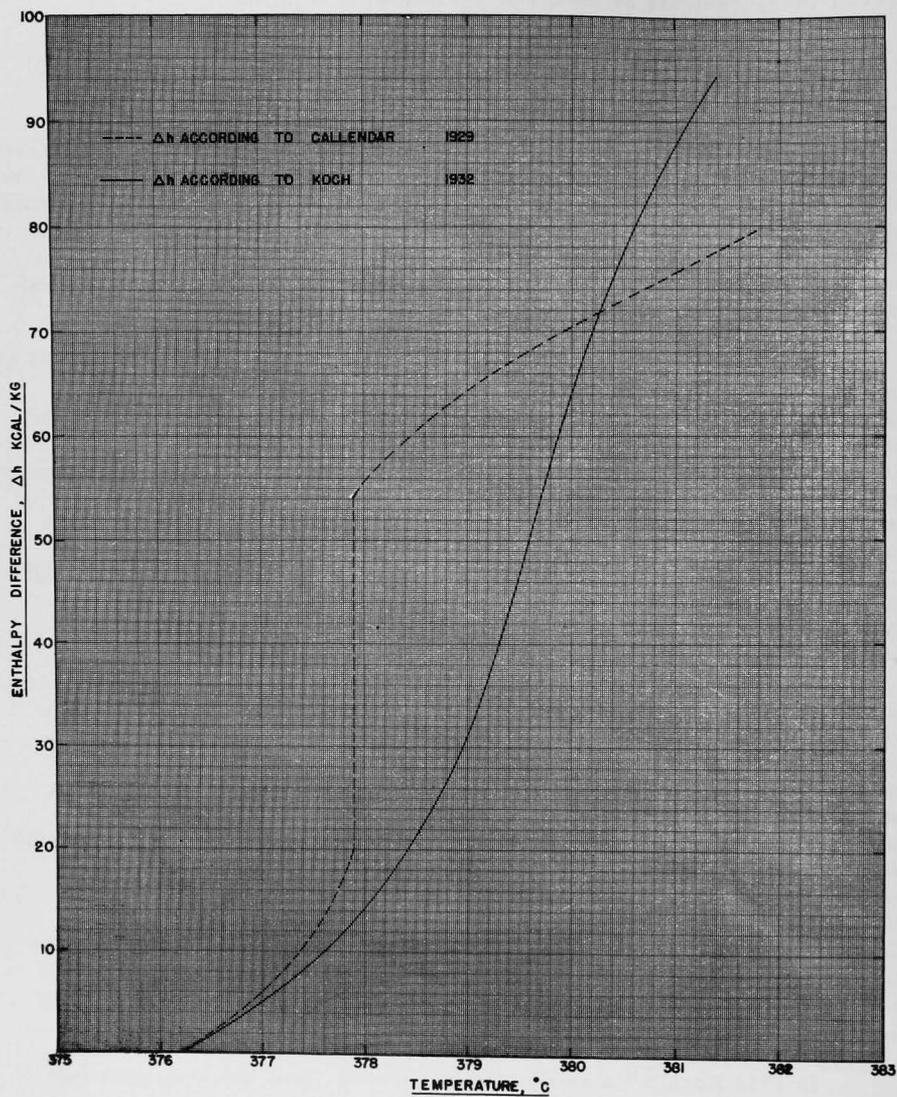


Fig. 1. Variation of  $\Delta h$  with Temperature at a Pressure of  $240 \text{ kg/cm}^2$

The temperature differences employed in the calorimeter ranged between 3.6 and 18°F (2 to 10°C). He estimated that the inlet temperature fluctuated between 0.036 and 0.09°F (0.02 and 0.05°C) and that the temperature reduction due to throttle effects was measured and determined to within 0.018°F (0.01°C).

If it is assumed that there were no heat losses, then the apparent error in his mean specific heat measurements is three and one-half per cent. Koch noted the maximum deviation of his measurements from a "best line" was around three per cent. It is reasonable to estimate therefore that the apparent error in Koch's specific heat measurements was nearly three per cent.

The investigations of Havlicek and Miskovsky<sup>(24)</sup> on the specific heat of water and water vapor extended well into the critical region. Instead of adding heat to the water vapor in the calorimeter, heat was removed as the water vapor flowed through the calorimeter. The water vapor flow rate employed during a typical experiment was between 6.6 and 35 lb<sub>m</sub>/hr. (3 and 16 kg/hr), and was determined accurately to within 0.025%. The heat removal during most experiments was around 1600 B/hr (400 kcal/hr). The additional heat removal which occurred due to heat losses and which was not determined by the calorimeter but by calibration was about 160 B/hr (40 kcal/hr). They estimated that the total heat removal, as determined by the water calorimeter and by calibration was known accurately to within one-half per cent. The corresponding temperature changes measured with resistance thermometers varied from 1.5 to 36°F (0.75 to 20°C). Havlicek and Miskovsky stated that these differences in temperatures between the entrance and exit of the calorimeter were measured to within 0.05°F (0.03°C). The temperature reduction caused by a throttling effect was probably quite insignificant since the pressure difference between the inlet and outlet of the calorimeter was less than 0.2 psia. If these estimates are correct, the apparent error in their mean specific heat determinations probably did not exceed four per cent.

Timrot<sup>(25)</sup> at the All Union Institute, VTI, was the first to conduct investigations on the specific heat of water and water vapor after World War II. In these experiments a predetermined amount of heat was transferred to a known amount of water vapor as it flowed through a well insulated calorimeter. The increase in temperature of the water vapor was measured with precision thermocouples. The flow rate of water vapor during the tests was between 4 to 16.5 lb/hr (1.8 to 7.5 kg/hr) while the heat input to the water vapor ranged from 160 to 320 B/hr (40 to 80 kcal/hr). The temperature difference of the water vapor between the entrance and exit sections of the calorimeter ranged from 0.4 to 43°F (0.2 to 24°C).

Timrot<sup>(26)</sup> stated that the flow rate of the water vapor fluctuated by around one half per cent. He further estimated that the mean flow rate was known accurately to within a tenth of one per cent. Moreover, in the region of maxima of specific heat along the various isobars, the temperature difference of the water vapor was measured accurately to within three per cent. The corresponding heat addition to the water vapor was determined accurately to within three tenths of one per cent while the mean temperature was measured to within 0.18°F (0.1°C). In view of these estimates it may be assumed that the apparent error in his measured values of specific heat in the region of maxima was approximately within four per cent.

The specific heat investigations at the VTI were subsequently extended into the subcritical and supercritical regions by Sirota and Timrot,<sup>(27)</sup> Sirota,<sup>(28)</sup> and Sirota and Maltzev.<sup>(29)</sup> These latter investigations were conducted with a new apparatus. It was estimated by the above investigators that the specific heat measurements were accurate to at least one and one-half per cent. These measurements are probably the most accurate that have been made in the subcritical and supercritical region. Considerable refinement was achieved and effected on temperature measurement.

There are factors, though, which indicate that the above estimates<sup>(27,28,29)</sup> of apparent error are somewhat optimistic. For instance it was stated that the water vapor flow rate was measured to within two tenths of one per cent while the temperature of the water vapor at the entrance fluctuated between 0.018 and 0.036°F (0.01 and 0.02°C). The minimum temperature difference between entrance and exit was around 2.2°F (1.25°C). Thus, even if the heat losses were insignificantly small, the apparent error in the measurements would appear to be around two per cent in the region of maxima along the various isobars. In addition to this Sirota and Maltzev<sup>(29)</sup> stated that there were sudden fluctuations in water vapor flow which interfered with the control of pressure and temperature. Therefore in the region of maxima, the error in their measurements are probably somewhat higher than two per cent due to the difficulty of controlling test conditions.

According to Romadin<sup>(30)</sup> and Sheindlin,<sup>(31)</sup> the MPI developed a new non-stationary method for the measurement of  $C_p$ . Sheindlin<sup>(31)</sup> utilized certain principles of both the flow and a non flow calorimeter to measure specific heat by the new method. During these experiments the water vapor flow rate ranged between 8.5 and 26 lb<sub>m</sub>/hr (2 and 12 kg/hr). The corresponding temperature differences between entrance and exit sections of the flow calorimeter was between 1 and 18°F (0.6 and 10°C). Sheindlin estimated that the apparent error in his specific heat measurements was about two per cent. This work at the MPI was subsequently extended with slight modification to the equipment by Russkazov et al.<sup>(32)</sup> and by Vukalovich et al.<sup>(33)</sup>

### C. Measurements for Subcooled Water

Table 2 shows the extent of some of the direct and indirect measurements of the specific heat at constant pressure for subcooled water. Bridgman's values of specific heat at room temperature and very high pressures were computed from his volumetric measurements by a graphical method.<sup>(34)</sup>

Table 2

#### EXTENT OF $C_p$ MEASUREMENTS ON SUBCOOLED WATER

Investigator(s)	Type of Experiment	Temperature Range		Pressure Range	
		°C	°F	kg/cm <sup>2</sup>	psia
Bridgman, Reference 34	Indirect	0 to 80	32 to 176	1000 to 12,000	14,000 to 168,000
Trautz and Steyer, 1931 Reference 19	Indirect	0 to 370	32 to 698	50 to 300	710 to 4270
Koch, 1934 Reference 35	Direct	0 to 350	32 to 662	50 to 300	710 to 4270
Havlicek and Miskovsky, 1936 Reference 24	Direct	350 to 370	662 to 698	150 to 300	2130 to 4270
Timrot, 1950 Reference 25	Direct	350 to 373	662 to 703	225 to 300	3200 to 4270
Sirota and Maltzev, 1959 Reference 29	Direct	12 to 373	54 to 704	26 to 500	370 to 7100
Sheindlin, 1954 Reference 31	Direct	194 to 372	381 to 702	300 to 500	4270 to 7100
Russkazov and Sheindlin, 1957 Reference 32	Direct	280 to 374	536 to 705	300 to 500	4270 to 7100
Vukalovich, Sheindlin, Russkazov, 1958 Reference 33	Direct	280 to 365	536 to 689	550 to 700	7820 to 9940

Precise calorimetric measurements on subcooled water were undertaken by Koch<sup>(35)</sup> with the same apparatus which was used to measure the specific heat of water vapor.<sup>(22,23)</sup> The water flow rate was either 13 or 19 kg/hr (29 or 42 lb/hr). The temperature difference during these experiments ranged from 9 to 18°F (5 to 10°C). From the error analysis of Koch<sup>(35)</sup> the apparent error in the specific heat measurements may be estimated as being well within one per cent.

The apparatus and techniques which were used to measure the specific heat of subcooled water by Trautz *et al.*,<sup>(19)</sup> Havlicek *et al.*,<sup>(24)</sup> Timrot,<sup>(25)</sup> Sirota *et al.*,<sup>(29)</sup> and Sheindlin *et al.*,<sup>(31-33)</sup> were identical to that used by them to obtain the specific heat of superheated water vapor.

#### D. Comparisons

The results of the measurements on the mean specific heat of subcooled water and superheated water vapor are given in Tables 3 to 8. A comparison of the various measurements is given in Figure 2.

Table 3

#### MEASUREMENTS OF KOCH

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_P$ , B/lb °F
2844.7	695.44	3.96	4.246
	696.72	7.83	4.075
	697.31	7.36	3.933
	698.27	10.84	3.792
	703.13	7.48	3.122
	706.45	16.86	2.878
	730.64	8.80	1.822
	756.10	18.63	1.414
	782.94	8.23	1.187
	807.37	17.46	1.056
	807.39	17.64	1.050
	837.23	8.38	0.957
3413.5	710.6		7.5
	712.4		12.5
	714.7		25
	715.3		36
	716		32
	717.8		17

Table 4

## MEASUREMENTS OF HAVLICEK AND MISKOVSKY

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_p$ , B/lb °F
2844.7	682.86	5.04	3.41
	683.02	4.95	3.48
	694.80	3.94	4.42
	694.83	3.92	4.43
	750.56	33.95	1.499
	753.53	35.10	1.452
2986.91	705.63	11.34	4.175
	707.14	12.10	3.975
3129.2	689.65	13.73	3.183
	690.01	13.46	3.229
	696.78	17.99	4.92
	697.10	18.08	5.21
	705.99	2.43	7.50
	706.03	2.47	7.38
	713.84	11.29	4.301
	714.54	11.59	4.193
3200.3	681.69	18.50	2.373
	681.93	18.32	2.389
	695.46	11.45	3.869
	695.84	11.20	3.959
	702.88	3.83	11.84
	703.06	3.55	12.84
	707.18	3.11	15.92
	707.25	3.11	15.80
	712.18	7.36	6.655
	712.31	7.43	6.601
	723.20	13.73	3.580
	723.81	14.08	3.478
	740.12	21.06	2.351
	740.64	21.11	2.338
3413.6	713.21	2.43	20.18
	713.41	2.18	22.51
	715.24	1.39	35.63
	715.24	1.37	36.00

Table 4 (cont'd.)

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_p$ , B/lb °F
3413.6	717.37	2.72	18.17
	717.48	2.79	17.70
	721.47	5.89	8.345
	721.56	5.96	8.344
3555.9	683.46	8.26	2.116
	683.76	8.30	2.106
	684.97	19.37	2.147
	685.18	19.37	2.156
	691.52	7.49	2.373
	691.61	7.45	2.382
	702.19	15.89	3.131
	702.63	15.66	3.165
	714.33	7.36	6.723
	713.43	7.92	6.138
	717.84	4.18	11.86
	717.91	4.19	11.82
	721.60	2.48	20.45
	721.60	2.45	20.70
	724.57	3.73	13.79
	724.86	3.87	13.26
	730.36	7.07	6.970
	730.47	7.16	6.884
	738.68	11.66	4.308
	738.99	11.81	4.238
	739.44	4.57	4.056
	739.98	4.77	3.941
	744.98	5.56	3.376
	745.14	5.58	3.376
	750.88	6.88	2.900
	751.53	17.93	2.934
751.57	6.97	2.846	
753.06	18.56	2.824	
758.07	8.14	2.484	
758.93	8.24	2.475	

Table 4 (cont'd.)

