

THE CRITICAL PROPERTIES OF ELEMENTS AND COMPOUNDS

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I. INTRODUCTION

The ever-broadening field of chemistry and chemical engineering makes it necessary to plan and design research equipment, pilot, semiworks, and full-scale plants to produce new chemicals. Many data are needed for these designs, but when the literature is consulted, few data may be found. Such data as thermodynamic properties, compressibility factors, and heat-transfer coefficients, as well as other needed data, may be either fragmentary or completely absent. It therefore becomes the task of the engineer to estimate these data to the best of his ability. Many useful and relatively accurate correlations have been devised which are based on the law of corresponding states. The critical properties of the substance must be known in order to use these correlations. Many data concerning the critical state are presented in the literature, but a great deal of time and effort are consumed in conducting the literature search. It is the purpose of this report to collect, evaluate, and present the critical constants of all substances for which experimental data exist.

A brief review covering the phenomena of a substance at its critical state and the methods and apparatus used in the determination of the values of the critical constants is presented, so that the collation and evaluation of the data may be more fully understood.

II. CRITICAL PHENOMENA

A. THE CRITICAL POINT

The phenomenon of the critical point was discovered in 1822 by Baron Cagniard de la Tour (151a, 316), who rolled a ball within a heated, closed cannon barrel and noted the difference in the sound when the substance was a liquid and when it was a gas. König (166a) states that Schmidt (294a) in 1823 predicted the critical point on the basis that there would be no latent heat of vaporization.

In 1869, T. Andrews discovered the essential conditions for the liquefaction of gases. Prior to this time, many investigators had tried unsuccessfully to liquefy gases by the application of pressure and had come to the erroneous conclusion that there existed certain "permanent" gases which could not be liquefied. Andrews (6) found that carbon dioxide could not be liquefied above 31.1°C. even though a pressure of 300–400 atm. was applied. Subsequent investigations (8, 9) led to the concept that each gas has a temperature above which it can not be liquefied regardless of the applied pressure. This temperature is called the *critical temperature*, and the pressure (vapor pressure) required to liquefy a gas at this critical temperature is called the *critical pressure*. The volume of a unit mass of the substance at the critical temperature and pressure is called the *critical volume*.

On the basis of Andrews' work and van der Waals' equation, it was thought that this critical state was a unique point at which the meniscus dividing the

vapor and liquid disappeared and the two phases became a single, homogeneous phase.

B. THE KINETIC THEORY

According to the kinetic theory of gases there are two forces which are exerted on the molecules of a gas: the potential force of attraction and the kinetic force of translation. The former is a force which tends to cause the molecules to coalesce and form a liquid. The latter tends to separate the molecules into the random distribution associated with the gaseous state of matter. Since only the latter is a function of temperature, there is a temperature at which the kinetic energy of translation is equal to the maximum potential energy of attraction. At any temperature greater than that, only the gaseous phase can exist.

This concept is entirely in accordance with the definitions set forth for the critical point, but does not rule out the possible existence of a critical region.

C. THE CRITICAL REGION

The classical or "Andrews-van der Waals" theory requires a unique critical point associated with the disappearance of the meniscus and the formation of a completely homogeneous phase. Objections to and the limitations of this theory have been summarized by Brescia (48), Clark (80), and Traube (318) among others. These objections are based largely on the fact that differences in density, refractive index, x-ray diffraction, and other physical properties exist between the two phases *after* the meniscus has disappeared.

The application of statistical mechanics to condensing systems has led Mayer and Harrison (203) to postulate that a region must exist between the temperature of the disappearance of the meniscus and the true critical temperature.

O. Maass and coworkers (186, 205, 206, 227) found viscosity and density hysteresis effects in the region of the critical temperature.

It has been postulated by these investigators that the coexistence curve has a finite horizontal flat segment at a temperature corresponding to the temperature at which the meniscus disappears and that a "steam-dome" region is superimposed on the coexistence curve above this flat segment. It is further assumed that the isotherms within this "steam-dome" region are horizontal over a finite range of volume.

In the recent work of Atack and Schneider (13, 188) on sulfur hexafluoride, it was shown that the coexistence curve was *not* a truncated parabola but rather a smooth parabola showing no evidence of a flat segment. The critical temperature as determined by the disappearance of the meniscus was the same as that determined from pressure-volume-temperature relations.

To determine the effect of hydrostatic head on the shape of the coexistence curve, Weinberger and Schneider (331), using very pure xenon, established the shape of the coexistence curve in bombs of two different lengths, 19 cm. and 1.2 cm. It was found that gravitational effects could account for a large part of the flat-topped segment of the coexistence curve. The effects of molecular clustering may also play some part in this phenomenon and, if so, would be expected to vary from compound to compound.

At the present time it is not possible to say with certainty that a critical region exists or that it does not exist. Hence, it is impossible to state whether the temperature at which the meniscus disappears is or is not the same as the critical temperature determined from pressure-volume-temperature relations.

Moreover, it must be remembered that the range of difference between the temperature of the disappearing meniscus and the true critical temperature varies from zero for non-associated liquids to a few degrees for highly associated substances. Therefore, those critical values which were determined by the application of the criterion of the disappearance of the meniscus should not be relegated to obscurity but indeed may prove to be more accurate than some values determined from P - V - T relations.

III. METHODS AND APPARATUS

A. THE CRITICAL TEMPERATURE

Since the determination of the critical constants by P - V - T relations gives the true critical temperature, these methods will be discussed first.

1. P - V - T relations

(a) *Method of Beattie and coworkers:* The apparatus used by Beattie (18) is illustrated in figure 1. The bomb, F, consisted of a glass-lined steel container of about 200-ml. capacity. A weighed sample of gas was placed in the bomb in such a way as to insure the exclusion of air. The volume of the bomb was varied by the introduction or removal of mercury by means of the mercury compressor, C, of about 210-ml. displacement. The temperature of the gas was controlled by the thermostat, G, and the platinum-resistance thermometer, T^1 , and measured by the platinum-resistance thermometer, T. The pressure was measured by the Amagat dead-weight tester, B. The pressure was transmitted by oil from the rizer block, D, to the gage.

The gage constant was determined by calibration against carbon dioxide at 0°C. The constant did not vary more than 0.02 per cent in the range of 1-500 atm.

The thermostat was constructed of outer and inner vessels separated by 85 per cent magnesia insulation. Three 50-ft. 20-ohm heaters were wound on the inner can. The liquid was agitated by nine stirrers mounted on three shafts which were geared together to rotate at 1700 R.P.M. The temperature was measured and controlled by the platinum-resistance thermometers, which were calibrated at the ice point and boiling point of water.

The overall accuracy of the pressure determinations was 0.01 per cent at low pressure and room temperature and 0.03 at high pressure and high temperature. The temperature was measured with a precision of 0.002°C., and the volume was accurate to within 0.1 per cent.

A series of P - V isotherms in the neighborhood of the critical temperature were determined and plotted on pressure-volume coordinates. That isotherm which showed a point of horizontal inflection was selected as the critical isotherm. The critical pressure and volume were then obtained from the coordinates of the point of inflection.

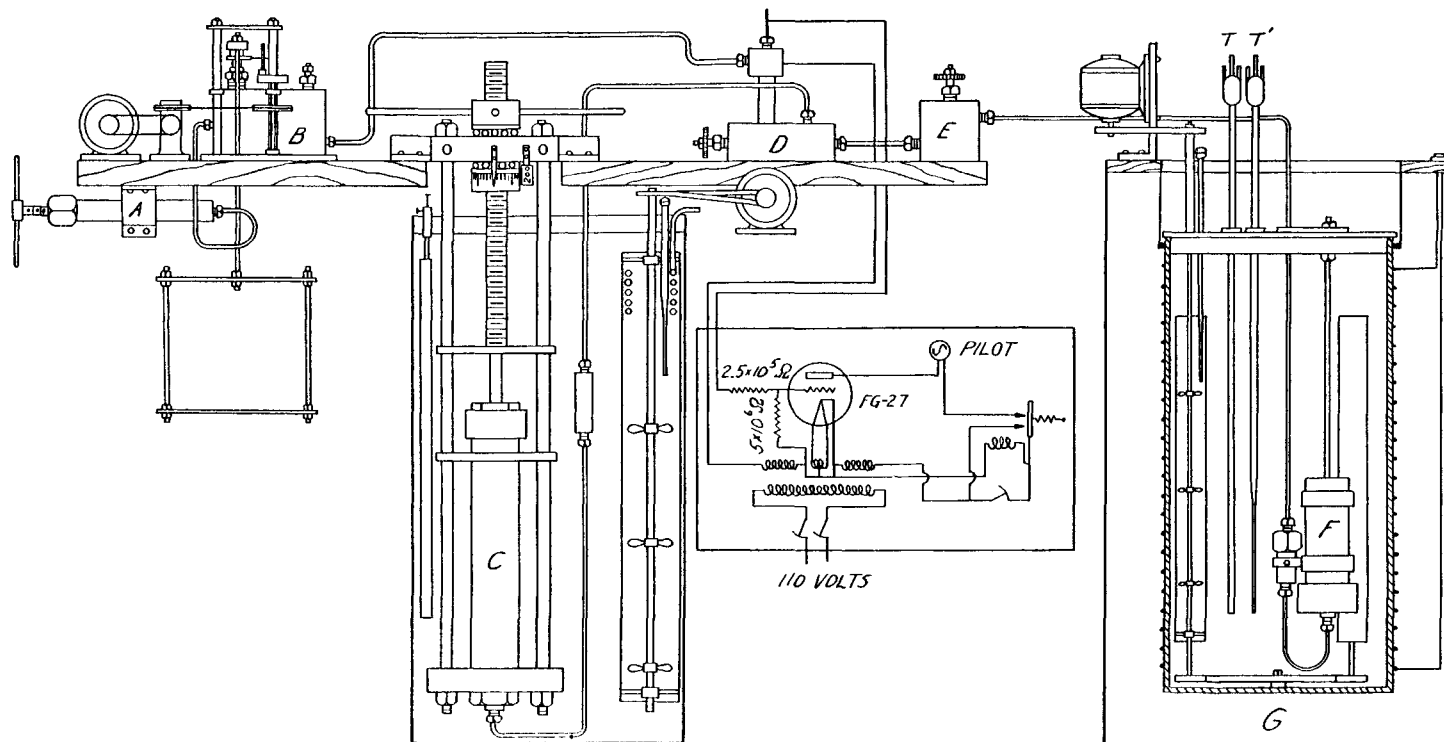


FIG. 1. Compressibility apparatus of Beattie²

²The authors wish to thank Professor James A. Beattie for the loan of the original drawing of this apparatus.

This method of determination is very reliable but requires the use of good equipment and extreme care in the operation of the equipment.

(b) *Method of Cailletet and Colardeau:* The method proposed by Cailletet and Colardeau (59) in 1888 depends upon the fact that the pressure of coexisting phases of vapor and liquid is independent of the relative volumes of either. Above the critical temperature no liquid can exist and the pressure must be a function of the volume (mass) of the sample. Therefore, the procedure consists in filling a steel bomb with different volumes of liquid sample and measuring the pressure at increasing values of temperature (the total volume is held constant). The data are then plotted on a pressure-temperature diagram and the critical temperature and pressure are determined as shown in figure 2.

(c) *Method of Ipatieff and Monroe:* The rotating-bomb method was developed by Ipatieff and Monroe (149) in 1942. The criterion of the critical point is analogous to that of the method of Cailletet and Colardeau. The pressure is

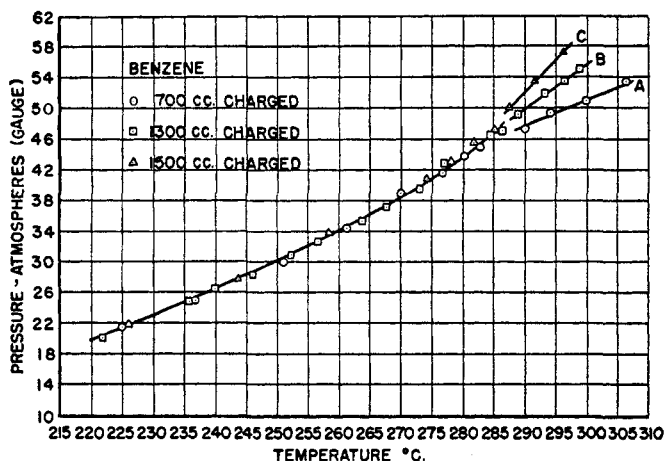


FIG. 2. Critical temperature and pressure by the method of Cailletet and Colardeau

measured at various values of increasing temperature and the results plotted on a pressure-temperature diagram. Only one filling of the bomb is made and the critical temperature and pressure occur at the discontinuity of the vapor-pressure curve, as is shown in figure 3. Hydrogen may be added to accentuate the break in the vapor-pressure curve.

The bomb is constructed of steel and is rotated in a thermostated bath at an angle of 28 degrees from the horizontal. The bomb assembly is illustrated in figure 4. The pressure gage is inclined in such a manner that the bomb may be stopped and the pressure determined while the gage is in a vertical position. The temperature is measured by a thermocouple so placed as to indicate the temperature of the liquid sample. The bomb is also equipped with vapor and liquid sample lines for use in the studies of equilibrium compositions of binary systems.

Although the determination of critical temperature and pressure is relatively

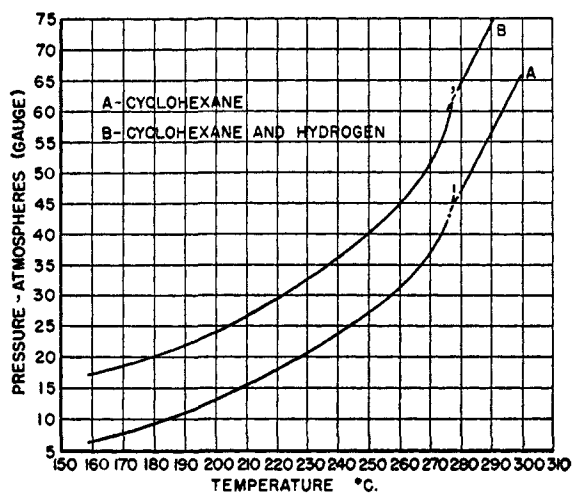


FIG. 3. Apparatus for determination of critical temperature and pressure by the method of Ipatieff and Monroe.

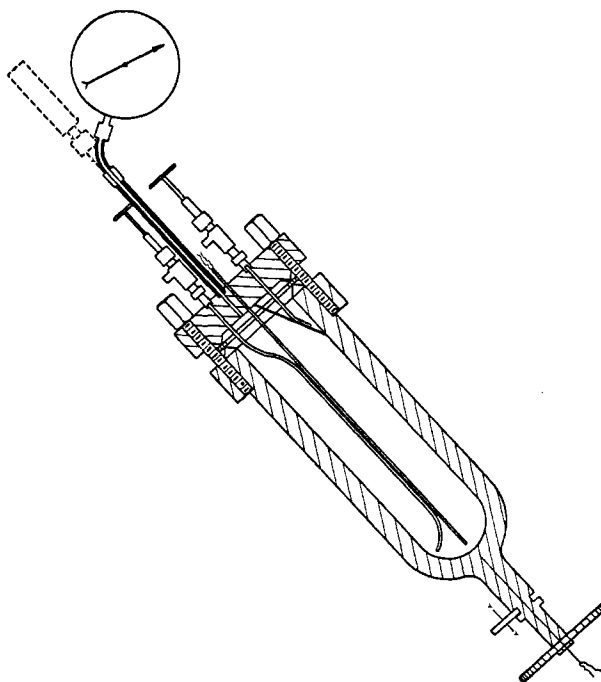


FIG. 4. The rotating bomb of Ipatieff and Monroe

simple by this method, the accuracy is only $\pm 2^\circ\text{F}$. and the method is therefore not suited for highly accurate determinations.

2. The disappearing meniscus

(a) *Method of T. Andrews:* The apparatus used by Andrews (6) was constructed of two copper cylinders interconnected by a cylinder of smaller diameter such that the overall shape was that of the letter H (see figure 5). Into the bottom of each cylinder was placed a large-diameter screw, the threaded part of which could be screwed well up into the cylinders. A capillary tube was fitted into the top of either cylinder. One of the capillaries was filled with the gas under investigation and the other with air. The metal cylinders were filled with water, and the water and gas samples were separated by slugs of mercury. Pressure

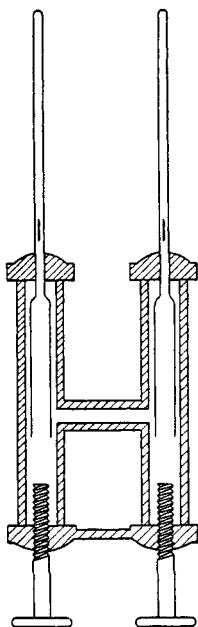


FIG. 5

FIG. 5. The apparatus of T. Andrews

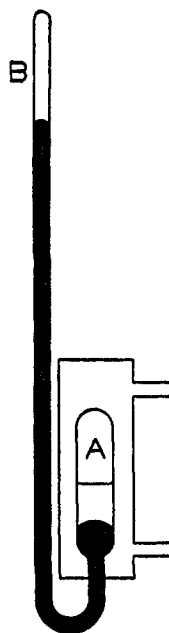


FIG. 6

FIG. 6. The apparatus of C. de la Tour

was applied to the system by means of the screws. The entire apparatus was immersed in a thermostated bath in order to maintain the desired temperature.

The capillaries were calibrated for capacity, and the pressure in the system was determined by the temperature-volume relations of air. Thus, the apparatus was suited for the determination of the critical constants by P - V - T relations, but Andrews noted that the disappearance of the meniscus occurred at the critical temperature, and he adopted this phenomenon as the criterion of the critical temperature; this led other investigators to use the disappearance of the meniscus as the sole criterion of the critical temperature.

(b) *Method of C. de la Tour:* The apparatus used by C. de la Tour (116) con-

sisted of a glass bulb, A, which contained the sample under investigation. A mercury-air manometer, B, was attached to the bulb as shown in figure 6. The bulb was then encased by a jacket so that a heated fluid could be circulated

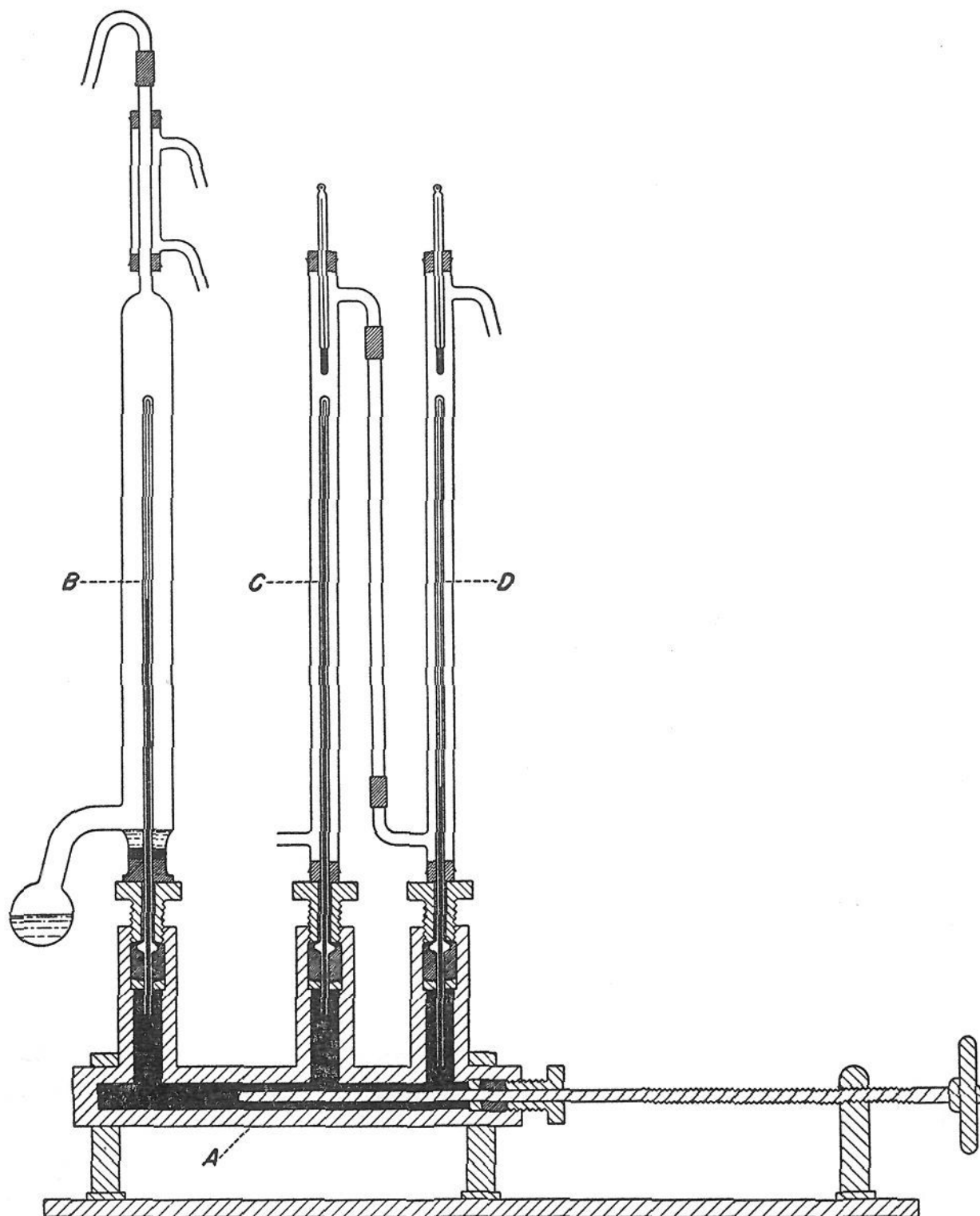


FIG. 7. The apparatus of S. Young

around the bulb. Although this method is crude as outlined, it is readily adaptable to refinements and ramifications such that accurate determinations may be carried out. Indeed, many investigators have used the basic principles of this method.

(c) *Method of S. Young*: A modification of the apparatus of Andrews was used by S. Young (350). It was made of a long wrought-iron tube, A, with three short tubes set at right angles to it, as illustrated in figure 7. One end of tube A was sealed and the other end was fitted with a screwed plunger. Capillaries of about 1.5-mm. internal diameter were fitted to the three short wrought-iron tubes and the lower portion was filled with mercury. These capillaries were accurately calibrated for capacity, and each capillary was enclosed in a jacket so that the temperature could be regulated.

Capillary B was filled with the substance to be investigated by means of a special technique explained in detail in the original article. This capillary was heated by liquids boiling under known reduced pressure, and the temperature was determined from the vapor-pressure data of the heating media. Carbon disulfide, ethyl alcohol, chlorobenzene, bromobenzene, aniline, and quinoline were used up to 280°C.

Capillaries C and D were maintained at a constant temperature by means of thermostated circulated water. The temperature was determined by thermometers, which were placed at the top of the jackets. The pressure in the system was varied by the screw plunger and transmitted to the sample and the air manometers by the mercury. The pressure was calculated from the volume-temperature relations of air with corrections for deviations from ideal gas by means of the data of Amagat, for differences in the heights of the mercury columns, for the column of the liquid sample, and for the thermal expansion of mercury. The air-manometer, C, was used for moderate pressures, and manometer D was used for high pressures.