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_p$ , B/lb °F
4267.0	680.97	25.02	1.717
	681.10	24.95	1.727
	702.82	21.51	2.096
	704.64	21.06	2.135
	720.57	17.93	2.723
	722.10	17.24	2.811
	735.67	12.29	4.131
	736.03	12.08	4.172
	745.59	8.44	6.087
	745.93	8.35	6.175
	753.91	8.01	6.619
	753.96	7.99	6.636
	761.83	9.70	5.613
	762.21	9.83	5.523
	773.40	14.09	3.983
	773.87	14.13	3.944
	788.05	19.64	2.872
788.61	19.85	2.850	

Table 5

## MEASUREMENTS OF TIMROT

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_P$ , B/lb °F
3200.3	684.27	4.40	2.52
	688.24	4.07	2.85
	696.47	4.84	4.26
	699.26	3.94	5.20
	700.16	3.69	5.56
	701.60	2.457	8.64
	703.38	1.06	20.69
	713.48	4.32	6.04
	716.16	5.13	5.08
	733.89	10.22	2.64
	752.49	13.23	2.05
	767.30	16.24	1.69
	771.80	17.10	1.62
	787.73	18.72	1.47
	788.77	19.08	1.43
	797.09	22.14	1.33
	800.71	21.15	1.32
3271.4	681.84	9.59	2.28
	682.23	9.49	2.30
	692.62	7.24	3.028
	698.59	5.71	3.97
	703.06	4.00	5.61
	704.01	3.73	5.98
	704.68	3.28	6.83
	705.09	2.853	7.91
	705.69	2.115	10.64
	706.28	1.440	15.67
	706.64	0.940	24.48
	707.27	0.603	37.60
	708.35	0.326	75.65
	711.59	2.358	11.19
	714.87	3.681	7.17
	716.85	4.19	6.25
	722.12	5.94	4.60
726.80	7.31	3.72	
747.61	12.47	2.32	

Table 5 (cont'd.)

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_P$ , B/lb °F
3413.6	685.18	4.99	2.29
	705.85	4.41	4.86
	707.90	3.64	5.98
	708.58	3.413	6.41
	709.30	3.281	6.68
	710.06	2.655	8.23
	711.41	2.30	9.62
	711.68	2.09	10.51
	712.15	1.471	15.19
	713.14	0.968	23.29
	714.38	0.709	31.78
	716.00	0.837	30.38
	717.66	1.530	16.94
	719.33	2.68	9.39
	720.37	2.95	8.82
	724.87	4.55	5.75
	731.30	6.44	4.10
743.36	9.54	2.85	
752.92	11.23	2.42	
3555.8	680.58	6.98	2.00
	685.89	5.895	2.07
	688.73	12.46	2.18
	692.56	5.78	2.38
	694.90	11.56	2.49
	699.21	3.87	2.85
	702.37	4.45	3.04
	703.98	3.879	3.20
	704.88	3.321	3.36
	707.09	3.465	3.52
	710.02	4.63	4.40
	712.47	2.734	5.19
	714.38	1.921	6.37
	716.77	1.494	9.37
	718.30	1.921	11.54
	719.49	1.550	14.43
	719.94	1.345	16.69
	720.68	1.215	18.54
	721.85	1.125	20.34
	722.41	0.794	18.11
723.88	1.471	15.19	
725.49	1.912	11.86	

Table 5 (cont'd.)

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_p$ , B/lb °F
3555.8	727.47	2.79	8.54
	728.46	2.961	8.06
	731.95	3.861	5.83
	742.17	6.62	3.84
	752.43	14.94	2.78
	764.19	19.42	2.26
	768.11	22.79	2.12
	777.76	25.36	1.85
	778.10	22.18	1.86
	779.54	25.20	1.84
3698.1	685.22	10.78	1.99
	692.82	9.43	2.26
	702.68	7.79	2.80
	712.02	5.73	3.83
	712.94	5.54	3.95
	717.10	4.27	5.20
	718.75	3.71	6.04
	720.00	3.26	6.85
	722.44	2.45	9.21
	723.52	2.174	10.44
	724.64	1.822	12.67
	725.54	1.696	13.95
	727.27	1.674	13.65
	727.45	1.670	13.61
	728.08	1.734	13.09
	728.85	1.82	12.49
	732.20	2.54	9.59
	737.64	4.03	6.25
	743.90	5.44	4.62
	757.22	8.66	3.02
760.01	9.20	2.85	
775.58	12.02	2.25	
3911.4	691.61	12.11	2.06
	692.28	11.72	2.10
	717.49	7.065	3.54
	726.03	5.29	5.60
	726.21	5.58	5.48
	731.23	3.470	8.54
	732.85	3.181	9.26
	733.91	2.851	10.31

Table 5 (cont'd.)

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_p$ , B/lb °F
3911.4	734.70	3.13	10.61
	735.49	2.745	10.64
	736.54	3.181	10.00
	738.61	3.20	10.07
	740.21	3.429	9.39
	741.63	3.681	8.64
	745.61	4.37	6.98
	750.15	5.51	5.62
	752.94	6.408	4.86
	763.32	13.19	3.35
	764.85	9.94	3.18
	777.63	17.64	2.55
	785.70	20.48	2.19
	800.56	15.41	1.88
4124.8	684.59	6.30	1.77
	703.78	9.40	2.20
	724.19	6.28	3.33
	728.24	5.38	3.83
	728.98	5.45	3.95
	732.11	4.52	4.65
	735.75	3.85	5.46
	738.14	3.375	6.25
	740.25	3.159	6.76
	742.01	2.90	7.37
	743.65	2.745	7.83
	748.58	2.77	7.86
	750.07	2.997	7.41
	752.86	3.321	6.72
	756.14	3.85	5.83
	761.09	4.81	4.71
768.60	6.39	3.64	
776.28	7.69	3.07	
4267.0	685.15	10.75	1.65
	703.94	8.82	1.99
	711.25	7.56	2.13
	715.30	9.16	2.36
	719.92	7.011	2.58
	726.94	5.67	3.15
	728.60	5.33	3.32
	732.51	4.68	3.77
	735.12	5.49	4.06

Table 5 (cont'd.)

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_p$ , B/lb °F
4267.0	738.46	3.62	4.69
	739.15	4.36	4.74
	743.18	3.78	5.58
	747.23	3.267	6.43
	749.16	3.141	6.65
	752.20	3.168	6.82
	755.87	3.26	6.62
	760.10	3.67	5.95
	766.22	4.54	4.83
	777.92	6.39	3.44
	790.95	6.71	2.58
	791.78	8.55	2.61
	806.20	9.05	2.10
	806.41	10.85	2.07

Table 6

## MEASUREMENTS OF SHEINDLIN

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_p$ , B/lb °F
4267.0	709.83	2.79	2.16
	712.60	3.08	2.25
	719.67	2.89	2.57
	720.05	2.56	2.57
	721.81	2.43	2.67
	723.25	2.38	2.70
	724.28	2.56	2.80
	731.68	1.75	3.60
	731.97	1.60	3.88
	732.11	1.63	3.89
	732.16	1.80	3.82
	732.23	1.67	4.03
	739.54	1.31	5.12
	740.10	1.31	5.19
	745.00	1.21	6.07
	745.23	1.17	6.21
	745.75	1.17	6.34
	751.95	1.06	7.04
	755.50	1.12	6.81
	755.54	1.12	6.82
	756.63	1.10	6.77
	762.01	1.37	5.71
	762.51	1.46	5.31
768.47	1.75	4.54	
777.03	1.80	3.54	
778.01	1.87	3.33	
788.51	2.34	3.22	

Table 7

## MEASUREMENTS OF RUSSKAZOV AND SHEINDLIN

Pressure P, psia	Mean Temperature $T_m$ , °F	Mean Specific Heat $C_p$ , B/lb °F
4267.0	685.90	1.73
	686.37	1.75
	686.93	1.78
	692.73	1.86
	693.05	1.83
	693.21	1.84
	726.82	3.16
	726.89	3.15
	726.98	3.14
	732.81	3.75
	733.14	3.80
	733.46	4.00
	747.39	6.43
	747.57	6.52
	747.73	6.65
	748.89	6.87
	749.17	6.96
	749.34	6.97
	750.13	7.01
	750.78	7.06
	751.28	7.11
	752.40	7.03
	752.41	7.02
	753.06	7.02
	754.63	6.95
	769.42	4.45
	768.90	4.55
	770.65	4.20
	779.16	3.20
	779.65	3.15
779.86	3.25	
788.36	2.70	
789.98	2.60	
793.85	2.51	
806.56	2.06	

Table 8

## MEASUREMENTS OF SIROTA AND MALTZEV

Pressure P, psia	Mean Temperature $T_m$ , °F	Inlet Temp - Outlet Temp $T_2 - T_1$ , °F	Mean Specific Heat $C_p$ , B/lb °F
4267.0	698.56	7.022	1.930
	706.50	6.277	2.148
	714.90	5.560	2.418
	721.72	4.853	2.742
	728.17	4.163	3.196
	735.15	3.334	3.978
	738.28	2.957	4.483
	741.36	2.601	5.085
	744.84	2.254	5.860
	746.58	2.590	6.238
	748.26	2.482	6.529
	749.32	2.722	6.662
	751.22	2.837	6.831
	751.95	2.812	6.850
	752.43	2.803	6.856
	753.39	2.984	6.827
	753.73	3.013	6.813
	754.11	2.999	6.782
	754.92	3.011	6.711
	755.56	2.783	6.644
	757.38	2.889	6.380
	759.20	3.100	6.065
	761.36	2.344	5.684
	764.87	2.637	5.075
768.47	2.963	4.534	
773.92	3.476	3.878	
779.04	3.827	3.416	
788.99	4.979	2.780	
797.74	5.794	2.418	

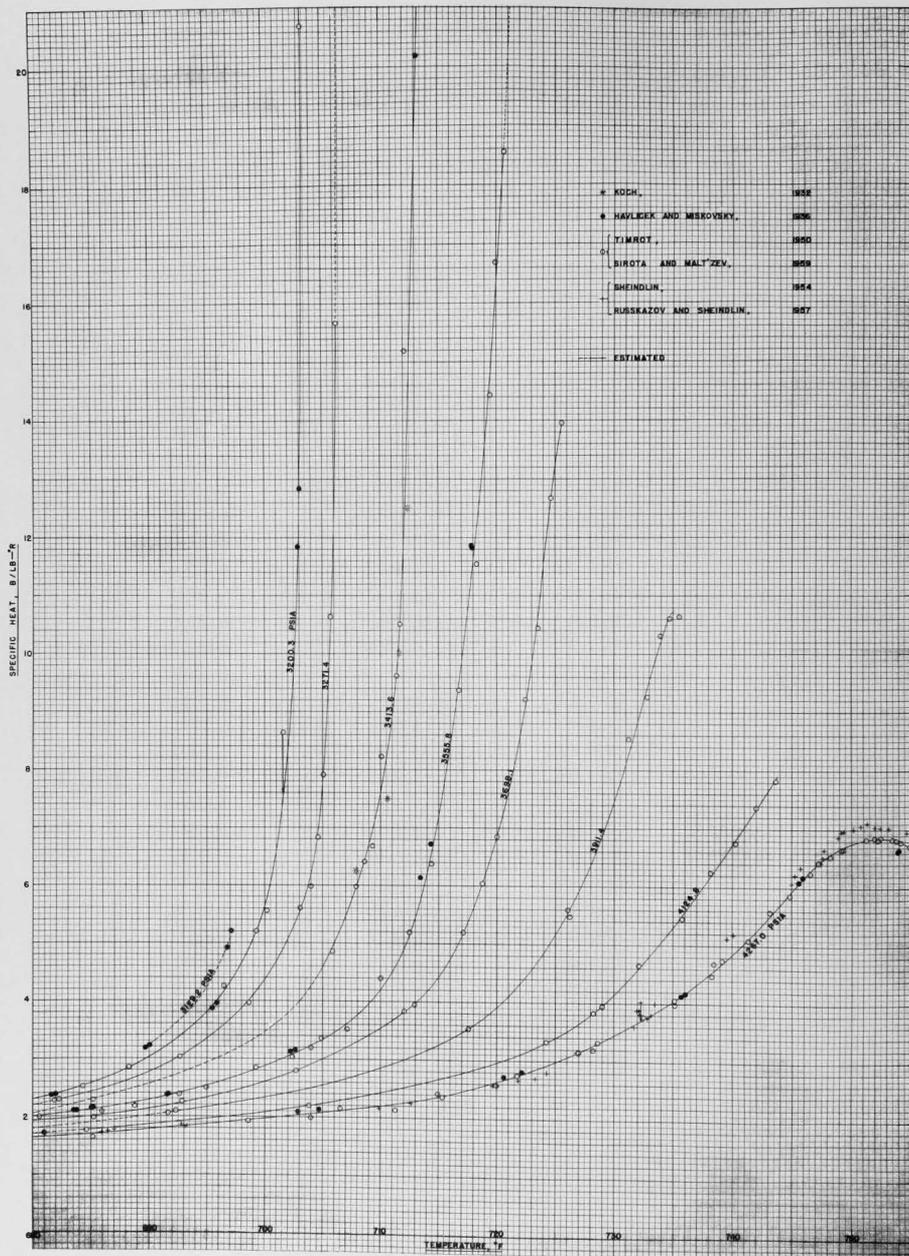


Fig. 2A. Experimental Values of Specific Heat Increasing with Temperature.

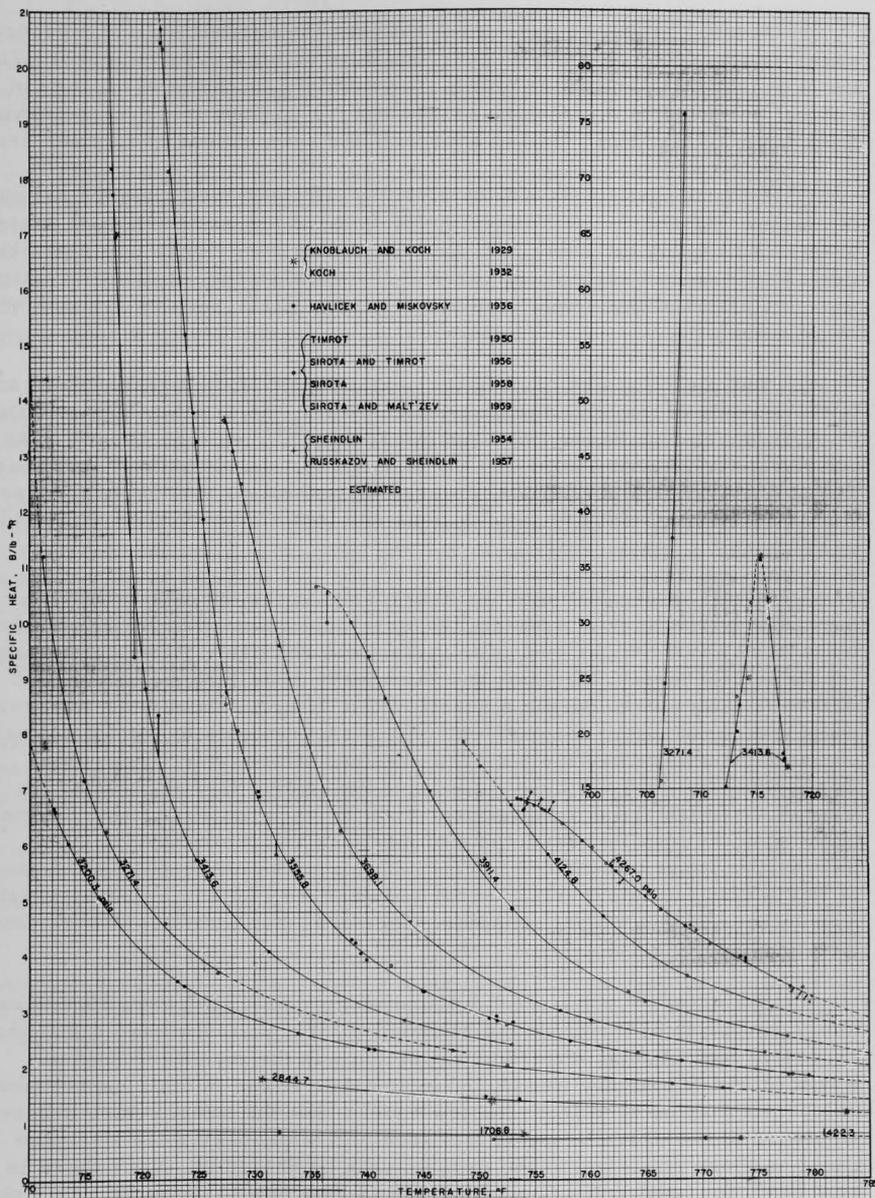


Fig. 2B. Experimental Values of Specific Heat (Decreasing with Temperature)

In most cases the agreement between the various sets of measurements is about four to five per cent, which is within estimated error. There are some notable exceptions to this; for example, in the near vicinity of the critical point and in the regions of maxima for various isobars, the deviations from a "best line" tend to approach and even exceed twenty per cent.

Several reasons have been given by different investigators for such deviations. Moreover each investigator favored his own particular measurements as being the most reliable. They also considered that a combination of random and systematic error in the experiments of other investigators were the cause of the disagreement. A review of the various reasons will be given below.

Timrot<sup>(26)</sup> stated that, in the near vicinity of the critical point and in the regions of maxima along various isobars, the error in the specific heat measurements of Havlicek and Miskovsky<sup>(24)</sup> could be greater than ten per cent. Timrot stated that the reasons for the error in the measurements of Havlicek and Miskovsky were due to the fact that the heat losses were only accounted for by calculations and that a poor method was used to measure the temperature.

It will be recalled that the heat losses in the specific heat determinations of Havlicek and Miskovsky were determined by special calibration tests to be about ten per cent of the total heat removal. After correcting for these heat losses, Havlicek and Miskovsky state that the enthalpy differences measured during a specific heat determination were in agreement with their highly accurate enthalpy measurements to within one-half per cent. Furthermore the temperatures and temperature differences were measured with specially calibrated resistance thermometers. In view of these factors it would appear that the error attributed by Timrot to the specific heat measurements of Havlicek and Miskovsky is quite pessimistic while the apparent error which may be estimated on the basis of Havlicek's and Miskovsky's error analysis may be somewhat optimistic. The authors of this report consider, therefore, that both sets of experimental data are equally reliable.

Sheindlin<sup>(31)</sup> subsequently found disagreement between his measurements and those of Havlicek and Miskovsky.<sup>(24)</sup> Sheindlin stated that the excessive temperature differences employed in the measurements of Havlicek and Miskovsky introduced systematic error in their experimental values. It may be seen from Tables 4 and 6 that the temperature differences employed in the experiments of Havlicek and Miskovsky were about the same as those employed in the experiments by Sheindlin. Thus there is no real basis for preferring Sheindlin's measurements to those by Havlicek and Miskovsky.

Sirota and Maltzev<sup>(29)</sup> on the other hand found agreement between their own measurements and those by Havlicek and Miskovsky.<sup>(24)</sup> They further considered that the large temperature differences employed by Havlicek and Miskovsky caused only a systematic error of less than one-half per cent in the regions of maxima.

Sirota and Maltzev<sup>(29)</sup> found that the deviation between their measurements and those by Sheindlin et al.,<sup>(31-33)</sup> was between five and seven per cent. They found also that the data of Sheindlin et al., were systematically higher than their measurements by around three or four per cent. Sirota and Maltzev attributed this deviation to the fact that the heat conduction through Sheindlin's resistance thermometer under calibration conditions differed from that during experimental conditions.

It is apparent that inconsistent reasons have been given for the disagreement between the various sets of measurements. The most important point that must be established is whether or not the disagreement is due to random error, such as in measurements of temperature or pressure, or systematic error, resulting from the use of large temperature differences. It is entirely possible that the present disagreement is a result of a combination of both of the above factors. An attempt has been made to resolve this dilemma and details will be found in Chapter V.

#### E. Summary

1. The majority of the measurements on the specific heat at constant pressure were obtained by the flow calorimeter method. The apparent overall error of the measurements were estimated to be within approximately one to five per cent. Figure 2 shows that when equal weight is given to the data of Koch,<sup>(23)</sup> Havlicek and Miskovsky,<sup>(24)</sup> Timrot,<sup>(25)</sup> Sheindlin et al.,<sup>(31-33)</sup> and Sirota and Maltzev,<sup>(29)</sup> they form a set of data which is adequate in tracing out the true variation of specific heat with temperature along various isobars.

2. In the near vicinity of the critical point and in the region of maximum specific heat for various isobars deviations tend to approach and even exceed twenty per cent. The cause for the deviations exceeding the limit of apparent error is not yet fully known.

## CHAPTER III

### FORMULATIONS PROPOSED FOR THE SPECIFIC HEAT AT CONSTANT PRESSURE

#### A. General

The various measurements on the mean specific heat reviewed in Chapter II formed the basis for several empirical formulations for the instantaneous specific heat at constant pressure. It was found that all of these formulations are unreliable in that part of the supercritical region, where the specific heat first increases with temperature, attains a maximum value and then subsequently decreases with temperature. Moreover to make practical use of these formulations high speed computing machines must often be employed. Nevertheless in spite of these factors a careful review will be given here of the various formulations proposed for the specific heat of water during the past thirty years. It is hoped that by combining certain of the underlying principles of each formulation a more reliable formulation may be attained.

#### B. Formulations Proposed by Various Investigators

Table 9 lists all of the formulations proposed for the specific heat at constant pressure during the past thirty years. These were all based on one or more of the various sets of experimental data given in Tables 3 to 8.

The formulation derived by Koch in 1932 is based solely on his measurements of mean specific heat at constant pressure.<sup>(23)</sup> A comparison may be obtained from Figure 3 of his measured and computed values of specific heat. In general the agreement between the computed and measured values is within experimental error (three per cent). There is however a paucity of data in the near vicinity of the vapor saturation line. In view of this and of the rapid variation of specific heat with temperature and pressure near the saturation line it is probable that near saturation conditions the error in computed values is in excess of three per cent.

Keyes et al.,<sup>(36)</sup> derived a formulation for  $C_P$  from their equation of state. This  $C_P$  formulation is the basis for the smoothed values in References 37, 38, and 39. The formulation is valid from the vapor saturation line to temperatures of about 460°C for pressures below 160 kg/cm<sup>2</sup>. The computed values agree with the measured values of Koch<sup>(23)</sup> to well within two per cent, i.e. entirely within experimental uncertainty. The formulation of Keyes et al.,<sup>(36)</sup> is valid for pressures higher than 200 kg/cm<sup>2</sup>. However, Keyes et al., do not calculate specific heat along isobars above 200 kg/cm<sup>2</sup>. It may be assumed that the Keyes' specific heat formulation is valid in the same region where their equation reproduces experimental P-V-T data satisfactorily.

Table 9  
EMPIRICAL EQUATIONS FOR  $C_p$  OF SUPERHEATED WATER VAPOR

Investigator(s)	Temp. Range °C	Press. Range kg/cm <sup>2</sup>	Equation*	Parameters**
Koch, 1932 Ref. 23	330 to 460	120 to 200	$C_p = A + BT^{-3.5} + CT^{-19} + DT^{-50} + BT^{-130}$	A = 0.49 B = $1.55 \times 10^7 P + 14 \times 10^7$ C = $6.036 \times 10^{39} (P + 80)^{5.58}$ D = $7.4302 \times 10^{130} (P-71)^{4.41}$ E = $7.9652 \times 10^{315} (P-19)^{21.79}$
Keyes et al., 1936, Ref. 36	100 to 460	1 to 200	$C_p = C_{P0} + AP + BP^2 + CP^4 + DP^{13}$	A, B, C and D are functions of temperature.
Schmidt, 1948 Ref. 40	100 to 460	1 to 300	$C_p = C_{P0} + \frac{A'}{D} + \frac{P}{(T/D)^{3.82}} + \frac{P^3}{D} \left\{ \frac{B'}{(T/D)^{15}} + \frac{C'}{(T/D)^{32.6}} \right\}$	A' = 9.62 B' = $0.9162 \times 10^{-2}$ C' = $1.503 \times 10^4$ D = 100
Vukalovich 1952, Ref. 2	100 to 700	1 to 300	$C_p = C_V + \frac{.1102 \left[ 1 + \frac{1}{V} \left( A + \frac{1}{V} \left\{ 8 - C \left[ 1 + \frac{.0069}{V} - \frac{35.57}{10^9 V^3} \right] \right\} \right) \right]^2}{1 - \frac{1}{V} \left( A_1 + \frac{1}{V} \left[ B_1 - C_1 \left\{ 1 + \frac{.0092}{V} - \frac{71.14}{10^9 V^3} \right\} \right] \right)}$	A = $\frac{5.2478}{(T/100)^{3.468}} + 8.5 \times 10^{-4}$ B = $\frac{4.69 \times 10^{-3}}{(T/100)^{3.468}}$ C = $(T/100)^{-6.936} \left\{ 107.25 - \frac{2639.6}{T/2} \right\}$ A <sub>1</sub> = $\frac{2.6863}{T} + \frac{4.2527}{(T/100)^{3.468}} - .0017$ B <sub>1</sub> = $\frac{.00571}{(T/100)^{3.468}}$ C <sub>1</sub> = $(T/100)^{-6.936} \times \left\{ 54.203 - \frac{1230.4}{T/2} \right\}$
Timrot, 1952 1958, Ref. 5 and 6	100 to 600	1 to 300	$C_p = C_{P0} + AP + BP^2 + CP^3 + DP^{3.8} + EP^9$	A, B, C, D and E are empirical functions of temperature.
Timrot, 1952 1958, Ref. 5 and 6	100 to 500	1 to 300	$Z = \frac{1}{0.3707} \left[ y - A(1 + y/B) \sqrt{1 - y/C} \right]$ $A = \frac{100}{2.74 x^3 + 9.3 x^2 + 5.8 x + 1.4019}$ $B = \frac{78.4}{x + 0.9284}$ $C = \frac{1}{x} \left\{ 150 + \frac{140}{x + 2.35} \right\}$ $x = (C_p - C_{P0})/K$ $K = 1.01 \left\{ 1 + \frac{a - \sqrt{a^2 - 42.8 (P \cdot 10^{-6}) - 10.19 P^2 \cdot 10^{-12} - 43.3}}{100} \right\}$	y = T - 648.16 Z = P - 227.82 a = $04244P - 6.353$
J.S.M.E. 1955, Ref. 7	100 to 550	1 to 300	$C_p = A + \frac{BT}{100} + \frac{C}{T/100} + \frac{DP}{(T/100)^{3.7}} + \frac{EP + FP^2 + GP^6}{(T/100)^{9.4}}$ $+ \frac{HP^6}{(T/100)^{31.5}} + \frac{JP^{26}}{(T/100)^{148}}$	A = 0.34618 B = 0.01832 C = 0.14047 D = 1.56229 E = 8081.1 F = 583.43 G = $-5.5785 \times 10^{-9}$ H = $6.0001 \times 10^{11}$ J = $6.3886 \times 10^{59}$
Sirota and Timrot, 1956 Ref. 44		20 to 120	$C_p = C_{P0} + \frac{PTN}{100 - PT}$	$\tau = 0.00261 \left\{ \frac{14350}{T} - 1 \right\}$ N = $647 \left\{ \frac{1}{273} - \frac{1}{T} \right\}$

\*All formulations are only valid in regions where the upper limit of the specific heat is between 1.0 and 4.0 kcal/kg°C (4.0 Btu/lb °F).

\*\*P = pressure kg/cm<sup>2</sup>; T = absolute temperature, °K; C<sub>p</sub> = specific heat, kcal/kg°C.