The criterion of the critical temperature was taken as the point where the meniscus had vanished but would reappear when the volume was increased suddenly by a small amount (adiabatic cooling). The critical volume was determined by the application of the rule of rectilinear diameters (see determination of the critical volume). The curvature of the rectilinear diameter was taken into consideration by the addition of a quadratic term to the equation.

3. *Miscellaneous methods*

(a) *Method of O. Maass and coworkers*: Maass and coworkers (186, 205, 206, 227) developed an apparatus which consisted of two bombs, B' and B, which were connected by a capillary tube as shown in figure 8. Bomb B' was filled with carbon dioxide in such a way that there were always two phases present. The pressure in the system was regulated by the temperature at which bomb B' was maintained. The pressure was determined from the vapor-pressure data of carbon dioxide. A magnetic stirrer was provided to insure equilibrium.

Bomb B was filled with the substance to be investigated and was immersed in a separate thermostat from that in which bomb B' was immersed.

The densities of the liquid and vapor phases were determined by the float suspended from a quartz spiral. The volume and weight of the float and the spring constant of the quartz spiral were accurately determined; thus, the density of the fluid was calculated from the buoyancy effect.

Pressure-volume isotherms were determined and plotted, and the critical state was selected as that isotherm which showed a unique point of inflection.

Maass and coworkers (191) also developed the shaking-bomb method. Two bombs were filled with sample and fixed to a vertical wheel which was rotated at 30 R.P.M. in a bath. The meniscus was viewed through a telescope and was seen to disappear very sharply at the same temperature at which it reappeared on cooling. The attainment of equilibrium was given as the reason for these phenomena.

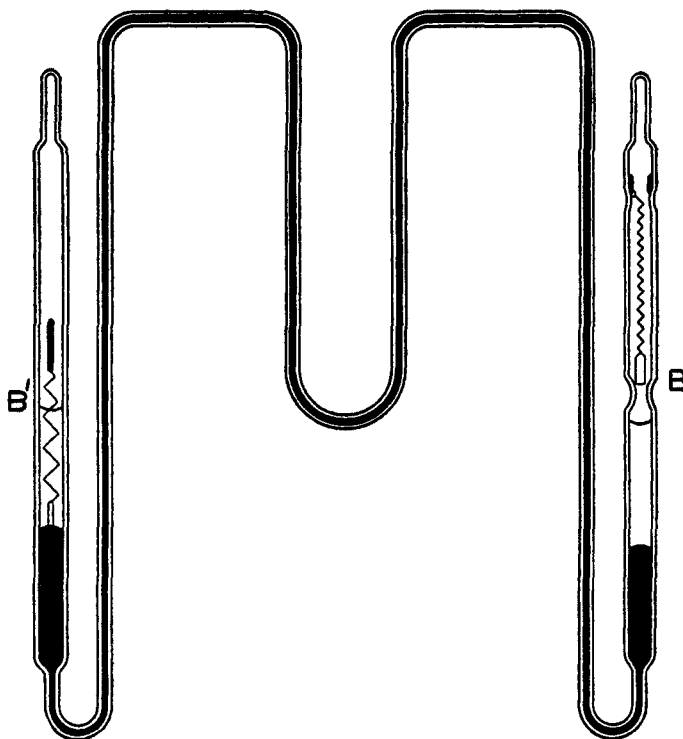


FIG. 8. The apparatus of O. Maass

(b) *Method of Cardoso and coworkers:* The apparatus used by Cardoso and Bell (68) was similar to that of Young with two exceptions: (1) the sample was stirred by a magnetic stirrer and (2) the pressure was determined by a Bourdon-tube pressure gage instead of by air manometers. The great difference, however, lay in the criterion of the critical state. As was previously stated, Young used the disappearance of the meniscus, whereas Cardoso and workers used the disappearance of critical opalescence. This opalescence occurred after the meniscus had disappeared and was due to the formation and breaking-up of liquid agglomerates within the vapor phase.

(c) *Method of Fischer and Reichel:* The method of Fischer and Reichel (109) consisted in heating the sample in a capillary tube and observing the phenomena

through a telescope. The criterion of the critical state was the disappearance of small droplets of liquid after the meniscus had disappeared. These authors stated that the disappearance of the meniscus was difficult to ascertain with certainty and reproducibility and selected the disappearance of the droplets as the criterion of the critical state because this phenomenon was sharp, clearly defined, and reproducible.

(d) *Method of Bond and Williams:* Bond and Williams (43) developed a method of determining the critical temperature of highly corrosive materials such as hydrogen fluoride. The apparatus consisted of an air thermostat, an assay balance, and a sample tube 10 mm. in diameter and 153 mm. in length. The equip-

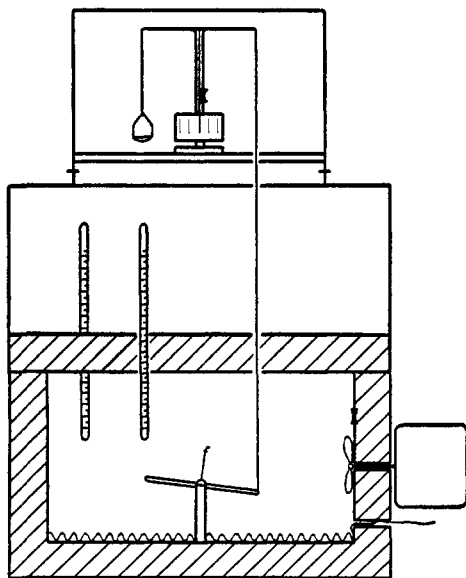


FIG. 9

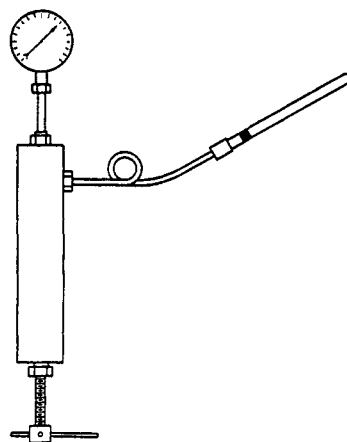


FIG. 10

FIG. 9. The apparatus of Bond and Williams

FIG. 10. The apparatus of Altschul

ment assembly is illustrated in figure 9. The sample was sealed in the tube and the tube placed in the pivots located in the furnace. The furnace was heated to several degrees above the critical temperature and the temperature was held at that point for at least 30 min. to insure thermal equilibrium within the sample tube. The tube was set at an angle of 20 degrees to the horizontal and the balance adjusted to the zero point. The furnace was allowed to cool slowly, and the temperature was noted when the balance was first disturbed. The movement of the pointer indicated that a liquid phase had formed, and this movement of the pointer was selected as the criterion of the critical state.

Since a visual observation of the meniscus is not required in this method, the sample tube may be made of an opaque substance such as stainless steel, monel metal, or the like for use with highly corrosive substances.

Methods involving pressure–volume–temperature measurements are suited for the determination of critical pressure and volume as well as the critical temperature. The methods of the disappearing meniscus may be adapted to give the critical pressure in addition to the critical temperature. The special method of Bond and Williams is designed to yield only the critical temperature.

B. THE CRITICAL PRESSURE: METHOD OF ALTSCHUL

The method of Altschul (4) was designed for only the determination of the critical pressure. The criterion for the critical state was the disappearance of the meniscus. A capillary tube was inclined at about 45 degrees from the vertical. The upper end was sealed and the lower attached to a compression pump to which a pressure gage was fixed. The apparatus is illustrated in figure 10.

The upper end of the sample tube was maintained at a temperature higher than the critical temperature, while the lower end was kept at a temperature

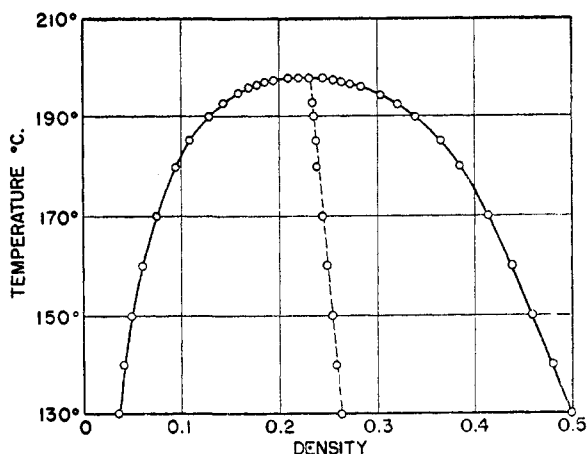


FIG. 11. Determination of the critical density by the law of rectilinear diameters

lower than the critical temperature. As the pressure was increased, the meniscus moved up the tube to the point at which the meniscus disappeared. The pressure was then noted as the critical pressure.

C. THE CRITICAL DENSITY (VOLUME)

Because of the extreme compressibility of a gas in the neighborhood of the critical temperature a large change in volume is brought about by a small change in pressure; hence it is difficult to determine the critical volume directly.

Method of Cailletet and Mathias: In 1886, Cailletet and Mathias (60) proposed a method for the determination of the critical density. It was noted that the mean of the densities of saturated vapor and liquid was a linear function of the temperature. The locus of the mean values is known as the *rectilinear diameter*.

The rectilinear diameter for many substances approaches a straight line, but S. Young (350) pointed out that the line of mean density may be slightly curved, and he introduced a quadratic term into the equation for the diameter.

In order to use this method, a plot of temperature *versus* saturated vapor and liquid densities is made, as shown in figure 11. The vapor and liquid densities form a continuous parabolic curve and become equal at the critical point. The line of mean density is then determined, and the intersection of the parabolic curve and the line of mean density is the critical point. This intersection may be ascertained graphically or the equation for the rectilinear diameter may be obtained and the results determined analytically:

$$\frac{d_L + d_V}{2} = a + bt$$

but at the critical point:

$$\frac{d_L + d_V}{2} = d_c = a + bt_c$$

Young (350) found that the slight curvature of the rectilinear diameter is best corrected for by use of a quadratic equation:

$$\frac{d_L + d_V}{2} = a + bt + ct^2$$

where d_L = liquid density,

d_V = vapor density,

t = temperature in °C., and

a, b, c = empirical constants.

The orthobaric densities (density of vapor and liquid coexisting at the same temperature) may be determined in several ways. The method of Maass and coworkers (186, 205, 206, 227), which utilizes the float and quartz spring, is adaptable, as is the method of Traube (318), which makes use of a number of balls of different known densities.

The most used method for the determination of orthobaric densities is that of Young (350). The volumes of the liquid, V_L , and of the vapor, V_G , are determined for two different amounts of the substance, m and m' , at the same temperature. The densities, d_L and d_G , are then obtained by a simultaneous solution of the two equations:

$$m = d_L V_L + d_G V_G$$

$$m' = d_L V'_L + d_G V'_G$$

Many variations of the methods for the determination of the critical constants summarized herein are readily apparent and have been used by many investigators in the field.

IV. GENERALIZED CORRELATIONS

Because many compounds decompose below the critical temperature and the critical constants of many compounds have not been experimentally determined, numerous correlations have been proposed for estimating the critical

constants. The correlations are also useful for comparison of experimentally determined values.

A. THE CRITICAL TEMPERATURE

1. *Studies of Guldberg*

One of the first attempts to estimate the critical temperature was made by Guldberg (119), who observed that the ratio of the absolute temperature of the normal boiling point to that of the critical point was two-thirds for many substances. This is a very approximate relation and is not in general use.

2. *Studies of Prud'homme*

A rather simple but inaccurate relation which relates the melting point, the boiling point, and the critical point was proposed by Prud'homme (264):

$$T_b + T_f = T_c$$

where T_b = the normal boiling point in °K.,

T_f = the fusion temperature in °K., and

T_c = the critical temperature in °K.

3. *Studies of Ramsay and Shields*

Ramsay and Shields (268) studied the Eötvös rule, which is based on the Law of Corresponding States, and proposed a relation for the critical temperature, t_c , from the molar surface energy, $\gamma(M_v)^{2/3}$.

$$\gamma(M_v)^{2/3} = K(t_c - t - 6)$$

where M_v = molar volume,

γ = surface tension, and

K = the Ramsay-Shields constant.

The constant K , known as the Ramsay-Shields constant, has a value of 2.12 for "normal" substances, but since it is not a true constant, the entire relation is of limited accuracy.

4. *Studies of Lewis*

One of the first attempts to predict critical values by use of the parachor was made by D. T. Lewis (181). The concept of the parachor, $[P]$, was developed by Sugden and is expressed by an equation which relates liquid and vapor densities, d_L and d_v , and surface tension, γ , all measured at the same temperature, for a molecular weight, M , of the substance.

$$[P] = \frac{M\gamma^{0.25}}{d_L - d_v}$$

With few exceptions the parachor is not dependent on the temperature. Values for the atomic and structural parachors have been proposed by Sugden (306) and by Mumford and Phillips (220) from which the molecular parachor can be determined quite accurately.

The relation proposed by Lewis (181),

$$T_c = 2.33[P] + 63$$

is not very accurate, however, for many compounds.

5. *Studies of Meissner and Redding*

The relations proposed by Meissner and Redding (210) were developed by the correlation of the critical temperatures of a number of homologous series. The following relations are based on these correlations:

For substances boiling below 235°K.:

$$T_c = 1.70T_B - 2$$

For substances containing halogens or sulfur and boiling above 235°K.:

$$T_c = 1.41T_B + 66 - 11F$$

For aromatic compounds and naphthalenes:

$$T_c = 1.41T_B + 66 - r(0.383T_B - 93)$$

For other compounds:

$$T_c = 1.027T_B + 159$$

In these equations, the symbols are defined as follows:

T_c = the critical temperature in °K.,

T_B = the normal boiling point in °K.,

F = the number of fluorine atoms in the molecule, and

r = the ratio of non-cyclic carbon atoms to cyclic carbon atoms.

The reliability of the equations is about 5 per cent.

6. *Studies of Herzog*

R. Herzog (136) correlated the critical temperature with the parachor and the normal boiling point and proposed a series of equations which are applicable to specific homologous series. Some 140 compounds were divided into six groups and an equation of the type

$$T_c/T_B = a - b \log [P]$$

was fitted to the data of each group by the method of least squares. In these relations a and b are constants for a particular series and $[P]$ is the parachor of Mumford and Phillips (220).

Because of the complexity of the grouping system, the values of the constants a and b are not reproduced here. These may be found in the article (136) together with a tabulation of the atomic, structural, and strain parachor values of Mumford and Phillips (220). The reliability of the predictions is stated to be about 5 per cent based on the *maximum* deviations.

7. *Studies of Meissner*

Meissner (209) has developed relations which correlate the critical temperature with the parachor and the molar refraction. The molar refraction, $[R]$, is, theoretically, an exact property of a substance which is independent of the temperature and which is defined by:

$$[R] = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d_L}$$

where n is the refractive index of a liquid of density d_L , both determined at the same temperature. The refractive index must be measured at infinite wave length of the incident light. Since in practice the sodium D line is used, the ideal molar refraction is not obtained but rather a value which is related to the ideal molar refraction. As with the parachor, the molar refraction may be estimated accurately by summing the atomic refractions of the component elements in the molecule. The relation as proposed by Meissner is

$$T_c = 20.2T_B^{0.60} - 143 - 1.2[P] + 10.4[R_D]$$

where $[P]$ is the parachor of Mumford and Phillips and $[R_D]$ is the molar refraction of the sodium D line.

8. *Studies of Watson*

In 1931 Watson (330) proposed a relation for predicting the critical temperature of non-polar and slightly polar compounds. The relation is

$$\frac{T_*}{T_c} = (0.283) \left(\frac{M}{d_B} \right)^{0.18}$$

where T_* is the temperature at which the specific volume of the vapor is 22.4 l. per gram-mole, and d_B is the liquid density at the normal boiling point. T_* is a function of the normal boiling point and may be determined from a graphical representation given in the article (330).

B. THE CRITICAL PRESSURE

The attempts to correlate and predict the critical pressure are not as numerous as those for the critical temperature, but some of the more useful of these relations are considered.

1. *Relation proposed by Meissner and Redding*

The relation proposed by Meissner and Redding (210), based on both the critical temperature and the critical volume, is:

$$P_c = 20.8T_c/(V_c - 8)$$

Hence, any errors in the values for T_c or V_c will be carried into the value for P_c . The reliability is about 20 per cent.

2. *Relations proposed by Herzog*

The relations proposed by Herzog (136) are divided into six groups, as in the case for the predictions of the critical temperature. The equation for P_c is:

$$\log P_c = a' - b' \log [P]$$

where a' and b' are constants for a particular homologous series and $[P]$ is the parachor of Mumford and Phillips.

3. *Relation proposed by Meissner*

The relation of Meissner (209) is based on a correlation of the parachor, the molar refraction, and the critical temperature:

$$P_c = 60.3T_c/(1.5[P] + 9 - 4.34[R_D])^{1.226}$$

where the symbols are the same as defined under the discussion of the critical temperature.

4. Relation proposed by Gamson and Watson

A correlation for the critical pressure of hydrocarbons has been proposed by Gamson and Watson (144). The relationship was derived from an empirical vapor-pressure equation which they had found to represent satisfactorily over forty compounds of various types. The proposed relationship is:

$$P_c = P'_c + \frac{\Delta p}{(n_c + c)}$$

where P'_c , Δp , and c are determined from charts and tables in *Chemical Process Principles* (144).

C. THE CRITICAL DENSITY (VOLUME)

The critical volume is best estimated by expressions which correlate this constant with the parachor.

1. Relation proposed by Sugden

One of the first attempts to predict the critical volume was made by Sugden (306). The relation is

$$V_c = \frac{[P]}{c}$$

where $[P]$ is the parachor. The constant c was determined as 0.78 but later was found to vary from 0.93 for water to 0.635 for octadecane.

2. Relation proposed by Meissner and Redding

Meissner and Redding (210) proposed a relation for all compounds (except water) which was based on the parachor of Sugden, $[P]$.

$$V_c = (0.377[P] + 11.0)^{1.25}$$

3. Relations proposed by Herzog

Herzog (136) proposed two relations which relate the critical volume to the parachor and the critical temperature or the critical pressure. The relations are

$$V_c = c[P]/P_c^{0.25}$$

and

$$V_c = K[P]_c^{1.2}/T_c^{0.3}$$

The values of the constants c and K are parameters which are varied according to the specific substance under consideration. The reliabilities are 6–10 per cent for the former and 5–8 per cent for the latter. The best results are obtained if the experimental values are used. However, an error of 5 per cent in the critical temperature will yield only a 2 per cent error in the value predicted for the critical volume.

4. Relation proposed by Meissner

The relation proposed by Meissner (209) does not involve the use of the critical temperature or the critical pressure:

$$V_c = (0.55)(1.5[P] + 9 - 4.34[R_D])^{1.155}$$

Many other correlations have been proposed for all three of the critical constants but they are too numerous to discuss here. The best known and most generally useful have been presented. A complete evaluation is beyond the scope of this paper, but it is believed that these relations will allow one to predict or correlate critical constants within the limits of engineering accuracy.

V. EXPERIMENTAL CRITICAL DATA

The units of the critical data which are tabulated in the pages that follow are as follows: critical temperature, t_c , in °C.; critical pressure, p_c , in normal atmospheres; and critical density, d_c , in grams per cubic centimeter.

The methods that have been used to establish the critical values were numerous; hence the following key has been prepared:

KEY	METHOD
1.....	Disappearance of the meniscus (usually the average value of the temperatures of disappearance and reappearance of the meniscus)
2.....	Disappearance of the meniscus upon a very slight volume increase (pressure decrease)
3.....	Disappearance of critical opalescence
4.....	Disappearance of droplets after the meniscus has broadened
5.....	Pressure-volume-temperature relations: $\left(\frac{\partial P}{\partial V}\right)_T = 0$
6.....	Disturbance of a balanced tube
7.....	Rotating bomb
8.....	Method of Cailletet and Colardeau
9.....	Plot of enthalpy <i>versus</i> temperature
10.....	Break in the specific gravity curve
11.....	Change in dielectric constant
12.....	Equal viscosities of vapor and liquid
13.....	Calculation from some physical property
14.....	Survey
15.....	Method of Altschul
16.....	Extrapolation of vapor-pressure curve
17.....	Calculation from vapor-pressure equation
18.....	Plot of enthalpy <i>versus</i> pressure
19.....	Law of rectilinear diameters

A. INERT GASES (SEE TABLE 1)

1. Helium

The work of K. Onnes is known for extreme precision and the critical data are assumed to be highly accurate even though there is no basis for comparison. The

final value (1915) reported for the critical temperature is the 1911 value corrected for thermal molecular pressure in the constant-volume helium thermometer. The precision in the measurements is: temperature, $\pm 0.1^\circ\text{C}$.; pressure, ± 0.01 atm.; density, 0.5 per cent.

2. Helium³

The He³ samples were obtained from the decay of tritium gas which had been prepared by neutron irradiation of lithium in a chain-reacting pile. The tritium was separated from He⁴ by diffusion through a heated palladium thimble. The He³ was purified by passing it through a U-tube immersed in liquid helium. The sample contained 0.03 ± 0.03 mole per cent He⁴ according to a mass-spectrograph analysis.

3. Neon

Onnes, Crommelin, and Cath removed hydrogen from their impure neon by exploding it with oxygen. The neon was frozen a number of times and distilled over charcoal cooled in liquid air. Traces of impurity were still present, as was evidenced by an increase in pressure when the gas was liquefied at constant temperature. The temperature was thought to be within a few tenths of a degree of the true critical temperature.

Crommelin used the same procedure as Onnes, Crommelin, and Cath, except that he passed neon through a coil immersed in liquid hydrogen. The pressure of the neon was maintained at 12 mm. of mercury (approximately its vapor pressure) to remove nitrogen and oxygen that might have been present. The neon was then solidified and fractionated, the first portion being rejected.

The rectilinear diameter was determined by Mathias and Crommelin, using the same neon sample as was used by Crommelin to determine the critical temperature.

4. Argon

The data of Olszewski are not considered, since there was doubt as to the purity of the sample used in the determination. Ramsay and Travers used a crude cryostat in their work, which did not permit the necessary accuracy.

The argon used by Crommelin was extracted from air by absorbing oxygen and nitrogen with calcium carbide and calcium chloride. The gas was purified by passing it over a mixture of quicklime, magnesium, and sodium. Crommelin stated that exact measurements were not made because of suspected impurities; hence the data are rounded to three figures. The value selected for the critical density was determined by the application of the rule of rectilinear diameters.