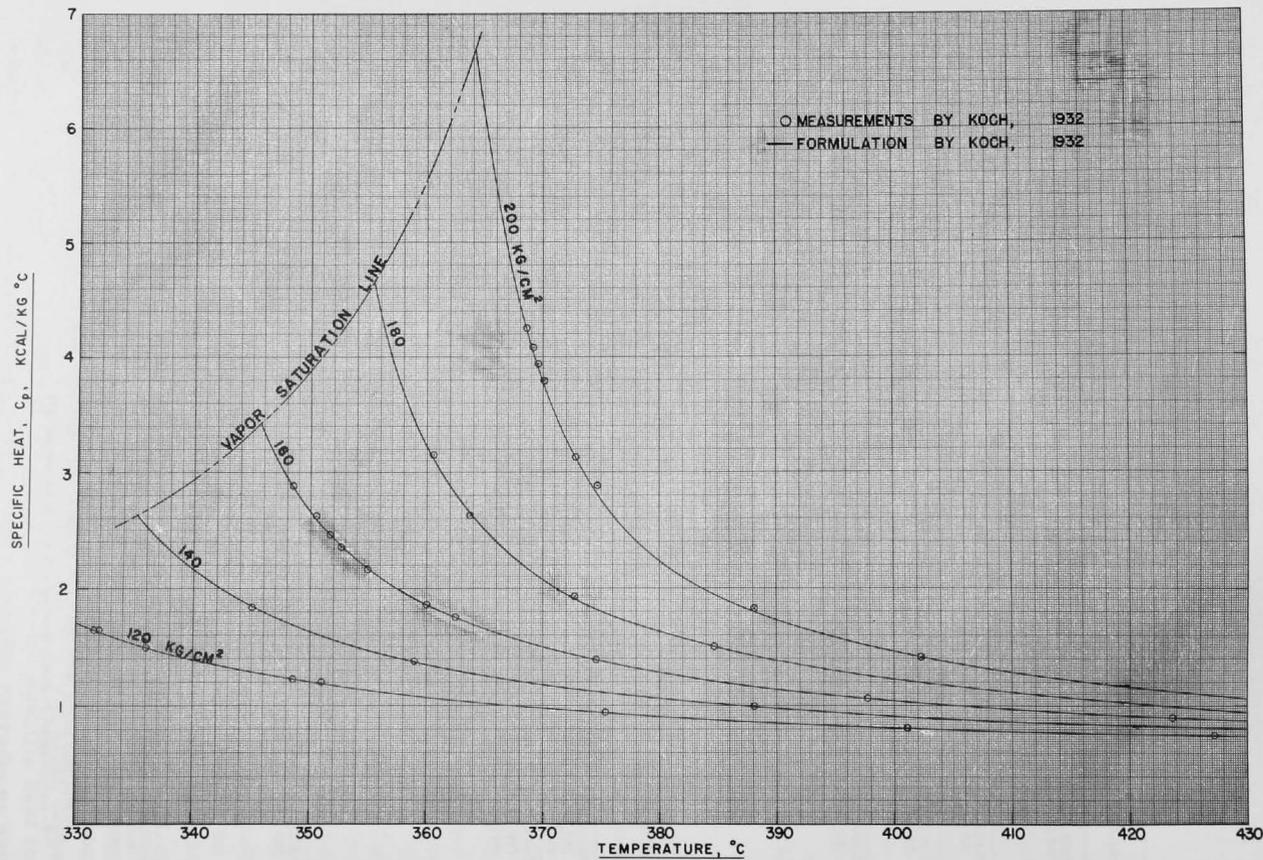


Fig. 3. Smoothed and Experimental Values of Specific Heat

Keyes *et al.*,<sup>(36)</sup> found that in the subcritical region, near the vapor saturation line, the specific heat values of their formulation were systematically lower than the measured values of Knoblauch and Koch.<sup>(18)</sup> The authors of this work estimate that a maximum deviation of around seven per cent occurs between the above computed and measured values along the 100 kg/cm<sup>2</sup> isobar. Interestingly enough Sirota and Timrot<sup>(27,28)</sup> found that their measured values of specific heat were systematically lower than the measured values of Knoblauch and Koch.<sup>(18)</sup> Deviation between these two sets of measurements approach a maximum of eight per cent along the 100 kg/cm<sup>2</sup> isobar near saturation conditions.

Both Keyes *et al.*,<sup>(36)</sup> and Sirota and Timrot<sup>(27,28)</sup> thought that measurements of Knoblauch and Koch<sup>(18)</sup> were invalidated near the saturation line as a result of droplets of liquid water being entrained in the water vapor. However, this is a conjecture and further investigations may show that the true specific heat is between the measurements of Sirota and Timrot<sup>(27,28)</sup> and those of Knoblauch and Koch.<sup>(18)</sup> For the time being though, the smoothed values of Keyes *et al.*, and the measured values of Sirota and Timrot may be considered as being the best available in the subcritical region.

Schmidt<sup>(40)</sup> derived the formulation given in Table 9 by starting with the following fundamental relation,

$$\left[ \frac{\partial C_P}{\partial P} \right]_T \equiv -T \left[ \frac{\partial^2 V}{\partial T^2} \right]_P \quad (7)$$

Integration of Equation 7 yields

$$C_P \equiv C_{P_0} - T \int_0^P \left[ \frac{\partial^2 V}{\partial T^2} \right]_P dP \quad (8)$$

Koch's equation of state<sup>(41,42)\*</sup> was subsequently employed to evaluate the integrand of Equation (8).

Schmidt<sup>(40)</sup> stated that, at high pressures and also in the immediate vicinity of the critical point, his formulation (Table 9) does not represent experimental data faithfully. The highest values of specific heat at constant pressure that may be computed from the formulation is 2.4 B/lb°F. It is reasonable to assume therefore, that his formulation is not valid in that part of the critical region for  $C_P > 2.4$  B/lb°F.

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\*Neither Schmidt<sup>(40)</sup> nor the steam tables by Schmidt or Koch<sup>(42)</sup> give the exact region where Koch's equation<sup>(41)</sup> is valid.

The formulation proposed by Vukalovich<sup>(2,3)</sup> was derived by starting with the relation,

$$C_P \equiv C_V - T \left[ \frac{\partial P}{\partial T} \right]_V \left[ \frac{\partial V}{\partial P} \right]_T \quad (9)$$

He used his equation of state<sup>(2,3)</sup> to evaluate  $(\partial P/\partial T)_V$ ,  $(\partial V/\partial P)_T$  and the specific heat at constant volume,  $C_V$ . Vukalovich's formulation is not valid in that part of the critical region where  $C_P$  is greater than  $2.8 \text{ B/lb}^\circ \text{R}$ .

Vukalovich's newer steam tables<sup>(4)</sup> unlike his older steam tables<sup>(2,3)</sup> gives no information for  $C_P$ . It may be seen from Equations (8) and (9) that various derivatives, i.e.,  $(\partial^2 V/\partial T^2)_P$ ,  $(\partial P/\partial T)_V$  and  $(\partial V/\partial P)_T$ , must be evaluated in order to compute specific heat at constant pressure. It follows therefore that the most probable reason for the absence of specific heat values in the newer tables of Vukalovich<sup>(4)</sup> and even those of Koch *et al.*,<sup>(42)</sup> are due to the fact that the equations are not yet tested in the subcritical and critical region or due to the fact that the derivatives from their equations of state are unreliable.

Attention is directed to some recent work done by the authors on the graphical differentiation of P-V-T data. The data used was estimated to be accurate to a few parts in ten thousand. The values obtained for  $(\partial V/\partial T)_P$  by several reliable methods were found to be accurate to within five per cent. The various equations of state are not valid in the critical region. However, even in the subcritical or supercritical regions they probably do not represent P-V-T data to a greater accuracy than that in the P-V-T data used by the authors of this work. Thus the derivatives from the various equations of state probably have an error in them which may be greater than five per cent.

The two specific heat formulations of Timrot<sup>(5,6)</sup> were derived from his measurements<sup>(24)</sup> and those of Knoblauch and Koch<sup>(18)</sup> and Koch.<sup>(23)</sup> The first formulation is similar in form to that derived by Keyes *et al.*,<sup>(36)</sup> It is valid only in the region where the specific heat is less than  $1.0 \text{ B/lb}^\circ \text{R}$ . Even in this region it is not valid on or near the saturation line. Timrot's second equation is valid in the following region,  $1.0 \leq C_P \leq 4.0 \text{ B/lb}^\circ \text{R}$ , and on and in the vicinity of saturation curve. In order to solve for specific heat using the second formulation it is necessary to solve a fifth order polynomial.

Figure 4 shows the limits for application of Timrot's equation. The agreement between computed and experimental values is, in the large majority of cases, satisfactory. However, there are regions where the deviations exceed 'apparent error.'

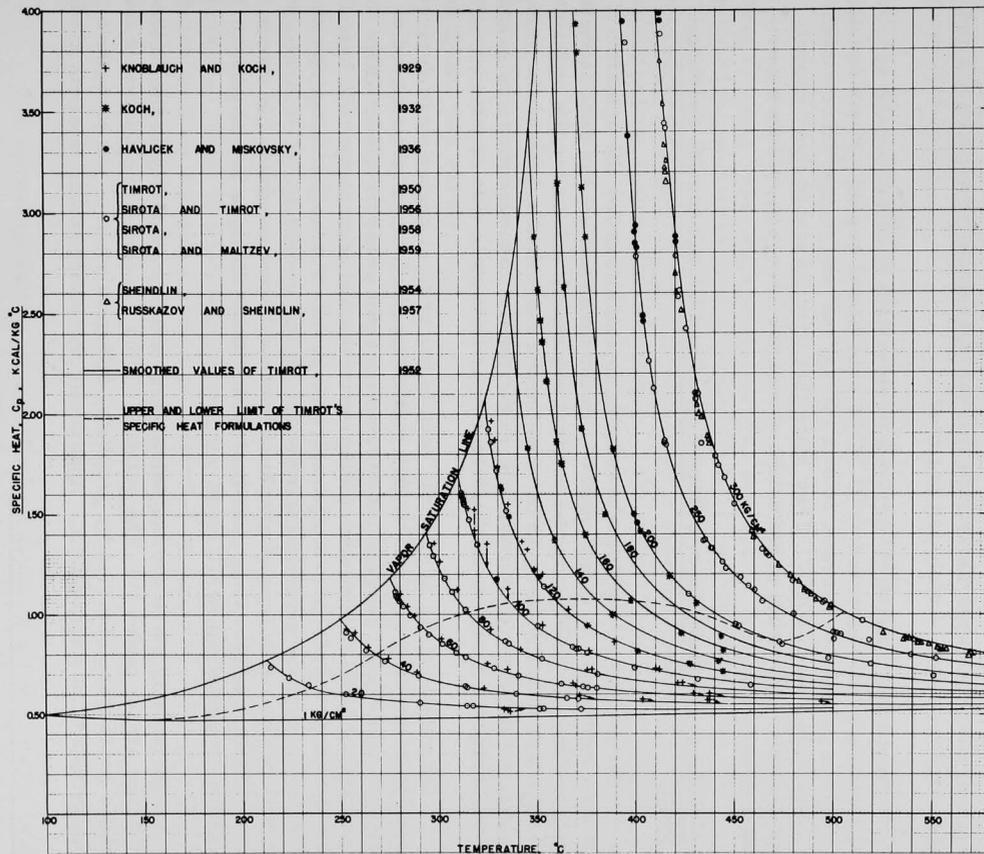


Fig. 4. Comparison Between Smoothed Values Derived by Timrot with Various Experimental Data

The formulation in the J.S.M.E. Steam Tables<sup>(7)</sup> was derived from Tanishita's equation of state.<sup>(43)\*</sup> Apparently the formulation for the specific heat at constant pressure is only valid in that region where the magnitude of the specific heat is less than 3 B/lb°R (3kcal/kg°C). A preliminary check has indicated that values from it are in good agreement (five per cent) with the smoothed values of Koch<sup>(23)</sup> and Keyes et al.<sup>(36)</sup> However, near the vapor saturation line the agreement is not as good and there are deviations of up to ten per cent.

Sirota and Timrot<sup>(44)</sup> derived an empirical equation for the specific heat from their measurements<sup>(27)</sup> in the subcritical region. Their equation is valid for pressures between 20 and 120 kg/cm<sup>2</sup> and temperatures from the saturation line to 400°C. They state that it represented their experimental data<sup>(27)</sup> to within a few tenths of one per cent, i.e., within experimental uncertainty.

### C. Graphical Methods Used to Derive Smoothed Values for the Specific Heat

The preceding section showed that formulations for the specific heat were only valid in that region where the magnitude of the heat capacity was less than 4.0 B/lb°R. In the critical region the values for the specific heat,  $C_P$ , are much larger. In this region the smoothed values of the various steam tables were derived from experimental measurements by graphical techniques. A review of these technique follows in this section.

Smoothed values of specific heat in the critical region were derived by Havlicek and Miskovsky.<sup>(24)</sup> The method used essentially consisted of constructing a  $C_P - t$  diagram at various constant pressures from their measurements.<sup>(24)</sup> From such a diagram lines of constant specific heat were drawn on a pressure-temperature diagram. A small scale graph of the latter diagram is given in their paper. In the immediate vicinity of the critical point this type of graphical method becomes unreliable due to the very large change of specific heat with minute changes in either the pressure or temperature.

No basis is given for the values presented graphically in the Keenan and Keyes steam tables.<sup>(1)</sup> The authors of this present work think that the specific heats were obtained by graphical differentiation of the smoothed enthalpy data\*\* of Reference 1. Apparently the temperature interval used

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\*The authors of this work were unable to obtain Tanishita's paper. Therefore, the basis of Tanishita's equation is not known with certitude.

\*\*The smoothed values of enthalpy in Reference 1 were essentially derived from the enthalpy measurements of Havlicek and Miskovsky.<sup>(24)</sup>

in evaluating the specific heat at constant pressure  $C_{P\text{mean}} \equiv (\Delta h / \Delta T)_P$  was ten degrees. In the vicinity of maxima along various isobars,  $P > P_C$ ,  $C_P$  values so derived could be in considerable error.

Smoothed values of specific heat are derived in the Timrot steam tables<sup>(5,6)</sup> solely from Timrot's measurements.<sup>(25)</sup> These values were obtained from isobars of  $C_P$  versus  $T$  constructed according to Timrot's measurements.

Vargaftik<sup>(58)</sup> by means of an unspecified graphical method derived  $C_P$  values from the measurements of Timrot,<sup>(25)</sup> and Havlicek and Miskovsky.<sup>(24)</sup>

Sheindlin et al.,<sup>(45,46)</sup> derived smoothed values for the specific heat of water vapor by a unique graphical method. Specifically they interpolated the measurements of Koch,<sup>(23)</sup> Havlicek and Miskovsky,<sup>(24)</sup> Timrot,<sup>(25)</sup> Sirota and Timrot,<sup>(27)</sup> Sirota<sup>(28)</sup> and Sheindlin et al.<sup>(31-33)</sup> The technique essentially consisted of first plotting measured values of specific heat against specific volume, with pressure as a parameter. The noteworthy feature of such a diagram is that isobars do not intersect. From this diagram, isochoric profiles were obtained, i.e.,  $1/C_P$  as a function of pressure with specific volume as a parameter. Such profiles along a constant volume line were found to have comparatively small curvature in the critical region. This again must be considered as noteworthy. From this diagram, a  $C_P - V$  diagram and then finally a  $C_P - T$  diagram was constructed.