5. Krypton

The sample used by Ramsay and Travers was separated from 30 l. of liquid air. The oxygen and nitrogen were evaporated and traces in the residue were removed by explosion with hydrogen and absorption by a mixture of lime and magnesium, respectively. The resulting mixture (argon, krypton, and xenon) was fractionated to remove the argon (spectrographically). The xenon was

TABLE 1

Inert gases

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
1. Helium						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1908	-268	2.3		Onnes	13	(240)
1909	-268	2.75		Onnes	1	(241)
1911	-267.6		0.065	Onnes	13	(242)
1911	-267.85	2.26	0.066	Onnes	3	(243)
1915	-267.90	2.26		Onnes and Weber		(249)
1925			0.06930	Mathias <i>et al.</i>	19	(199)
Values selected.....	-267.9	2.26	0.0693			
2. Helium ^s						
1949	-269.82	1.15		Sydoriak <i>et al.</i>	5	(307)
1950	-269.84	1.13		Abraham <i>et al.</i>	1	(1)
1950	-269.81	1.17		Abraham <i>et al.</i>	5	(1)
		\pm 0.03				
Values selected.....	-269.82	1.15				
3. Neon						
1909		29		Onnes	1	(241)
1911	-212			Rankin	13	(271)
1917	-228.36	26.86		Onnes, Crommelin, and Cath	5	(244)
1923	-228.72			Crommelin	5	(86)
1923			0.4835	Mathias, Crommelin, and Onnes	19	(198)
Values selected.....	-228.7	26.9	0.484			
4. Argon						
1895	-121.0	50.6		Olszewski	?	(259)
1901	-117.4	52.9		Ramsay and Travers	?	(259)
1910	-122.44	47.996	0.509	Crommelin	5	(259)
1912			0.53078	Mathias, Onnes, and Crommelin	19	(259)
Values selected.....	-122	48.0	0.531			

TABLE 1—Continued

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
5. Krypton						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1901	-61.5	54.3		Ramsay and Travers	1	(269)
1909			0.775	Rudorf	13	(280)
1937	-63.77	54.270		Meihuizen and Crommelin	5	(208)
1937			0.9085	Mathias, Crommelin, and Meihuizen	19	(200)
Values selected.....	-63.8	54.3	0.908			
6. Xenon						
1901	14.7	58.0		Ramsay and Travers	1	(269)
1907			1.126	Happel	13	(127)
1912	16.6	58.2	1.155	Patterson <i>et al.</i>	1, 15, 19	(254)
1951	16.65	57.89	1.09	Beattie <i>et al.</i>	5	(19)
1952	16.590		1.105	Weinberger and Schneider	1	(331)
Values selected.....	16.59	58.0	1.105			

removed by additional fractionation. The final sample consisted of only 0.03 g.

Meihuizen and Crommelin purified krypton by passing it through a cold trap (-115°C.) to freeze out water and carbon dioxide and then condensing the krypton by liquid air. The krypton was next solidified and the gas above it was exhausted. The krypton was then evaporated and the middle portion resolidified, the gases again being exhausted. The middle fraction was stored. Spectroscopic and vapor-pressure checks indicated that a small amount of xenon was still present. The gas was then purified by rectification in a spiral column designed for low-temperature work. A vapor-pressure check indicated a much purer sample of krypton.

The data of Crommelin and coworkers are selected as the most probable, because of the purity of their sample and the techniques that were used in the Leiden Laboratories.

6. Xenon

Ramsay and Travers prepared xenon by fractionally distilling liquid air. Oxygen was removed by phosphorus and by sparking with hydrogen. The sample was repeatedly fractionated. It consisted of only 3 cc. at normal temperature and pressure.

Patterson, Cripps, and Whytlaw-Gray worked with a sample which was the residue of 120 tons of liquid air. The sample was repeatedly fractionated and

liquefied, and the non-condensable gases were removed by evacuation of the gas phase. The sample then occupied about 120 cc. under normal conditions. The xenon was allowed to boil away and the final 20 cc. was collected for use in the determinations.

Beattie, Barriault, and Brierley used a sample of xenon from the Linde Air Products Company. Mass-spectrometer analysis showed that the sample contained 0.105 mole per cent krypton but neon, argon, oxygen, and nitrogen were not detected. A precise determination of the critical constants was not made; the reported values were said to be approximately correct.

The xenon used by Weinberger was obtained from the General Electric Company and was said to contain less than 100 parts per million of krypton. No krypton (i.e., less than 0.01 per cent) or any other impurities were detected on analysis with a mass spectrometer. The effect of contaminants from gasket material was discussed by the authors. The precision of the work was given as $\pm 0.001^\circ\text{C}$. for the critical temperature.

The high precision of the work of Weinberger and Schneider warrants the selection of their data for the critical temperature and density. The critical pressure was taken as the average of the values of Beattie *et al.* and Patterson *et al.*

B. ELEMENTARY GASES (SEE TABLE 2)

1. Chlorine

The data prior to 1913 are reported for historical value only.

Estreicher and Schnerr did not mention the method used for preparation and purification of the sample. The mean of twenty determinations made in two tubes was 143.4°C . with a range of 142.2 to 144.15°C .

Pellaton prepared chlorine by the decomposition of gold chloride. Purified gold was heated to 300°C . in a stream of air to insure complete dryness. The chlorination was carried out at 200°C . The sample tubes were evacuated to 0.005 mm. of mercury and heated. The chlorine which was given off by the heated gold chloride was condensed therein. The thermometer was calibrated at 100° , 130° , and 54°C . against water, chlorobenzene, and bromobenzene. The results obtained with four sample tubes were as follows:

TUBE NO.	t_c	TUBE NO.	t_c
1.....	143.99	3.....	143.95
2.....	143.98	4.....	144.05

2. Bromine

The sample used by Nadejdine was thought to contain impurities such as water, organic matter, and hydrobromic acid. No information is available as to how the sample was prepared or how the critical state was determined.

Scheffer and Voogd distilled bromine many times through a potassium bromide solution containing zinc oxide and then dried the bromine over phosphorus

pentoxide. The critical pressure was determined by extrapolating the vapor-pressure curve ($\log p$ vs. $1/T$) to the critical temperature. The value is believed to be accurate to 1 atm.

The data of Scheffer and Voogd are selected as being more reliable than those of Nadejdine, although the latter's value for the critical density is retained for lack of other data.

3. Iodine

No information is available concerning the preparation and purification of the sample. There is no basis for selecting a more probable value of the critical temperature.

4. Hydrogen (normal)

The first experimental work was done by Olszewski in 1895 but insufficient cooling hindered the efforts. In 1905 observations of the meniscus (again by Olszewski) showed that the meniscus disappeared at a pressure of 20 atm. and reappeared at 13.4 atm.

The work of Bulle was discredited by Onnes, because it seemed unlikely that temperatures were uniform throughout the bath.

The work of Onnes *et al.* is probably the most reliable to date, since these workers have available the best low-temperature apparatus known. The hydrogen was purified by fractional distillation. Isothermals were determined above and below the critical point and the parabola drawn on a p - V diagram. The pressure at the vertex was taken as the critical pressure, and the critical temperature was determined by extrapolating the vapor-pressure curve and the critical pressure. The uncertainty in the temperature was 0.1°C . The fact that the isothermals (below the critical) were straight and parallel to the volume axis indicated (1) that the hydrogen was pure and (2) that the temperature could be maintained to 0.01°C .

White, Friedman, and Johnston prepared hydrogen electrolytically. The sample was purified by three successive liquefactions and distillations. The total impurity was less than 0.002 per cent. The precision was as follows: temperature, $\pm 0.02^\circ\text{C}$.; pressure, 1 part in 30,000 at 25 atm. No attempt was made to correct for the ortho-para shift. It was thought that the maximum change was 2-3 per cent during the longest runs. The workers stated that they did not observe any evidence of critical opalescence.

The data of White and of Onnes are in excellent agreement and consequently are selected as the most reliable.

5. Homologs of hydrogen

The hydrogen and deuterium samples used by Hoge and Lassiter were catalyzed to equilibrium (ortho-para) at 20.4°K . The uncertainties in their determinations were 0.04 - 0.045°C . for the temperature, 30-40 mm. of mercury for the pressure, and ± 2 per cent for the volume.

The sample used by Friedman, White, and Johnston was obtained from the

TABLE 2
Elementary gases

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
1. Chlorine						
	$^{\circ}\text{C}.$	<i>atm.</i>	<i>g./cc.</i>			
1878	148.			Ladenburg	?	(173)
1884	141.	83.9		Dewar	?	(90)
1890	146.0	93.5		Knietsch	?	(166)
1913	143.2			Estreicher and Schnerr	1	(104)
1915	144.0	76.1	0.573	Pellaton	1, 19	(257)
Values selected...	144.	76.1	0.573			
2. Bromine						
1885	302		1.18	Nadejdine	?	(147)
1926	311	102		Scheffer and Voogd	1, 16	(292)
Values selected...	311	102	1.18			
3. Iodine						
1902	512			Radice	1	(266)
1920	553			Rassow	?	(272)
4. Hydrogen (normal)						
1882	-174.2	98.9	0.050	Sarrau	13	(287)
1885	-240.4	13.3		Wroblewski	13	(340)
1895	-234.5	20.0		Olszewski	1	(238)
1905	-240.8	13.4-15.0		Olszewski	1	(239)
1913	-241.15	11.0		Bulle	?	(56)
1917	-239.9*	12.80	0.0310	Onnes, Crommelin, and Cath	5, 19	(245)
1921			0.03102	Mathias, Crommelin, and Onnes	19	(197)
1950	-239.92	12.797		White, Friedman, and Johnston	1	(333)
Values selected...	-239.9	12.80	0.0310			
5a. Equilibrium hydrogen						
1951	-240.22	12.770	0.0326	Hoge and Lassiter	5	(14)
5b. Hydrogen deuteride						
1951	-237.25	14.645	0.0209	Hoge and Lassiter	5	(14)

* Ice point taken to be 273.09°K.

TABLE 2—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
5c. Equilibrium deuterium						
1951	°C. −234.90	atm. 16.282	g./cc. 0.0151	Hoge and Lassiter	5	(14)
5d. Normal deuterium						
1951	−234.82 (−234.81)	16.421 (16.432)		Friedman, White, and Johnston	1	(112)
6. Nitrogen						
1882	−123.8	42.1	0.2719	Sarrau	13	(287)
1884		39.2		Olszewski	1	(233)
1884	−146	35.0		Olszewski	1	(234,238)
1884	−146	35.0		Dewar	?	(90)
1885	−146	33.0		Wroblewski	?	(341,342)
1886			0.44	Wroblewski	?	(344)
1888	−146.5			Wroblewski	?	(345)
1904			0.3269	Dewar	?	(91)
1914	−147.13	33.490		Onnes, Dorsman, and Holst	1	(246)
1914			0.31096	Mathias, Onnes, and Crommelin	19	(202)
1915	−144.7	33.65		Cardoso	1	(63)
1951	−146.90	33.54		White, Friedman, and Johnston	1	(334)
Values selected...	−147.0	33.5	0.311			
7. Oxygen						
1882	−105.4	48.7	0.3637	Sarrau	?	(287)
1883	−113			Wroblewski	1	(346)
1884	−113.0	50	0.63	Dewar	?	(90)
1885	−118	50		Wroblewski	1	(343)
1885	−118.8	50.8		Olszewski	1	(238)
1904			0.400	Mathias	?	(193)
1904			0.4407	Dewar	?	(91)
1907			0.433	Happel	?	(126)
1911			0.4299	Mathias and Onnes	19	(201)
1914	−118.83	49.71		Onnes, Dorsman, and Holst	1	(246)
1915	−118.0	49.30	0.430	Cardoso	3	(67)
1950	−118.38	50.14	0.38	Hoge	5	(139)
Values selected..	−118.4	50.1	0.41			
8. Ozone						
1922	−5	67	0.537	Riesenfeld and Schwab	1,17,19	(277)

Stuart Oxygen Company and was said to be 99.7 atomic per cent hydrogen. The impurity was hydrogen deuteride. The second value (in parentheses) is the value corrected for the 0.3 atomic per cent hydrogen (assumed to be linear with position).

6. Nitrogen

The data prior to 1914 are presented for historical value only.

The nitrogen used by Onnes, Dorsman, and Holst was made by boiling sodium nitrite and sodium sulfate with ammonia and was then passed through concentrated sulfuric acid. The purity was ascertained by condensing the vapor at a constant temperature. The pressure was constant to within a few hundredths of an atmosphere, indicating a nearly pure sample. The precision of the determination of the critical point was: temperature, $\pm 0.1^\circ\text{C}$.; pressure, ± 0.05 atm.; density, 1 per cent.

Cardoso prepared nitrogen by heating purified potassium trinitride and passing the gas over calcined barium oxide and then over phosphorus pentoxide. The constancy of the pressure during isothermal condensation indicated a sample of high purity.

Johnston and coworkers used a sample of nitrogen from the Linde Air Products Company which contained less than 0.01 mole per cent impurities. They used a copper-constantan thermocouple with an uncertainty of temperature measurement of less than 0.02°C . and a dead-weight tester which gave pressure measurements with an uncertainty of less than 1 part in 10,000. They stated that no opalescence was noted in their determinations.

The data of Johnston and of Onnes are in good agreement; hence average values of these workers are selected as the most reliable data.

7. Oxygen

Only the data since 1911 will be considered in the final selection.

The oxygen used by Onnes, Dorsman, and Holst was prepared by heating pure recrystallized potassium permanganate. The gas was passed over heated platinized gauze and condensed by means of liquid air. It was then allowed to evaporate slowly to eliminate water vapor and carbon dioxide. The sample exhibited a constant pressure during isothermal condensation.

Cardoso prepared oxygen from pure crystallized potassium permanganate and passed the gas over solid potassium hydroxide and phosphorus pentoxide.

Hoge also prepared oxygen by heating potassium permanganate. The first 1 per cent of the gas evolved was discarded and the sample was collected until approximately 80 per cent of the crystals had decomposed. The purity was checked by melting-point depression and the tests showed that the impurities comprised $2-4 \times 10^{-5}$ mole per cent of the sample; hence no further purification was made. The precision of the measurements was: temperature, $\pm 0.03^\circ\text{C}$.; pressure, ± 0.07 atm.; density, ± 1 per cent.

The discrepancy between the values of Hoge and those of Onnes, Dorsman, and Holst may be thought to be due to the criterion used in determining the

critical point. However, Hoge stated that only about one-half of the difference could be attributed to this factor.

The values selected are those of Hoge for the critical temperature and pressure. The value for the critical density is an average of the values of Hoge and those of Mathias and of Mathias and Onnes.

8. Ozone

The only experimental data for ozone were obtained by Riesenfeld and Schwab. No information on the sample purity was given, but it was noted that the temperature at which the meniscus disappeared became lower and lower and approached the value for the critical temperature of oxygen. In view of this fact, the data may not be very accurate. The critical pressure was calculated by the method of Byk (57) and may be as much as 7 per cent from the true value.

C. ALIPHATIC HYDROCARBONS

1. Paraffins (see table 3)

(a) Methane

The data of Sarrau, Wroblewski, Dewar, Olszewski, and Mathias are reported for historical reasons only, since little or no information was given as to methods of sample preparation and purification.

Cardoso prepared methane by the action of water on methylmagnesium iodide. The methane was stored over water for several days and then passed through potassium hydroxide solution and concentrated sulfuric acid. The gas was then dried over solid phosphorus pentoxide and fractionally distilled ten times at liquid-air temperature.

Keyes, Taylor, and Smith prepared methane by heating a mixture of dry sodium acetate and soda lime. Acetone was removed by 20 per cent fuming sulfuric acid and the sulfur trioxide fumes were removed by 98 per cent sulfuric acid. The gas was then passed through a sodium hydroxide solution, solid sodium hydroxide, and phosphorus pentoxide. The impurities were believed to be less than 1 part in 500 (the limit of analytical accuracy).

Wiebe and Brevoort prepared methane by the Grignard reaction, using methyl iodide in an excess of ether. Water was used to decompose the reagent, and the methane was passed successively through a condensation bulb (to remove ether), fuming sulfuric acid, concentrated sulfuric acid, 30 per cent sodium hydroxide, solid potassium hydroxide, and solid phosphorus pentoxide. The methane was then liquefied and fractionally distilled several times, the first and last portions being rejected each time. The melting point was measured as $-182.9^{\circ}\text{C}.$, as compared to a literature value of $-184^{\circ}\text{C}.$, indicating a possible trace of impurity.

Corcoran, Bowles, Sage, and Lacey determined the critical values, using the enthalpy data of Wiebe and Brevoort and the vapor-pressure data of Eucken and Berger (105). The uncertainty in the enthalpy values was stated to be less than 0.5 B.T.U. per pound.

TABLE 3
Aliphatic hydrocarbons: paraffins

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
(a). Methane						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1882	-75.7	46.8	0.145	Sarrau	?	(287)
1884	-73.5	56.8		Wroblewski	?	(340)
1884	-99.5	50.0		Dewar	?	(90)
1885	-81.8	54.9		Olszewski	?	(236)
1904			0.145	Mathias	?	(193)
1913	-82.85 (-82.29)*	45.6	0.1623 (0.1618)	Cardoso	1, 19	(62)
1922	-82.11	45.79	0.1613	Keyes, Taylor, and Smith	1, 19	(162)
1930	-82.13			Wiebe and Brevoort	9	(335)
1945	-82.5	45.8	0.1381	Corcoran, Bowles, Sage, and Lacey	9, 18, 5	(83)
A.P.I.	-82.5	45.80	0.162			
Values selected ...	-82.1	45.8	0.162			
(b). Ethane						
1884	35	45.2		Dewar	?	(90)
1889	34	50.2		Olszewski	?	(238)
1894	32-40	50		Hainlan	1, 16	(122)
1895	32.2			Kuenan	?	(169)
1897	32	48.8		Kuenan	?	(170)
1902	31.95	48.43	0.206	Kuenan and Robson	?	(171)
1912	32.1	48.85		Cardoso and Bell	3	(68)
1915	32.32	48.13		Prins	1	(263)
1937	32.6	48.85	0.212	Sage, Webster, and Lacey	5, 19	(284)
1939	32.27	48.20	0.203	Beattie, Su, and Simard	5	(29)
1940	32.23			Mason, Naldrett, and Maass	10	(191)
A.P.I.	32.27	48.20	0.203			
Values selected ...	32.3	48.2	0.203			
(c). Propane						
1889	97.	44.		Olszewski	?	(238)
1894	102.	48.5		Hainlan	1, 16	(122)
1905	97.5	45.		Lebau	1	(177)
1921	95.6			Maass and Wright	1	(187)
1934	100.1	43.77	0.2323	Sage, Schaafsma, and Lacey	5	(283)
1935	96.81	42.01	0.226	Beattie, Poffenberger, and Hadlock	5	(27)
1939	98.9	43.28		Scheeline and Gilliland	5	(289)
1940	96.85	42.1	0.224	Deschner and Brown	1, 19	(88)
1942			0.2194†	Meyers	19	(213)
1949			0.220†	Reamer, Sage, and Lacey	19	(274)
A.P.I.	96.81	42.01	0.220			
Values selected ...	96.8	42.0	0.220			

TABLE 3—Continued

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
(d). <i>n</i> -Butane						
	°C.	atm.	g./cc.			
1911	150.8	37.5		Kuenan	?	(174)
1913	150.8	37.5		Visser	?	(174)
1915	153.2	35.67		Siebert and Burrell	1	(301)
1935	150.7			Harand	1	(128)
1938	152.8	36.00	0.232	Edmister	?	(101)
1939	152.01	37.47	0.225	Beattie, Simard, and Su	5	(28)
1940	152.2	37.46	0.228	Kay	1, 19	(153)
1946	152.0	37.50	0.228	Hanson	14	(125)
A.P.I.	152.01	37.47	0.228			
Values selected . . .	152.0	37.5	0.228			
(e). Isobutane						
1915	133.7	36.54		Siebert and Burrell	2	(301)
1946	134.8	35.9	0.227	Hanson (Sage and Lacey)	5, 19	(125)
1949	134.98	36.00	0.221	Beattie, Edwards, and Marple	5	(22)
A.P.I.	134.98	36.00	0.221			
Values selected . . .	134.9	36.0	0.221			
(f)(1). <i>n</i> -Pentane						
1910	197.2	33.03	0.2323	Young	2, 19	(350)
1942	197.2	33.6	0.229	Sage and Lacey	5	(282)
1948	196.62	33.31	0.232	Beattie, Douslin, and Levine	5	(20)
A.P.I.	196.62	33.31	0.232			
Values selected . . .	196.6	33.3	0.232			
(f)(2). Isopentane (2-methylbutane)						
1882	194.8			Pawlewski	1	(255)
1893	187.1	33.3		Altschul	1	(4)
1910	187.8	32.9	0.2343	Young	2, 19	(350)
A.P.I.	187.8	32.9	0.234			
Values selected . . .	187.8	32.9	0.234			

TABLE 3—Continued

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
(f)(3). Neopentane (2,2-dimethylpropane)						
1951	160.60	31.57	0.238	Beattie, Douslin, and Levine	5	(20)
A.P.I.	160.60	31.57	0.238			
Values selected . . .	160.6	31.6	0.238			
(g)(1). <i>n</i> -Hexane						
1882	250.3	30.	0.2343	Pawlewski	1, 19	(255)
1893	234.5	29.		Altschul	1	(4)
1906	234.8			Winkelman	1	(336)
1910	234.8	29.6	0.2344	Young	2, 19	(350)
1926			0.2344	Germann and Pickering	19	(148)
1937	234.7	29.6		Merckel	?	(212)
1942	236.	30.		Ipatieff and Monroe	7	(149)
1946	234.7	29.94	0.233	Kay	1, 19	(154)
A.P.I.	234.7	29.92				
Values selected . . .	234.7	29.9	0.234			
(g)(2). 2,3-Dimethylbutane						
1910	227.35	30.74	0.2411	Young	2, 19	(350)
1946	227.1	30.99	0.241	Kay	1, 19	(154)
A.P.I.	227.1	30.99	0.241			
Values selected . . .	227.1	30.9	0.241			
(g)(3). 3-Methylpentane						
1946	231.2	30.83	0.235	Kay	1, 19	(154)
1951	231.5	30.75		Day and Felsing	5, 17	(87)
A.P.I.	231.2	30.83	0.235			
Values selected . . .	231.5	30.8	0.235			

TABLE 3—Continued

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
(g)(4). 2-Methylpentane						
1946	°C. 224.7	<i>atm.</i> 29.95	<i>g./cc.</i> 0.235	Kay	1, 19	(154)
A.P.I.....	224.9	29.95	0.235			
Values selected...	224.7	29.9	0.235			
(g)(5). 2,2-Dimethylbutane						
1946	216.2	30.67	0.240	Kay	1, 19	(154)
A.P.I.....	216.2	30.67	0.240			
Values selected...	216.2	30.7	0.240			
(h)(1). <i>n</i> -Heptane						
1910	266.85	26.88	0.2341	Young	1, 19	(350)
1929	269.5	27.65		Edgar and Calingaert	1	(99)
1937	267.01	27.00	0.241	Beattie and W. C. Kay	5	(24)
1938	267.4	27.0	0.235	W. B. Kay	1, 19	(152)
1939	265.2			Khalilov	12	(163)
A.P.I.....	267.01	27.01	0.235			
Values selected...	267.0	27.0	0.235			
(h)(2). Isomers of heptane						
HEPTANES	t_c	p_c	d_c			
	°C.	<i>atm.</i>	<i>g./cc.</i>			
2-Methylhexane.....	257.9‡	27.2‡	0.234			
3-Methylhexane.....	262.4‡	28.1‡	0.240			
3-Ethylpentane.....	267.6‡	28.6	0.241			
2,2-Dimethylpentane.....	247.7‡	28.4‡	0.248			
2,3-Dimethylpentane.....	264.6‡	29.2‡	0.247			
2,4-Dimethylpentane.....	247.1‡	27.4‡	0.239			
3,3-Dimethylpentane.....	263	30				
2,2,3-Trimethylbutane.....	258.3‡	29.75‡	0.254			