They estimated that smoothed values so obtained were accurate to within two per cent, except in the region of maxima along various isobars. The uncertainty in the measured values in the region of maxima is significantly larger than that in the values far removed from the region of maxima. It was mentioned previously that Figure 2 shows deviation between various experimental values of five per cent in the regions far removed from the region of maxima and of up to twenty per cent in the region of maxima. Thus, it would appear that the Sheindlin et al., estimate of the error in their smoothed values is somewhat optimistic. However, the techniques employed by Sheindlin et al., appear to be both rational and fundamental.

#### D. Smoothed Values

The smoothed values of specific heat found in various steam tables and other reference sources for water vapor in the critical region are given in Figure 5. There is fair agreement between the smoothed values of various steam tables in the subcritical region, i.e., where specific heats are less than 4.0 B/lb/°F. The disagreement in the critical region and in the region of maximum specific heats reaches some thirty per cent.



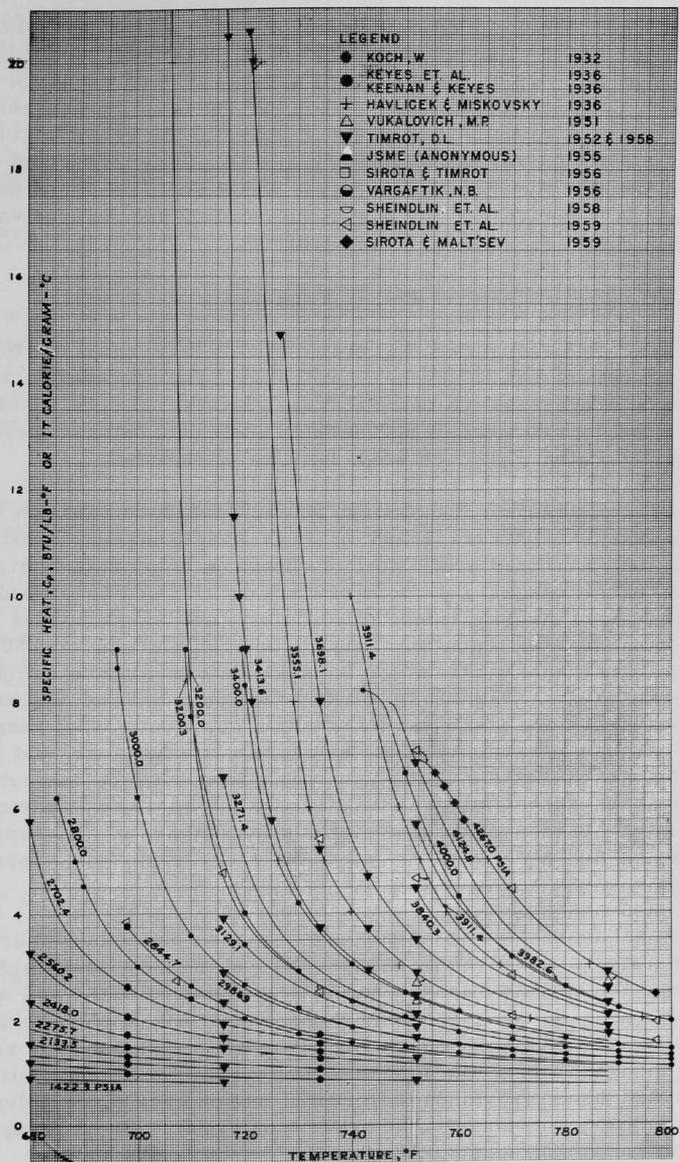


Fig. 5b. Smoothed Values of Specific Heat,  $C_p$ , For Water and Water Vapor.

One of the reasons for this discrepancy is due to the yet unexplained deviations among the experimental data of various independent investigations. However, since the latter amounts to at most twenty per cent, it becomes apparent that another reason for the larger disagreement among the data of various steam tables is due to the error introduced as a result of smoothing of the experimental data. This smoothing error becomes appreciable in the critical region where just one set of measurements are not adequate for the purpose of tracing out the true variation of  $C_p$  with either pressure and temperature.

#### E. Analytical Investigations Still in Progress

This report would not be complete if mention were not made of the various analytical investigations in progress. The fact that such investigations are in progress indicates that the variation of specific heat with pressure and temperature is still incompletely understood. Keyes<sup>(47)</sup> and Juza<sup>(48)</sup> stated that much work remains to be done.

Upon completion of extensive P-V-T measurements on water and water vapor,<sup>(36)</sup> Keyes embarked on several rigorous analytical investigations. Keyes utilized available P-V-T and enthalpy data to evaluate constants in the rational equations of state which were developed as a result of the above investigations. Specifically, his investigations led to the equations of state presented for water vapor in Reference 49, 50, and 51. Values of less than 4.0 B/lb°F for the specific heat may be computed from these formulations. Deviations between the computed and measured values of specific heat were small and were within "apparent experimental uncertainty." In the near vicinity of the saturation line however, and in the region where  $C_p$  approaches 4.0 B/lb°R, the deviations between computed and experimental measurements generally exceed the apparent experimental uncertainty.\* In view of these deviations the authors of this report think that this is a further demonstration of the underestimation of probable error in experimental values of  $C_p$ .

Apart from the theoretical investigations described, there have been machine programs devised by Skinner<sup>(52)</sup> and used by Boehringer<sup>(53)</sup> respectively, to compute thermodynamic properties of water and water vapor. A machine program was also used at the University of Manchester.<sup>(100)</sup> In these investigations Tchebichef's polynomials with as many as 400 coefficients were used in an attempt to formulate the thermodynamic properties of water and water vapor. In the critical region even these polynomial equations failed to represent the experimental data to within experimental uncertainty.

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\*Keyes further found that there were considerable deviations between  $C_p$  values obtained from equations based on P-V-T alone and enthalpy data alone. In some cases the deviations exceeded thirty per cent.

Juza<sup>(48)</sup> has devoted a considerable amount of time to the derivation of analytical formulations for the various thermodynamic properties. Currently he is revising his P-V-T formulations and one may presume that, subsequently, attention will be paid to such properties as the specific heat at constant pressure. It is noteworthy to mention that special attention is being paid by Juza to take into account the correct behavior of his formulation at the critical point.<sup>(54,55,56)</sup>

#### F. Summary

1. In the critical region the deviations between the various sets of experimental data are several times larger than the estimated apparent experimental error. Consequently the greater deviations between the various sets of smoothed data may be attributed in part to unexact and unreliable graphical methods of smoothing the existing data and in part to the yet unexplained differences in experimental data.

2. Various empirical equations proposed for specific heat are not valid in the critical region where the specific heat first increases with temperature, reaches a maximum, and then decreases with temperature.

3. A considerable number of analytical investigations are in progress throughout the world. This indicates that, in spite of extensive investigations which have been carried out, the theory of the equation of state for water vapor is incompletely understood.

## CHAPTER IV

### SPECIFIC HEAT ALONG THE VAPOR SATURATION LINE

#### A. General

It is not possible to measure the specific heat of either saturated water or saturated water vapor by a direct method. Consequently, most smoothed values at saturation conditions were derived by extrapolating the different measurements of specific heat in the superheated water vapor and subcooled liquid region to the saturation line. However, it should be noted that the possibility of moisture entrainment in the water vapor increases as test conditions approach saturation conditions. If such entrainment of moisture occurs the measurements of specific heat at constant pressure are subject to considerable error. Thus, if experiments were carried out with droplets of water entrained in the water vapor, the smoothed values of specific heat along the saturation line obtained through the extrapolation of direct measurements become unreliable.

Values for the specific heat of saturated water vapor have recently been derived from a combination of calorimetric and volumetric data in conjunction with thermodynamic relations by Sheindlin et al.<sup>(57)</sup> This is described in detail in the next section. As the critical point is approached values for the specific heats of both saturated water and saturated water vapor become very large. Due to this rapid change of specific heat with temperature, the values of specific heat obtained by all methods tend to become unreliable.

#### B. Values Along the Vapor Saturation Line

It was stated in Chapter III that Koch derived an empirical formulation from his specific heat measurements on water vapor.<sup>(23)</sup> This formulation was used to derive values along the vapor saturation line in the range from 608 to 689°F (320 to 365°C). Figure 3 indicates that there is a paucity of measured values in the near vicinity of the saturation line. It will be recalled that the apparent error in Koch's measurement is around three per cent. In view of the paucity of experimental data and also in view of the fact that all measurements tend to become unreliable near the saturation line, it is probable that smoothed values given along the saturation line by the formulation have an error greater than three per cent.

The specific heat formulation derived by Keyes et al.,<sup>(36)</sup> is valid along the vapor saturation line to about 651°F (344°C). The maximum deviation between the values of Koch<sup>(23)</sup> and Keyes et al.,<sup>(36)</sup> is around five per cent. The equation of state developed by Keyes in 1949 was based on his P-V-T measurements.<sup>(36)</sup> Deviation between the values obtained from the specific heat formulation<sup>(49)</sup> and the values computed by Koch<sup>(23)</sup>

reach a maximum of 6.3% at a temperature of 662°F (350°C). In view of the probable uncertainty in Koch's derived values, this agreement may be regarded as satisfactory. Since no values are presented for the specific heat of saturated water vapor above 350°C, it would appear that the equation of state derived in Reference 49 is valid only to 662°F (350°C).

Values for the specific heat of saturated water vapor which are given in a small scale graph in Reference 7 were derived from a specific heat formulation based on the equation of state of Tanishita.<sup>(43)</sup> The values so obtained agree to within five per cent with those of Keyes et al.,<sup>(36)</sup> and Koch.<sup>(23)</sup> This agreement may be regarded as satisfactory since it is within the limit of experimental uncertainty.

Vargaftik<sup>(58,59)</sup> derived specific heat values for saturated water vapor by extrapolating the measurements of Timrot,<sup>(25)</sup> Havlicek and Miskovsky.<sup>(24)</sup> Details of the extrapolation are not given. However the values so obtained are in good agreement with the derived data of Koch,<sup>(21)</sup> Keyes et al.,<sup>(36)</sup> and the JSME.<sup>(7)</sup>

By an altogether different method Sheindlin et al.,<sup>(57)</sup> in 1958 derived specific heat values for saturated water vapor for temperatures between 100 and 370°C (212 and 698°F). There were no values given above 370°C, presumably because the method becomes unreliable in the near vicinity of the critical point. The method and techniques which were utilized have some theoretical basis to them and therefore they will be noted in detail.

Sheindlin et al.,<sup>(57)</sup> utilized the following differential equation for two phase equilibrium derived by Planck<sup>(60)</sup>

$$C_{P_g} = C_{P_f} + dh_{fg}/dT - h_{fg}/T + h_{fg}/V_{fg} [ \{ \partial V_g / \partial T \}_P - \{ \partial V_f / \partial T \}_P ]$$

Thus the specific heat along the vapor saturation line may be evaluated, in principle, by utilizing the various sets of reliable volumetric and calorimetric measurements available for water and water vapor at and near saturation conditions.

The values utilized for the specific heat of saturated water were those derived by Koch by extrapolation of experimental subcooled water data up to 350°C.<sup>(35)</sup> Sheindlin et al., do not explain the source of values for this property for temperatures from 350 to 370°C but it is thought they derived them from Koch's measurements.<sup>(101)</sup>

The formulations and tabulated data for the enthalpy of vaporization and the specific volume of vaporization of Osborne et al.,<sup>(61,62)</sup> were utilized to derive values for  $dh_{fg}/dT$ ,  $h_{fg}/T$ , and  $h_{fg}/V_{fg}$ . The precision of these values along the saturation line is both noteworthy and well-known (within 0.1%).

Sheindlin et al., evaluated  $\left\{ \frac{\partial V_f}{\partial T} \right\}_P$  by graphically differentiating the P-V-T data of Keyes and Smith.<sup>(63)</sup> They estimated that the derivatives so derived were accurate to within two per cent. The term  $\left\{ \frac{\partial V_g}{\partial T} \right\}_P$  was evaluated by several indirect methods from the P-V-T data of Keyes et al.,<sup>(64,65,66)</sup> and Timrot. The first method consisted of constructing a diagram with PV/RT as the ordinate and 1/V as the abscissa. The second method consisted of constructing a diagram having  $V(1 - PV/RT)$  as the ordinate and 1/V as the abscissa. Temperature was a parameter in both cases. Since isotherms in both systems of coordinates are almost linear it was relatively straightforward to measure the tangents and thence derive values for  $\left\{ \frac{\partial P}{\partial V} \right\}_T$ . Slopes along isometrics are easily measured. Thus from this knowledge of  $\left\{ \frac{\partial P}{\partial V} \right\}_T$  and  $\left\{ \frac{\partial P}{\partial T} \right\}_V$  the term  $\left\{ \frac{\partial V_g}{\partial T} \right\}_P$  was calculated from the following relation,

$$\left[ \frac{\partial V_g}{\partial T} \right]_P = - \frac{(\partial P / \partial T)_V}{(\partial P / \partial V)_T}$$

Sheindlin et al., found that the values of  $(\partial V_g / \partial T)_P$  obtained by the two methods were in good agreement. No estimate is given of the relative accuracy. However, Sheindlin et al., stated that the values obtained for the derivative  $\left\{ \frac{\partial V_g}{\partial T} \right\}_P$  by the two methods were in excellent agreement with values obtained from the equation of state of Keyes et al.,<sup>(67)</sup> for saturation temperatures to 300°C. Sheindlin et al., considered that the values for the derivative  $\left\{ \frac{\partial V_g}{\partial T} \right\}_P$  from the equation of state were not reliable for temperatures greater than 300°C.