TABLE 3—Concluded

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
(i)(1). <i>n</i> -Octane						
	°C.	<i>atm.</i>	<i>g./cc.</i>			
1893	296.4	25.2		Altschul	1	(4)
1910	296.2	24.64	0.2327	Young	2, 19	(350)
A.P.I.....	296.2	24.64	0.235			
Values selected.....	296.2	24.6	0.233			
(i)(2). 2,5-Dimethylhexane						
1883	270.8			Pawlewski	1	(255)
1910	276.8	24.55	0.2366	Young	2, 19	(350)
A.P.I.....	279.	25.0	0.239			
Values selected.....	276.8	24.6	0.237			
(i)(3). 2,2,4-Trimethylpentane						
1948	271.2	25.5	0.237	Beattie and Edwards	5	(21)
1951	270.676	25.308	0.243	Kay and Warzel	1, 19	(156)
A.P.I.....	271.15	25.50	0.237			
Values selected.....	270.9	25.4	0.243			
(i)(4). Other isomers of octane (A.P.I. Research Project No. 44)						
ISOMERS OF OCTANE				t_c	p_c	d_c
				°C.	<i>atm.</i>	<i>g./cc.</i>
2-Methylheptane.....				288	24.8	0.234
3-Methylheptane.....				292	25.6	0.239
4-Methylheptane.....				290	25.6	0.240
3-Ethylhexane.....				294	26.4	0.245
2,2-Dimethylhexane.....				279	25.6	0.245
2,3-Dimethylhexane.....				293	26.6	0.248
2,4-Dimethylhexane.....				282	25.8	0.245
3,3-Dimethylhexane.....				291	27.2	0.254
3,4-Dimethylhexane.....				298	27.4	0.253
3-Ethyl-2-methylpentane.....				295	27.4	0.254
3-Ethyl-3-methylpentane.....				305	28.9	0.263
2,2,3-Trimethylpentane.....				303	29.0	0.264
2,3,4-Trimethylpentane.....				295	27.6	0.256
2,2,3,3-Tetramethylbutane.....				270.8‡	24.5‡	0.238

* Values in parentheses have been corrected by Keyes *et al.* for thermometric error.

† Recalculated from data of Beattie, Poffenberger, and Hadlock.

‡ From unpublished work of Keyes.

§ These values are from Felsing and coworkers (107a) but upon checking, it was found that Felsing *et al.* did not determine the critical constants. Further investigation revealed that these values are data for diisobutyl, which in reality is 2,5-dimethylhexane and not 2,2,3,3-tetramethylbutane. It is believed that there are no experimental values for 2,2,3,3-tetramethylbutane.

The values selected for the critical temperature and pressure are those of Keyes, Taylor, and Smith, since this work was performed very precisely by direct observation (probably by the method of disappearing meniscus). The value for the critical temperature is substantiated by the work of Wiebe and Brevoort and of Cardoso. The value for the critical pressure is substantiated by work of Cardoso (62) and Corcoran, Bowles, Sage, and Lacey (83). The values have been rounded to three significant figures because of the uncertainties involved.

The value for the critical density is taken as the mean of the values of Cardoso and of Keyes, Taylor, and Smith (rounded to three significant figures). The value of Corcoran, Sage, and Lacey is obviously in error and is disregarded in the final choice.

(b) Ethane

The values of observers prior to 1912 are reported for historical reasons only.

The ethane used by Cardoso and Bell was prepared by two methods: The first method was the action of pure magnesium on ethyl iodide in ether solution. The ethane was liberated by adding etherized water. The gas was liquefied, distilled, and passed through alcoholic potassium hydroxide, bromine water, and concentrated sulfuric acid. This cycle was repeated seven times, after which the gas was fractionated nine times. The second method used was that of adding ethyl cyanide to sodium wire. The gaseous product was passed through potassium hydroxide and sulfuric acid, and dried over solid phosphorus pentoxide. Measurements made on ethane from each source checked very well.

Prins prepared ethane by the electrolysis of a sodium acetate solution. The gas was purified by passing it through bromine water and concentrated potassium hydroxide solution. It was then dried over soda lime and phosphorus pentoxide and fractionated at liquid-air temperatures.

Sage, Webster, and Lacey used 95 per cent ethane from the Carbon and Carbide Chemicals Corporation as a starting material. The impure gas was fractionated three times in a column packed with glass rings, the middle cut being used each time. The product was condensed at 1×10^{-4} in. of mercury. This material was then mixed with a larger quantity which had been previously purified by a similar method and two additional fractionations and partial condensations were carried out. A change in pressure of 0.2 p.s.i. from dew point to bubble point at 70°F. indicated only a trace of impurity.

Beattie, Su, and Simard used a bulk-stock ethane (99.9 per cent) from the Linde Air Products Research Laboratory. This was distilled three times using liquid air, the first and last portions being discarded each time.

Mason, Naldrett, and Maass passed ethane through a train consisting of saturated bromine water, potassium hydroxide, copper oxide at 300°C., and a trap immersed in a solid carbon dioxide-acetone mixture.

The value selected for the critical temperature (32.3°C.) is an average of the values reported by Beattie, Su, and Simard (29), Mason, Naldrett, and Maass (191), and Prins (263). Cardoso's value is slightly lower, since it was made by direct observation as opposed to the pressure-volume relationships used by the

other workers. The critical pressure was selected as 48.2 atm. on the basis of the work of Prins and of Beattie, Su, and Simard. (The value of Sage, Webster, and Lacey also is in good agreement if corrected to the same value of critical temperature.) The value for the critical density was chosen as 0.203 g./cc., because of the precision of the techniques of Beattie, Su, and Simard.

(c) Propane

The work prior to 1934 will be disregarded because of abundance of later data obtained using more advanced techniques.

Sage, Schaafsma, and Lacey used propane obtained from the Phillips Petroleum Company. The gas had purity specifications of no detectable impurities. Isothermal compression at 100°F. showed a difference of less than 0.5 p.s.i. in the bubble-point and dew-point pressures. No further purification was attempted.

The propane used by Beattie, Poffenberger, and Hadlock was obtained from the Linde Air Products Company and had a purity of 99.9+ per cent. The purity was checked by measuring the vapor pressure at 50°C. and 75°C. over wide ranges of vapor volume. The vapor pressure was constant within limits of measurement (± 0.001 atm.).

Scheeline and Gilliland used 99.9+ per cent propane from the Phillips Petroleum Company. The propane showed no absorption by strong bromine water and was used as received.

Deschner and Brown purified 98.27 per cent propane from the Phillips Petroleum Company by four distillations from which the middle one-third cuts were used. The propane was then frozen, and non-condensables were removed by a mercury diffusion pump.

The purity of the sample of Sage, Schaafsma, and Lacey is questionable on the basis of the pressure differential between dew point and bubble point. Thus from the standpoint of sample purity, only the data of Beattie, Poffenberger, and Hadlock, of Scheeline and Gilliland, and of Deschner and Brown will be considered.

From the standpoint of precision the values of Beattie, Poffenberger, and Hadlock are chosen for the critical temperature and pressure.

The method of evaluation of critical density by Beattie, Poffenberger, and Hadlock is not as accurate as the application of the law of rectilinear diameters; hence the values as determined by Meyers and by Reamer, Sage, and Lacey are averaged to obtain the selected value of the critical density.

(d) *n*-Butane

The work of Kuenan (174), Visser (174), and Siebert and Burrell (301) has been discussed by Pickering (259) and will not be considered here.

Beattie, Simard, and Su obtained *n*-butane from the Buffalo Laboratory of the Linde Air Products Company. The butane was fractionated five times to remove permanent gases. The vapor pressure increased 0.01–0.02 atm. during isothermal expansion, indicating a small amount of impurity, probably isobutane.

Kay used *n*-butane from the Phillips Petroleum Company analyzing 99.4

per cent *n*-butane and 0.6 per cent isobutane. The gas was passed through fuming sulfuric acid, through concentrated potassium hydroxide solution, and then over calcium chloride and phosphorus pentoxide. The material was then condensed in the boiling flask of a distillation apparatus and distilled at a high reflux ratio. The center cut showed a change of 0.2–0.7 p.s.i. (0.014–0.048 atm.) from dew point to bubble point, indicating a small amount of isobutane as impurity.

The values reported by Hanson are values selected from the work of Beattie, Simard, and Su (28) and Kay (153).

The source of Edmister's values is not known.

Harand reported only the critical temperature which was obtained by a micro-technique of questionable reliability; hence his values are not considered.

It is evident that a high degree of purity had been obtained by both Beattie, Simard, and Su (28) and Kay (153), with a slight advantage in favor of Beattie and coworkers. Beattie claims an overall accuracy of 0.03 per cent in pressure measurements and 0.002°C. precision in temperature measurements. (The claims of Kay are slightly less.) The values of the critical temperature and the critical pressure are in excellent agreement, but the values of Beattie, Simard, and Su are selected because of the evidence of higher purity and greater precision.

In the determination of the critical volume (density), Beattie, Simard, and Su read the value directly from the critical isotherm of a pressure–volume plot. Hanson reports a value for the critical density as determined by Cragoe, using data of Beattie *et al.* extrapolated by application of the rule of rectilinear diameters. Kay also determined the critical density by application of the law of rectilinear diameters. These values are in excellent agreement (14.21 and 14.24 lb./ft.).

Since it is believed that the extrapolation of the curve of mean density is the most accurate method for determining the critical volume (for non-polar substances), the value of Kay is selected as the most reliable.

(e) Isobutane

The isobutane used by Siebert and Burrell was prepared by electrolytic action of a zinc–copper couple on isobutyl iodide. The gas was collected over potassium hydroxide and solidified by liquid air. Any remaining gases were removed by evacuation. The gas was fractionally distilled ten times at -120°C . and later again fractionated at -98°C . The vapors were condensed isothermally with no perceptible rise in pressure. Several other tests showed that the isobutane was highly purified. The maximum variation in duplicate temperature determinations was 0.1°C. The pressure was measured by a calibrated air manometer (no limits of reproducibility were mentioned).

The data as reported by Hanson are in reality values as reported by Sage and Lacey (281). The critical temperature was determined by Sage and Lacey, using the data of Siebert and Burrell. The critical density was determined by extrapolation of the line of mean density to the critical temperature, and the critical pressure was determined by extrapolation of the vapor-pressure data.

Beattie, Edward, and Marple obtained their sample of isobutane from the Linde Air Products Company. The sample was distilled, solidified, and subjected to high vacuum several times to insure removal of non-condensable gases. A sample of exceptionally high purity was evidenced by the small increase in pressure with a decrease in vapor volume. The precision of the measurements was stated to be: temperature, $\pm 0.05^\circ\text{C}$.; pressure, ± 0.05 atm.; volume, ± 2 per cent.

Because of the techniques employed by Beattie, Edwards, and Marple, their values are selected as being the most probable for the critical values.

(f) Pentanes

The data of Pawlewski and Altschul are presented only for historical value.

The pentanes used by Young were obtained from an American petroleum fraction with a boiling range of $28\text{--}37^\circ\text{C}$. This fraction was treated with sulfuric acid, a sulfuric and nitric acid mixture, water, potassium hydroxide, and water. The material was then distilled from phosphorus pentoxide and fractionally distilled twenty-one times, giving pure samples of normal pentane and isopentane.