From the above calculation Sheindlin et al., reached the following conclusions: For saturation pressures between 8 and 16 kg/cm<sup>2</sup> their derived values for the specific heat of saturated water vapor were in satisfactory agreement with the extrapolated values of Knoblauch and Winkhaus.<sup>(68)</sup> Between 20 and 30 kg/cm<sup>2</sup> their derived values were in satisfactory agreement with the extrapolated data of Knoblauch and Raisch.<sup>(69)</sup> In the region of saturation pressures between 20 and 120 kg/cm<sup>2</sup>, their derived values were somewhat lower than these of Knoblauch and Koch<sup>(18)</sup> and also lower than that of Sirota and Timrot.<sup>(27)</sup> Better agreement, however, was secured with the latter set of data. For saturation pressures between 120 and 200 kg/cm<sup>2</sup> their derived values were found to be higher than the values computed by Koch.<sup>(23)</sup> Finally for values near the critical point their values were somewhat higher than the values derived by Vargaftik.<sup>(58,59)</sup>

It is interesting to note that Sheindlin et al., considered that in the vicinity of the saturation line the experiments of Knoblauch and Koch<sup>(18)</sup> and Sirota and Timrot<sup>(27)</sup> were invalidated because of entrained droplets of liquid water being in the superheated water vapor. Sheindlin et al. also considered that the values derived by Koch<sup>(23)</sup> were not reliable. He

stated that reliable values could only be obtained if there were more measurements near the vapor saturation line. Sheindlin et al., concluded that further theoretical and experimental investigations were needed to establish the cause of the various discrepancies (as high as 43% at 698°F), which far exceeded the estimated probable error.

Figure 6 shows various sets of smoothed values for the specific heat of saturated water vapor. It is evident that the deviations become larger as the critical point is approached.

The authors of this report near the end of its preparation found that very recently Sheindlin et al.,<sup>(70)</sup> derived new values of specific heat along the vapor saturation line in the range from 32 to 644°F (0 to 340°C). Time did not permit the authors to study the new analysis of Sheindlin et al.<sup>(70)</sup> However, the newer values of these authors agree with the derived (extrapolated) values of Vargaftik<sup>(58,59)</sup> to well within three per cent.

### C. Summary

1. Measurements of specific heat near the vapor saturation line are subject to considerable error when moisture is entrained in the water vapor.

2. The specific heat varies markedly with pressure and temperature near the vapor saturation line. In view of the paucity of measurements extrapolated values of specific heat in this region are subject to considerable error.

3. Sheindlin et al.,<sup>(57)</sup> found that his values derived by computation were significantly different to those obtained by extrapolation by Knoblauch and Koch<sup>(18)</sup> and by Vargaftik.<sup>(58,59)</sup>

4. Further work is necessary to establish correct values of specific heat along the vapor saturation line.

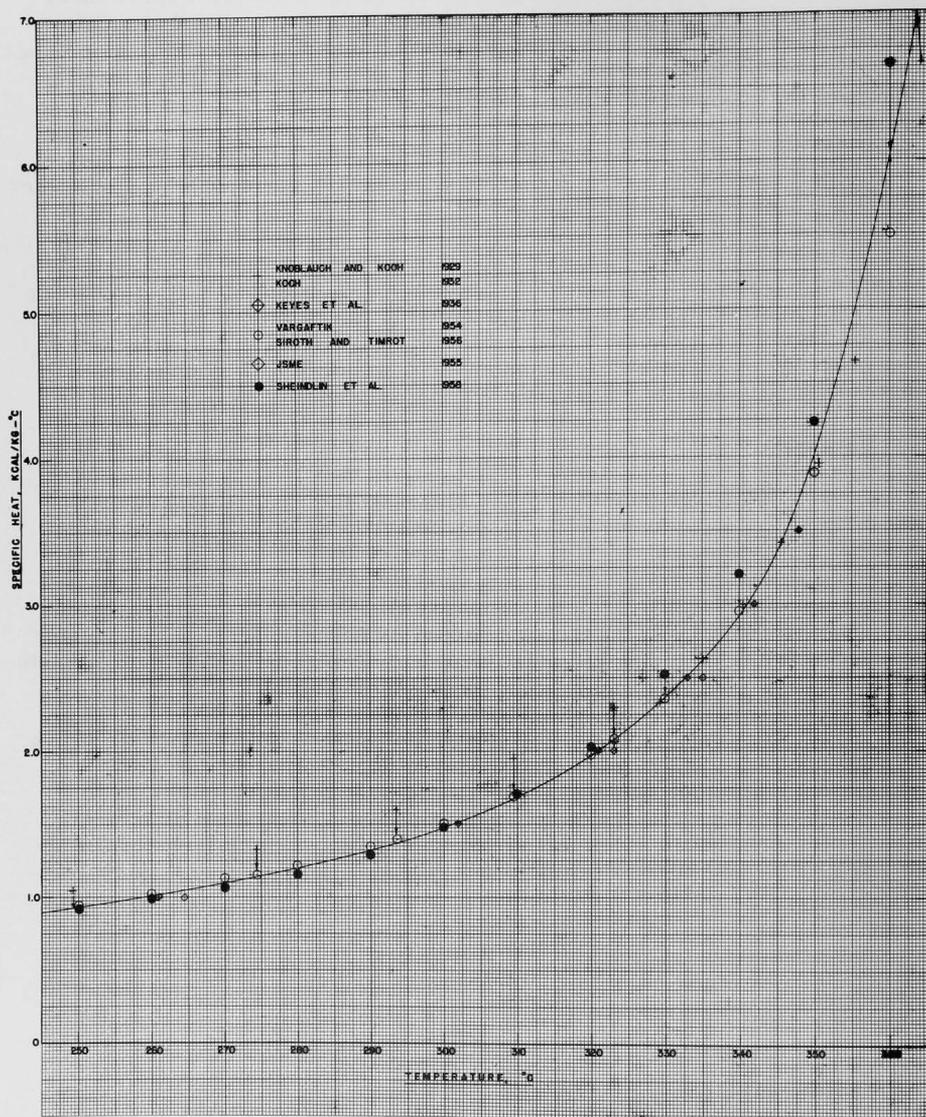


Fig. 6. Specific Heat of Saturated Water Vapor

## CHAPTER V

### AN ANALYSIS OF SPECIFIC HEAT

#### A. General

In the near vicinity of the critical point and also in the regions of maxima along various isobars, the disagreement between various experimental data for specific heat was found in Chapter II to be around twenty per cent. This is four to five times larger than the estimated apparent over-all error. Some investigators are of the opinion that this disagreement is attributable to the fact that temperature differences in the flow calorimeter were excessively large. Other investigators are of the opinion that the disagreement is attributable to erroneous temperature measurement techniques or experimental techniques. These conjectures were inconsistent and were made without any rational basis. The purpose of this chapter is to determine the actual causes for the above disagreement. The analysis consisted of deriving values for the specific heat at constant pressure from P-V-T data. A comparison was subsequently made between enthalpy differences obtained from the integration of  $C_P$  - T isobaric curves which were constructed from derived and measured data respectively. Details of the method used will be given in the event that it will form the basis of future analyses.

#### B. Derivation of $C_P$ - $C_V$ Relation

The relation

$$C_P - C_V = \frac{T}{J} \left[ \frac{\partial P}{\partial T} \right]_V \left[ \frac{\partial V}{\partial T} \right]_P \quad (11)$$

was derived by Nusselt<sup>(71)</sup> by means of a geometrical construction. Nusselt in his derivation considered that a subtangent of an isobar on a T-S diagram is  $C_P$  while the subtangent of a constant volume line on a T-S diagram is  $C_V$ . Equation (11) is applicable to a pure substance such as water and water vapor.

The partial derivative  $[\partial P/\partial T]_V$  represents the tangent of a constant specific volume line at a given pressure and temperature. The authors of this investigation made a recent analysis of the P-V-T measurements of Timrot<sup>(26)</sup> and Keyes et al.<sup>(36)</sup> This analysis, described in Reference 72, showed that the relation

$$\left[ \frac{\partial P}{\partial T} \right]_V = \frac{R'}{V}$$

where

$$R' = \left[ \frac{dP_s}{dT} \right]_{T_c} \left[ V_c \right]$$

was valid to within one per cent for specific volumes from 0.0400 to 0.1200 ft<sup>3</sup>/lb and temperatures from saturation to 752°F.

Substituting for  $[\partial P/\partial T]_V$  in Equation (11) yields

$$C_P - C_V = \frac{R'T}{J} \left\{ \frac{1}{V} \left[ \frac{\partial V}{\partial T} \right]_P \right\}$$

Since

$$\beta = \left\{ 1/V \right\} \left\{ \partial V/\partial T \right\}_P$$

the above becomes

$$C_P - C_V = \frac{R'T\beta}{J} \quad (12)$$

The constant  $R'$  may be evaluated from the following values which were considered in References 73 and 74 as the most reliable:

$$V_c = 0.0525 \pm 0.0005 \text{ ft}^3/\text{lb}$$

$$(dP_s/dT)_{T_c} = 21.4 \text{ psia}/^\circ\text{R}$$

Using these data Equation (12) becomes

$$C_P = C_V + \beta T/4.81 \quad (13)$$

where  $C_P$  and  $C_V$  are in B/lb °F,  $\beta$  is in °R<sup>-1</sup> and  $T$  is in °R.

### C. Evaluation of the Coefficient of Volume Expansion

The difference  $C_P - C_V$  may be computed by utilizing values for the volume expansion coefficient and Equation (13). Time did not allow the computation of  $C_P - C_V$  along all of the isobars in Figure 2. Consequently, the difference in specific heat was computed only along the 225, 250 and 275 kg/cm<sup>2</sup> isobars.

Precise P-V-T data must be utilized to derive reliable values for the volume expansion coefficient. In References 73 and 74 it was concluded that existing steam data were not of utility for deriving reliable values for the volume expansion coefficient. Such suitable P-V-T data<sup>(75)</sup> has since

been derived from the P-V-T measurements of References 24, 36, 76, 77, 78 and 79. Values for the coefficient of volume expansion<sup>(80)</sup> were derived from the newly derived P-V-T data<sup>(75)</sup> by two graphical methods. The coefficient of volume expansion data used in this present work were derived from the data and methods used in Reference 80. These are thought to be accurate to within five per cent except in the region of maxima where they are probably accurate to within thirty per cent.

#### D. Values of $C_V$ Derived by Various Methods

The purpose of this section is to show how the specific heat at constant volume varies with specific volume and temperature in the initial region. A survey of the literature indicated that there is a paucity of data in the critical region.<sup>(81)</sup> The survey also found that values obtained by various methods were not consistent with one another. A review of the various methods used and some of the values obtained follows.

##### 1. Measurements of $C_V$

It is beyond the scope of this report to consider in detail all of the various direct methods which may be used to measure  $C_V$ . However, according to Partington,<sup>(81)</sup> direct measurements of  $C_V$  yielded discordant values. Partington further stated that values of  $C_V$  obtained by Wohl and von Elbe,<sup>(82)</sup> by explosion of a dry mixture of  $2H_2 + O_2$  does not agree with that calculated by Einstein's equation. They found that values of  $C_V$  obtained upon exploding a moist mixture were in closer agreement with values from Einstein's equation. Partington gives no values for the discrepancies or makes any mention of  $C_V$  at higher pressures.

Apparently Amirkhanov and Karimov<sup>(83,84)</sup> were the first to conduct measurements for  $C_V$  of water vapor in the critical region. Their method consisted of adding a known amount of heat to water vapor contained in a constant volume calorimeter. The maximum overall error was estimated at around two and one-half per cent. The measurements of References 83 and 84, shown in Figure 7, indicate that  $C_V$  is a function of both specific volume and temperature; i.e.,  $C_V = C_V(V, T)$ .

##### 2. Computed Values of $C_V$

It was mentioned in Chapter III that Juza<sup>(55)</sup> was engaged in analytical investigations on the thermodynamic properties of water and water vapor. Juza's most recent equation of state is still not finalized. However, it is interesting to mention that P-V-T values obtained from the equation were in good agreement with the values of References 73 and 75 in the region  $V \geq V_C$ . Juza's values of  $C_V$  which were computed by means of the recent equation of state<sup>(55)</sup> are shown in Figure 8.

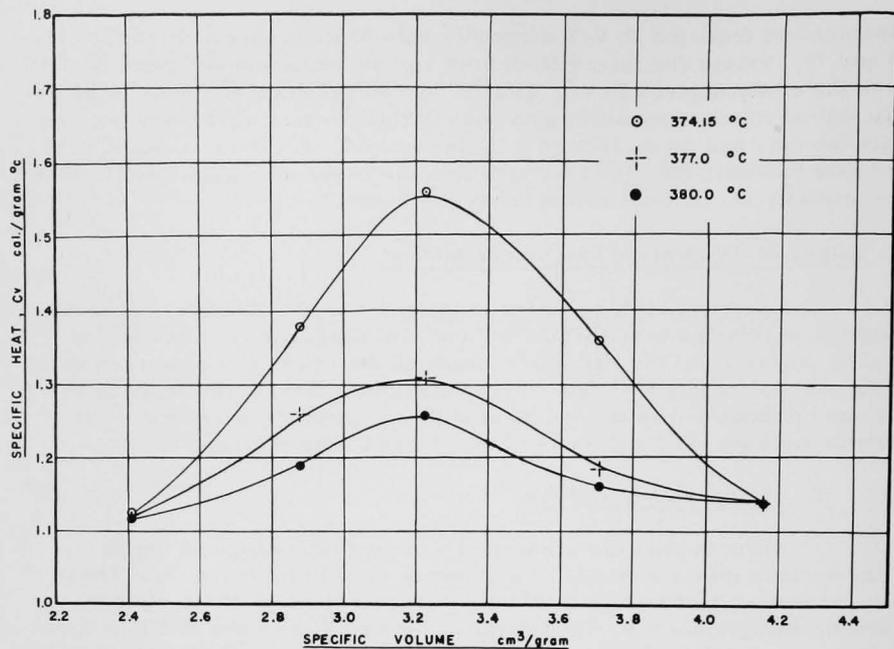


Fig. 7.  $C_v$  Measurements of Amirkhanov and Karimov

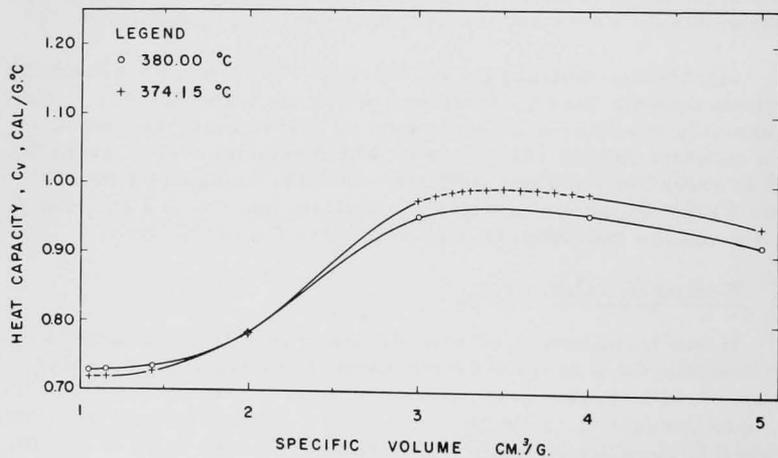


Fig. 8. Heat Capacity,  $C_v$ , According to Juza<sup>(55)</sup> Equation

It may be seen from Figures 7 and 8 that the experimentally observed values of  $C_V$  are not in agreement with the 'computed values.' For example, at the critical point the measured values<sup>(83,84)</sup> are some sixty per cent larger than the derived values of Juza.<sup>(55)</sup>

In view of these discrepancies the authors of this work attempted to derive some values of  $C_V$  in the critical region from internal energy data. The specific heat at constant volume is defined,

$$C_V \equiv \left\{ \frac{\partial U}{\partial T} \right\}_V \quad (14)$$

where  $U$  is the internal energy. Internal energy data was computed from enthalpy<sup>(24)</sup> and P-V-T data<sup>(75)</sup> by means of the relation

$$U = h - PV/J \quad (15)$$

By means of such internal energy data,  $C_V$  was derived for specific volumes between 0.0400 and 0.1000 ft<sup>3</sup>/lb and temperatures from the saturation line to 752°F. In view of the paucity of precise enthalpy data,<sup>(24)</sup> the variation of  $C_V$  with temperature along a constant volume line could not be evaluated. The available internal energy data, however, did indicate that such a variation is small. Even though the variation of  $C_V$  with temperature along an isometric could not be evaluated the authors did find a definite but small variation of  $C_V$  with specific volume at constant temperature. For example, it was found that  $C_V$  varied uniformly from 0.8 to 1.0 B/lb °F for specific volumes between 0.0400 and 0.0525 ft<sup>3</sup>/lb. For  $V > V_c$  no variation with either temperature or specific volume could be evaluated. Thus a good value for  $C_V$  in the region of specific volumes between 0.0400 and 0.1000 and temperatures from saturation temperature to 752°F is 1.0 B/lb °F. This value to within 0.2 B/lb °F is independent of temperature and specific volume.

P-V-T data may also be used to determine what variation of  $C_V$  occurs with temperature and specific volume. This may be accomplished by considering

$$\left[ \frac{\partial C_V}{\partial V} \right]_T = \left[ \frac{T}{J} \right] \left[ \frac{\partial^2 P}{\partial T^2} \right]_V \quad (16)$$

It was found in References 72, 73 and 75 that isometrics are very nearly linear in the region of pressures from 3000 to 4000 psia, specific volumes from 0.0400 to 0.1200 ft<sup>3</sup>/lb and temperatures from saturation to at least 752°F. Thus, this P-V-T data indicate almost zero change of  $C_V$  with specific volume along an isothermal. For volumes greater than the critical volume this is in agreement with that found in the analysis just described. This behavior for  $C_V$  of water vapor in the critical region is both surprising and interesting. If water vapor were a perfect gas,  $C_V$  would be independent of  $V$  and only at most dependent on  $T$ .

It is of interest to note that  $C_V$  is independent of specific volume for a Van der Waals as well as for a perfect gas. Glasstone<sup>(85)</sup> states for a gas obeying a Berthelot or a Beattie-Bridgeman equation of state, some variation of  $C_V$  with specific volume would be expected. However, the term  $\left\{\frac{\partial^2 P}{\partial T^2}\right\}_V$  is very small and consequently, Glasstone concludes that the variation of  $C_V$  with  $V$  would be small. Thus, Glasstone is of the opinion that for practical purposes  $C_V$  is independent of  $V$  for most gases. This statement may not have been intended for the variation of  $C_V$  with temperature and specific volume in the critical region. Nevertheless, the foregoing indicates that there may be gases (Van der Waals, Berthelot) which are not ideal but which possess the property of almost no variation of the specific heat at constant volume,  $C_V$ , with specific volume along an isotherm.

The above indicates that there is still considerable uncertainty about the absolute value of  $C_V$  and its variation with temperature and specific volume. Future analyses should be undertaken in order to rectify this situation. For purposes of calculation of  $C_P$ , the authors arbitrarily assigned a value of 1.0 B/lb °F to the specific heat at constant volume for specific volumes from 0.0400 to 0.125 ft<sup>3</sup>/lb and for temperatures from the saturation line to at least 752°F.

#### E. Comparison of the Derived and Computed Values for $C_P$

The equation that will be used to compute the specific heat at constant pressure is

$$C_P = 1 + \beta T / 4.81 \quad (17)$$

It is very difficult to estimate the probable error in the computed values of  $C_P$  since the factors contributing most to error will vary. For example, in the region of maxima the most important cause of error in  $C_P$  could be the error in  $\beta$ . In regions far removed from the region of maxima the possible error in the value chosen for  $C_V$  would be the major factor contributing to the error in  $C_P$ .

Figures 9 and 10 give a comparison between the derived and measured values of  $C_P$  along with values obtained by graphical differentiation of enthalpy data.\* Maximum deviations tend to occur in the region of maxima along various isobars. There is a large scatter of 'measured  $C_P$  values' above and below the derived  $C_P$  data of Equation (17). Thus, it would appear that Equation (17) reliably reproduces measurements in the critical region to within the limits of error in the specific heat at constant pressure measurements and in the values of the volume expansion coefficient.

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\*Details will be given of the graphical differentiation technique used to derive  $C_P$  from enthalpy measurements in a separate report.

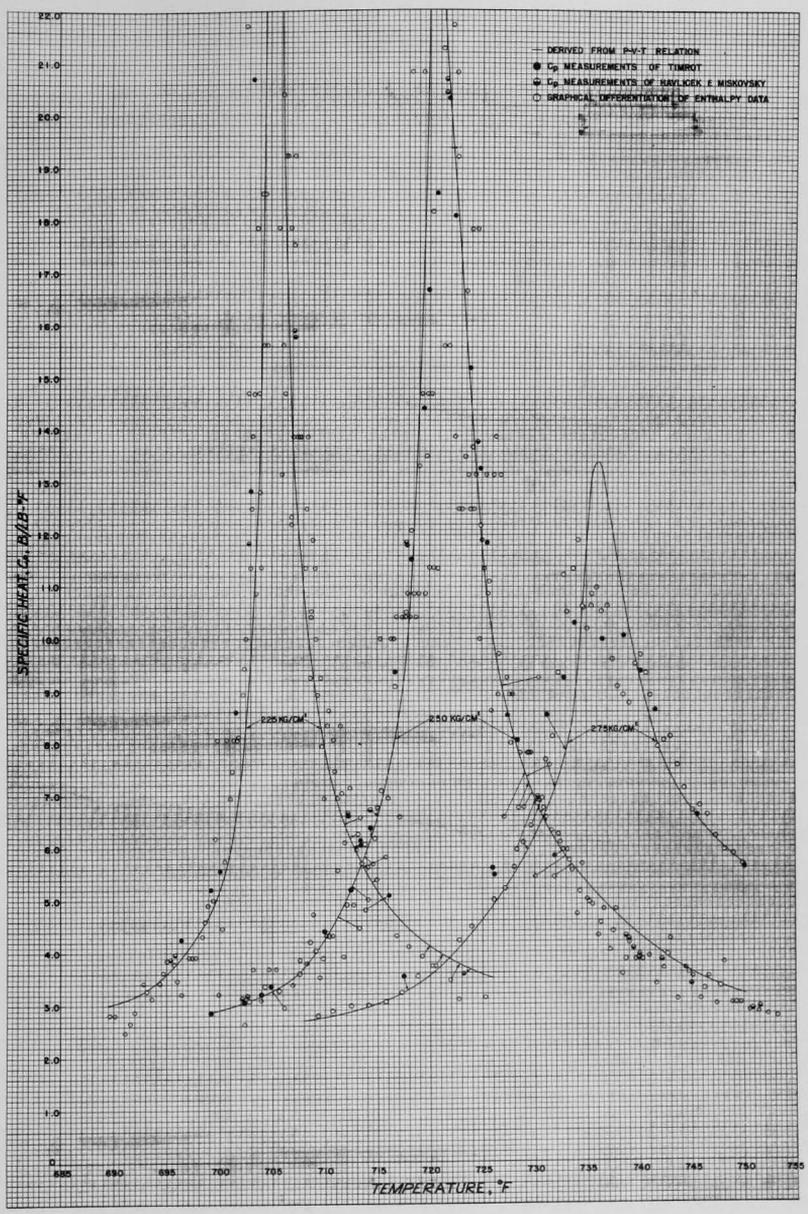


Fig. 9. Comparison Between Derived and Experimental Values of Specific Heat

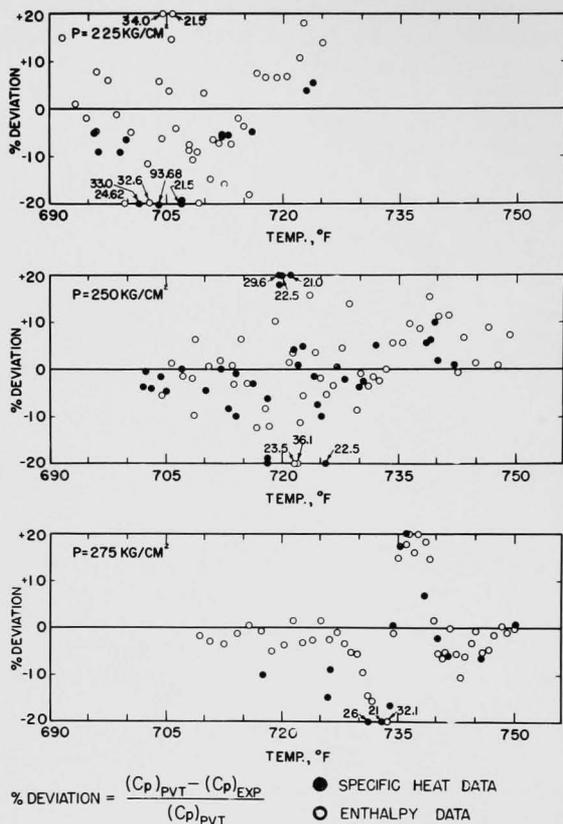


Fig. 10. Deviations Between Derived and Experimental Values of Specific Heat

Figure 11 compares experimental values of enthalpy difference with those obtained by integrating  $C_p - T$  isobars constructed from experimental values of specific heat and from values computed according to Equation (17). Along the 225 kg/cm<sup>2</sup> isobar values obtained from the curve based on Equation (17) are equally satisfactory as compared to that obtained from the curve based on experimental measurements of  $C_p$ . However, along the 250 and 275 kg/cm<sup>2</sup> isobars integrated values obtained from the curves constructed from experimental values of specific heat are superior to values obtained from the  $C_p - T$  curve constructed by means of Equation (17). The

values for the volume expansion coefficient derived along the 275 kg/cm<sup>2</sup> (3911 psia) isobar are high compared to values derived for the 3900 isobar of Reference 80. If values in Reference 80 are regarded as the best available, then it would appear that this factor would explain the somewhat higher values of  $C_p$  computed by Equation (17) for the 275 kg/cm<sup>2</sup>.

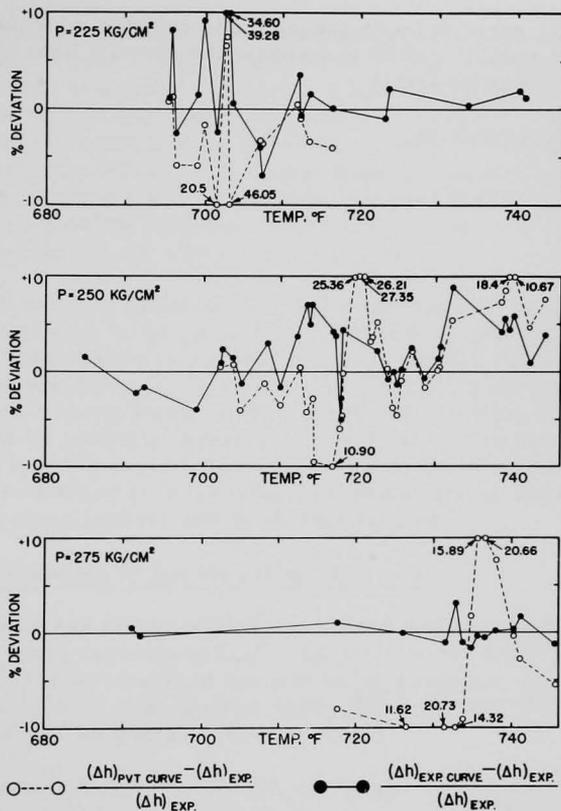


Fig. 11. Deviations Between Integrated and Experimental Values of Enthalpy Differences

## F. Summary

1. The principal reason for large errors in the experimental values of specific heat at constant pressure of various investigators is that excessively large temperature differences were employed in their measurements. This introduces considerable systematic error in the critical region.

2. The authors recommend that the following relation be used in the critical region encompassed by specific volumes of 0.4 to 0.12 ft<sup>3</sup>/lb and temperatures from the saturation line to 752°F.

$$C_P = 1 + \beta T/4.81 \quad .$$

3. In the event of more accurate and reliable information on  $C_V$ , the formula that should be used to compute the specific heat at constant pressure in the above region is

$$C_P = C_V + \beta T/4.81 \quad .$$

## CHAPTER VI

PRESSURE - VOLUME - TEMPERATURE VALUES  
CORRESPONDING TO MAXIMUM SPECIFIC HEATA. General

The pressure-temperature relations corresponding to maximum values of specific heat along isobars and isotherms has been the subject of a considerable amount of research. Euken<sup>(86)</sup> considered that structural changes without any observable heat of vaporization take place in the supercritical region along a curve on a pressure - temperature diagram defining  $(\partial C_P / \partial T)_P = 0$ . Euken probably considered that the pressure temperature curve locating the maximum specific heat along isobars represented the boundary between subcooled water and superheated water vapor in the supercritical region.

It was noted in Reference 73 that most engineering texts consider the critical isotherm to be the boundary between subcooled liquid and superheated water vapor in the supercritical region. None of these texts regarded this boundary as one where structural changes occur. Thus a comprehensive understanding of the fundamental aspects for an equation of state might be gained by studying information on the location of the maximum of specific heat along isotherms and isobars. Hence, a review of the results obtained from various attempts to locate the maximum of specific heat along isobars and isotherms follows.

B. Results of Studies to Locate  $(\partial C_P / \partial T)_P = 0$ 

Havlicek and Miskovsky<sup>(24)</sup> concluded that the maximum values of specific heat along isobars,  $(\partial C_P / \partial T)_P = 0$ , in the supercritical region occurred along an extension of the saturation pressure - temperature curve. Several investigators attempted to verify these pioneer observations by calculations based on phase transition theory.

Apparently Euken<sup>(86)</sup> and Trautz et al.,<sup>(87,88)</sup> pointed out that in the supercritical region the specific heat may be discontinuous at its maximum value. They considered also that the slope,  $(\partial C_P / \partial T)_P$ , may be discontinuous at the same point. These investigators considered that this discontinuity was due to a transition between liquid and vapor in the supercritical region. Thus, the curve of pressure versus temperature corresponding to the condition  $(\partial C_P / \partial T)_P = 0$  was termed a transition curve where structural changes are occurring even though the latent heat of vaporization is zero. They further considered that the phenomena of discontinuity was a phase shift of the third order in Ehrenfest's sense of the term.<sup>(89)</sup>

Jakob<sup>(90)</sup> extended the tangents at the inflection points of Havlicek and Miskovsky's isobaric specific heat curves as far as their point of intersection. He then made calculations according to the following equation derived by Ehrenfest,<sup>(89)</sup>

$$\frac{dP}{dT} = \frac{(\partial C_P / \partial T)_1 - (\partial C_P / \partial T)_2}{(\partial C_P / \partial P)_1 - (\partial C_P / \partial P)_2}$$

where the indices 1 and 2 refer to the two phases.

These calculations purported to show that the continuation of the saturation curve is a boundary between the two phases (liquid and vapor). In these calculations Jakob assumed that the curve of  $(\partial C_P / \partial T)_P = 0$  is coincident with the curve of  $(\partial C_P / \partial P)_T = 0$ .

Jakob was also able to show that the curve  $(\partial C_P / \partial T)_P = 0$ , did not deviate greatly from the critical specific volume line. He showed further that the maximum value of specific heat along a given isobar,  $P > P_C$ , was gradually displaced to greater values of density  $P > P_C$  as the pressure was increased. According to Jakob, Trautz and Ader<sup>(91)</sup> also suspected that the maximum values of specific heat along various isobars did not deviate greatly from the critical isochoric specific volume line.

According to Temperley,<sup>(92)</sup> Zimm<sup>(93)</sup> very recently suggested that the critical point of a gas or a liquid represents the end point of the phase transition curve. It is not clear whether or not Zimm considered that there is, or is not, a phase transition beyond the critical point and therefore more of these theoretical investigations are needed to clarify the situation.

Vargaftik<sup>(58,59)</sup> analyzed the specific heat measurements of Havlicek and Miskovsky<sup>(24)</sup> and Timrot.<sup>(25)</sup> He found that the pressure and temperature locating  $(\partial C_P / \partial T)_P = 0$  lies on an isochore which is somewhat smaller than the critical isochore. He concluded therefore that there was a linear relation between pressure and temperature corresponding to  $(\partial C_P / \partial T)_P = 0$  and that the line had a slope of  $dP/dT = 23.35 \text{ psia}/^\circ\text{F}$  ( $2.96 \text{ kg}/\text{cm}^2 \text{ }^\circ\text{C}$ ).

According to Vargaftik,<sup>(58,59)</sup> Timrot obtained the following relation for the maximum specific heat along various isobars,

$$C_{P \text{ max}} - C_{P_0} = \frac{A}{t_{\text{max}} - t_c}$$

An analogous relation was derived by Sheindlin et al.,<sup>(94)</sup> for pressures to  $500 \text{ kg}/\text{cm}^2$ . Sheindlin also considered that the above relation could be qualitatively obtained from the Van der Waal's equation of state.

Vukalovich et al.,<sup>(29)</sup> concluded from an analysis of their specific heat measurements that maximum values of specific heat along isobars lie on a curve which is a continuation of the saturation curve. They found however, that the relationship between  $C_{P_{\max}} - C_{P_0}$  and  $t_{\max} - t_c$  was not linear but had a very slight curvature.

Sirota and Maltzev<sup>(29)</sup> found that the maximum of specific heat along isobars becomes appreciably increased toward larger densities as the pressure is increased.

### C. Location of $(\partial C_P / \partial T)_P = 0$ by Means of Volumetric and Calorimetric Data.

The approach that will be used in this section is based on an analysis of precise volumetric data and also on various sets of experimental specific heat data. From the well-known thermodynamic relation

$$\left[ \frac{\partial C_P}{\partial P} \right]_T = - T \left[ \frac{\partial^2 V}{\partial T^2} \right]_P$$

It immediately follows that the condition defining the maxima of  $(\partial V / \partial T)_P$  along isobars coincides with the conditions of the maxima of specific heat,  $C_P$ , along isotherms. It was shown in Reference 80 that isobars of volume-temperature for pressures from the critical pressure to at least up to 4000 psia undergo inflection in the vicinity of the critical specific volume  $V_c = 0.0525 \text{ ft}^3/\text{lb}$ . Thus according to P-V-T data it may be concluded that  $(\partial C_P / \partial P)_T$  is zero in the vicinity of the critical specific volume.

Vargaftik<sup>(59)</sup> presents graphs of specific heat with both pressure and temperature as parameters. By means of this graph, the authors of this report recorded the various pressures and temperatures for which the specific heat attains a maximum value along isotherms, i.e.  $(\partial C_P / \partial P)_T = 0$ . Figure 12 shows excellent agreement between the pressure and temperature defining the critical specific volume and the various pressures and temperatures corresponding to where the specific heat attains a maximum. Thus, P-V-T and  $C_P$  data both indicate that the maximum values of specific heat along isotherm occurs along the critical isochoric line.

Near the completion of this report it was found that Sirota et al.,<sup>(95)</sup> concerned themselves with the location of maximum specific heat. They analyzed their own data<sup>(29)</sup> for pressures from 4300 to 7100 psia, (300 to 500  $\text{kg}/\text{cm}^2$ ), and found that the line  $(\partial C_P / \partial P)_T = 0$  does not coincide with the critical isochore. However they stated that it did lie very close to it.

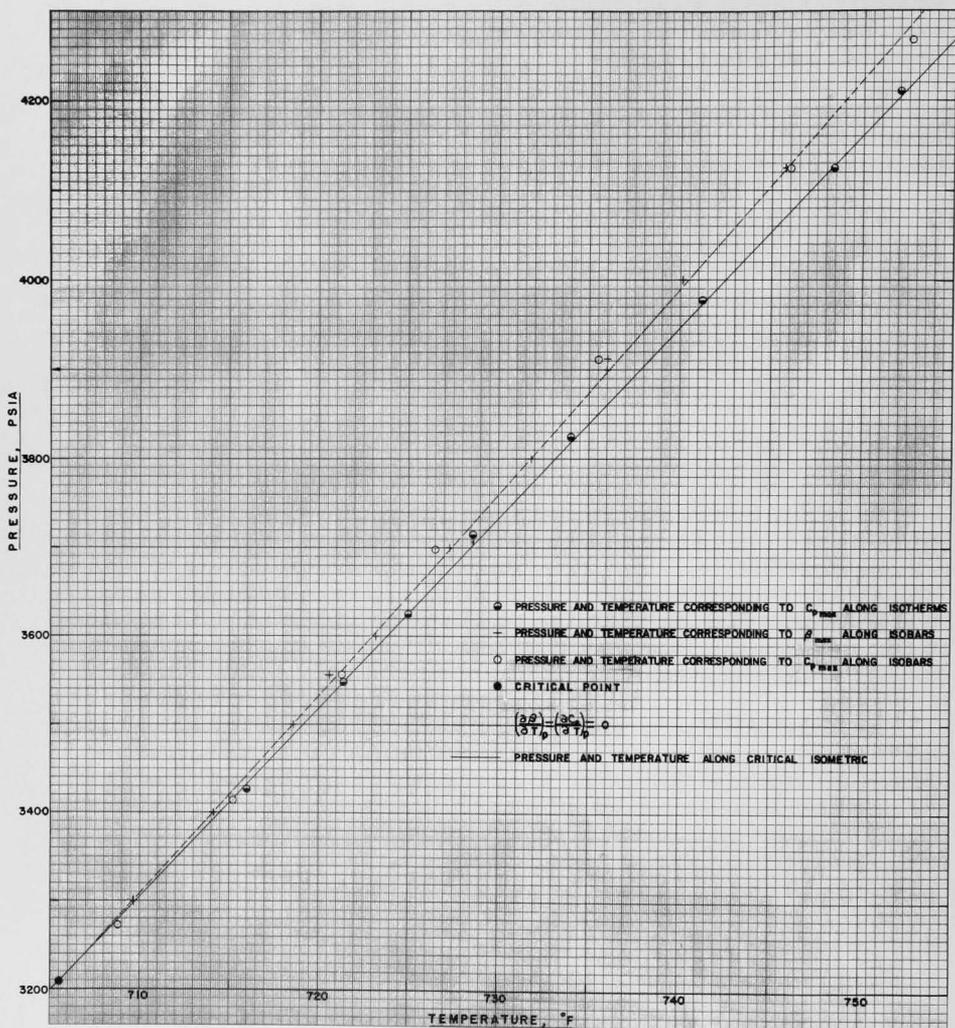


Fig. 12. Pressure and Temperature Corresponding to  $\beta_{max}$  and  $C_{p,max}$  Along Isobars and Isotherms

In Reference 80 it was found that the maximum value of the coefficient of volume expansion along a given isobar,  $P > P_c$ , occurred at a somewhat lower temperature than the point of inflection for an isobaric curve of specific volume against temperature. In view of this, the authors of this work decided to compare the locus of points for  $(\partial\beta/\partial T)_P = 0$  with the locus of points for the condition where  $(\partial C_P/\partial T)_P = 0$ . The curves of  $C_P - T$  shown in Figure 3 were used to obtain pressures and temperatures corresponding to the maximum values of specific heat along isobars. Figure 12 also shows the comparison between the pressures and temperatures defining the maxima of  $\beta$  along various isobars with that defining the maxima of  $C_P$  along various isobars. The agreement between the pressure and temperature defining  $\beta_{\max}$  and  $C_{P\max}$  along isobars is fair and a single curve may be assumed to represent both  $(\partial\beta/\partial T)_P = 0$  and  $(\partial C_P/\partial T)_P = 0$ .

One of the features of Figure 12 is that lines for  $C_P$  maxima on isobars,  $(\partial C_P/\partial T)_T = 0$ , and on isotherms,  $(\partial C_P/\partial P)_T = 0$  diverge slowly from one another as the pressure increases. For example at a pressure of 4200 psia, the difference between the curves is about three degrees. It may be definitely stated that the locus of points for  $(\partial C_P/\partial T)_P = 0$  and  $(\partial C_P/\partial P)_T = 0$  are not coincident. It was previously conjectured by Euken<sup>(86)</sup> and Jakob<sup>(90)</sup> that the locus of points for  $(\partial C_P/\partial T)_P = 0$  and  $(\partial C_P/\partial P)_T = 0$  form a single curve or at most a narrow band.

Sirota and Maltzev<sup>(95)</sup> stated that Kaganir<sup>(96)</sup> analyzed the maxima of  $C_P$  and  $(\partial V/\partial T)_P$  for a large group of gases and vapors. Kaganir found that the pressure and temperature lines defining the maxima of  $C_P$  and  $(\partial V/\partial T)_P$  on isobars diverge. Thus in view of this, the locus of points for  $(\partial C_P/\partial T)_P = 0$  and  $(\partial C_P/\partial P)_T = 0$  as shown in Figure 12 is typical of many vapors in addition to superheated water vapor in the supercritical region.

In Chapter V the following relation was derived between  $C_P$ ,  $C_V$ ,  $T$  and  $\beta$ ,  $C_P = C_V + \beta(T/4.81)$ . Differentiating with respect to pressure at constant temperature yields,

$$\left[ \frac{\partial C_P}{\partial P} \right]_T = \left[ \frac{\partial C_V}{\partial V} \right]_T \left[ \frac{\partial V}{\partial P} \right]_T + \frac{T}{4.81} \left[ \frac{\partial \beta}{\partial P} \right]_T$$

The term,  $(\partial C_P/\partial P)_T$  vanishes always at the critical specific volume. It was concluded in References 83, and 84,\* that  $(\partial C_V/\partial V)_T$  is zero along the critical isochoric line.

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\*This appears to be valid for other substances besides water and water vapor. Michels *et al.*,<sup>(97,98,99)</sup> found that  $(\partial C_V/\partial V)$  was zero along the critical isometric of  $CO_2$ . They found this to be true throughout the whole of the supercritical region.

Thus it may be assumed that the condition,  $(\partial\beta/\partial P)_T = 0$ , occurs always at the critical specific volume. It may be concluded that the pressure-temperature relations for  $C_{P_{\max}}$  and  $\beta_{\max}$  along isotherms are coincident with each other. It is not known whether the region enclosed by the two diverging lines of Figure 12 has any physical significance.

#### D. Summary

1. Various analyses previously made have given rise to the following conclusions;

- (a)  $(\partial C_P/\partial T)_P = 0$  for supercritical water vapor is an extension of the saturation pressure - temperature curve.
- (b)  $(\partial C_P/\partial T)_P = 0$  and  $(\partial C_P/\partial P)_T = 0$  are coincident and lie near the critical specific volume line.

2. The work of this report shows that the condition for which  $(\partial C_P/\partial P)_T = 0$  occurs always on the critical isometric, whereas  $(\partial C_P/\partial T)_P = 0$  occurs on a curved line gradually diverging away from the critical isometric.

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