Isopentane was also obtained by two additional methods: (1) as a product of the preparation of amylene from amyl alcohol and (2) by the reduction of amyl iodide using concentrated hydrochloric acid and copper-covered zinc in ethanol. In each case, amylene was removed by treatment with bromine. The specific gravities compared very well regardless of the method of preparation (all samples boiled at 27.95°C .).

Sage and Lacey used a sample of normal pentane containing 0.3 per cent of isopentane. This material was treated with concentrated sulfuric acid, neutralized with sodium carbonate, and dried over metallic sodium. After two fractionations, the center cut was stored until desired.

The neopentane used by Beattie, Douslin, and Levine was obtained from A.P.I. Research Project No. 6 and was certified to be 99.98 ± 0.012 mole per cent neopentane. The sample was subjected to six alternate freezings and meltings under vacuum to remove permanent gases and was then distilled into the sample bomb. The expected accuracies of the determinations were: temperature, $\pm 0.05^\circ\text{C}$.; pressure, ± 0.03 atm.; density, ± 1 per cent.

(g) Hexanes

The data prior to 1910 are presented for historical background only.

Young prepared *n*-hexane by the action of sodium on propyl iodide. The product was treated with concentrated sulfuric acid, concentrated nitric acid, caustic potash, and fractionally distilled. 2,3-Dimethylbutane was prepared in a similar manner, using isopropyl iodide in ether.

Ipatieff and Monroe used "practical" hexane, which they stated undoubtedly contained other isomers; hence their results are disregarded.

Kay obtained *n*-hexane, 2-methylpentane, and 3-methylpentane from a close-boiling fraction of petroleum naphtha. These compounds were purified by distillation in a 100-plate column operated at a reflux ratio of 50:1. The *n*-hexane

was further purified by silica gel to remove benzene (estimated to be 2 per cent by volume as determined by absorption spectra). 2,3-Dimethylbutane was prepared by the catalytic alkylation of isobutane and ethylene. The product was distilled in a 15-plate column at a high reflux ratio. A "pure neohexane" grade of 2,2-dimethylbutane was obtained from the Phillips Petroleum Company, treated with concentrated sulfuric acid, and distilled in a 60-plate column.

Day and Felsing used 3-methylpentane from the Phillips Petroleum Company which was certified by the Bureau of Standards to be 99.80 mole per cent pure. Day did not actually determine the critical temperature but showed that the value of 231.2°C. (Kay's value) was below the critical isotherm (showed a flat segment on a pressure-volume plot). Day *estimated* the correct value to be 231.5°C.

The work of Kay is characterized by extreme care in technique and sample preparation; hence his data are selected unless otherwise noted. The values of Young, of Pawlewski, and of Germann and Pickering for the critical density of *n*-hexane were selected. Day's estimated value for the critical temperature of 3-methylpentane was selected.

(h) Heptanes

Young extracted *n*-heptane from Jeffery pine oil. No mention of the method of purification was given but a high purity was ascertained by the following observations: (1) there was no perceptible rise of temperature during distillation, (2) the vapor pressure was independent of the relative amounts of liquid and vapor, (3) the phenomena in and about the critical point were normal, (4) the distillate collected in two fractions showed no difference in specific gravity, and (5) different samples gave results which checked.

Edgar and Calingaert obtained *n*-heptane from Jeffery pine oil as described by E. Kremers (168). The critical values were determined by Keyes and Kleinschmidt, using the same methods and apparatus used in the methane studies (162).

Beattie and Kay secured *n*-heptane from Jeffery pine oil. This material was washed with sulfuric acid and water and then refluxed over a sodium-potassium amalgam. The product was distilled, and a middle portion boiling over 0.01°C. was collected and redistilled (b.p., 98.52°C. \pm 0.01°). The precision of the measurements was as follows: temperature, \pm 0.02°C.; pressure, \pm 0.02 atm.; volume, \pm 1 per cent.

Kay distilled *n*-heptane from Jeffery pine oil and treated it with chlorosulfonic acid for 3 weeks. The sample was then neutralized with caustic, washed with water, dried over calcium chloride, and distilled over phosphorus pentoxide in a silvered, vacuum-jacketed bead column at a reflux ratio of 10:1. Of 500 ml. charged, only the middle 150 ml. was used in the determination. A reasonably high purity was obtained, as was evidenced by the pressure increasing less than 2 p.s.i. (usually less than 1) during the condensation of the vapors at 218°C.

No information is available concerning Khalilov's work except the value of the critical temperature.

The values selected for the critical temperature and pressure are those determined by Beattie and Kay. The work of Young and W. B. Kay substantiates the choice of these values. The value of W. B. Kay for the critical density has been selected as the most probable, since his method is more reliable than that used by Beattie.

All of the data for the isomers of heptane were reported by A.P.I. Project No. 44 (278a). Those data which are marked by the symbol ‡ were from unpublished work of Keyes. The preparation and purification of the sample were reported by Edgar, Calingaert, and Marker (100).

(i) Octanes

Young prepared *n*-octane from octyl iodide. After three fractionations, the distillate was shaken with concentrated sulfuric acid, a mixture of sulfuric and nitric acids, water, and caustic potash. The sample was distilled over phosphorus pentoxide and fractionated twenty-one times. Diisobutyl was prepared by the action of sodium on isobutyl bromide. The paraffin was separated from the bromide by fractional distillation. Final purification was effected by treatment with sulfuric and nitric acids, water, and caustic potash, followed by fractional distillation.

The data of Young are selected for *n*-octane and 2,5-dimethylhexane.

Beattie's sample was obtained from the Bureau of Standards and was used without further purification. Uncertainties of the measurements were as follows: temperature, $\pm 0.10^\circ\text{C}$.; pressure, ± 0.10 atm.; critical density, 3 per cent.

The sample used by Kay was obtained from the Phillips Petroleum Company and was said to contain 99.87 ± 0.05 mole per cent isoöctane. The sample was used without further purification except that it was distilled over phosphorus pentoxide into the sample tubes. The uncertainties of the measurements were as follows: temperature, $\pm 0.01^\circ\text{C}$.; pressure, ± 0.14 atm.; density, ± 0.001 g./cc.

It is extremely difficult to select the best values between two such investigations as those of Beattie and of Kay. Average values are selected as the most probable, except that Kay's value is selected for the critical density. Kay actually measured vapor densities, whereas Beattie estimated these densities by using the Law of Corresponding States with *n*-heptane as a reference substance.

2. Olefins (see table 4)

(a) Ethylene

The data prior to 1912 are presented for historical value only.

Cardoso and Arni prepared ethylene by the dehydration of ethyl alcohol with sulfuric acid and purified it by treatment with potassium hydroxide pellets, phosphorus pentoxide, and finally by ten fractionations.

Maass and Wright used ethylene prepared by the action of aluminum oxide on ethanol at 350°C . Water vapor was removed by phosphorus pentoxide and the

TABLE 4
Aliphatic hydrocarbons: olefins

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
(a). Ethylene						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1880	9.2	58	0.36	van der Waals	1	(321)
1882	1.5	43.5	0.148	Sarrau	13, 20	(287)
1882	13.0			Cailletet	1	(58)
1884	10.1	51.0		Dewar	?	(90)
1886	12.5		0.21	Cailletet and Mathias	1, 19	(60)
1895	10.0	51.0		Olszewski	1	(238)
1897	10.0			Villard	1	(325)
1912	9.50	50.65		Cardoso and Arni	3	(65)
1921	9.9			Maass and Wright	1	(187)
1937	9.50	49.98	0.2374	Maass and Geddes	1, 19	(186)
	± 0.01	± 0.01				
1938	9.50			McIntosh and Maass	1	(206)
1939	9.90	50.50	0.227	McIntosh, Dacey, and Maass	5	(205)
	± 0.01	± 0.01				
1940	9.21			Naldrett and Maass	1	(227)
	± 0.01					
1948	9.27	50.1		Kay	1	(155a)
A.P.I.	9.90	50.50	0.227			
Values selected ...	$\left\{ \begin{array}{l} t_m \ 9.2 \\ t_c \ 9.90 \end{array} \right.$	$\left\{ \begin{array}{l} 50.0 \\ 50.5 \end{array} \right.$	$\left\{ \begin{array}{l} \\ 0.227 \end{array} \right.$			
(b). Propene						
1883	97			Nadejdine	?	(222)
1915	92.6	45.34		Siebert and Burrell	1	(301)
1921	92.1			Maass and Wright	1	(187)
1933	92.0			Winkler and Maass	1	(339)
1940	91.4	45.5	0.233	Vaughan and Graves	1, 19	(322)
1940	91.9	44.6	0.234	Souders	?	(322)
1941	92.1	45.4		Lee, Newitt, and Ruheman	1	(184)
1949	91.76	45.61	0.220	Marchman, Pringle, and Motard	5	(189)
A.P.I.	91.9	45.4	0.233			
Values selected ...	91.8	45.6	0.233			

TABLE 4—Continued

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
(c)(1). 1-Butene						
	°C.	<i>atm.</i>	<i>g./cc.</i>			
1928	144			Coffin and Maass	1	(81)
1928	145			Coffin and Maass	13	(81)
1943	160.0	42.1		Doss (M. W. Kellogg Co.)	?	(94)
1943		39.2	0.2354	Cragoe	14, 19	(85)
1946	147.2	40.0	0.234	Olds, Sage, and Lacey	19	(230)
1949	146.4	39.7	0.233	Beattie and Marple	5	(26)
A.P.I.	146.4	39.7	0.233			
Values selected . . .	146.4	39.7	0.234			
(c)(2). 2-Butene (<i>cis-trans</i> mixture)						
1928	155			Coffin and Maass	1	(81)
1928	156			Coffin and Maass	13	(81)
1943	155	42.1		Doss (M. W. Kellogg Co.)	?	(94)
1943 <i>cis</i>	155.0	40.5	0.2359	Cragoe	14, 19	(85)
<i>trans</i> . . .	160.0	41.5	0.2398	Cragoe	14, 19	(85)
A.P.I.	155	41	0.238			
Values selected . . .	157	41	0.238			
(c)(3). Isobutylene (2-methylpropene)						
1928	143.5			Coffin and Maass	1	(81)
1928	147			Coffin and Maass	13	(81)
1939	149	39.7		Scheeline and Gilliland	1	(289)
1942	144.73	39.48	0.234	Beattie, Ingersoll, and Stockmayer	5	(23)
1942	144.6	39.5		Benedict	?	(23)
1943			0.2352	Cragoe	19	(85)
A.P.I.	144.73	39.45	0.234			
Values selected . . .	144.7	39.5	0.235			
(d)(1). Pentene						
1883	201.0			Pawlewski	1	(255)
1893	208.0			Altschul	1	(4)
1895	201.2			Pictet and Altschul	1	(260)
1903	202.4	40.4		Vespignani	1	(323)
1950	201			Day, Nicholson, and Felsing	5	(87a)
A.P.I.	201	39.9				
Values selected . . .	201	40.				

TABLE 4—Concluded

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
(d)(2). 2-Pentene						
1943	°C. 202.4	atm. 40.4	g./cc.	Doss (U.O.P.)	?	(94)
(d)(3). Isoamylene						
	191.6	33.9		Nadejdine	1	(174)
(d)(4). 2-Methyl-2-butene						
1943		35.3		Doss (U.O.P.)	?	(94)
1951	195-200			Kiyama, Suzuki, and Ikegami	5	(165)
1951	197.2	33.7		Kiyama, Suzuki, and Ikegami	1	(165)
Values selected . . .	197	34				
(e). Hexene						
1893	243.5			Altschul	1	(4)
(f). Octene						
1893	304.8			Altschul	1	(4)

ethylene was distilled several times. As a final purification, the ethylene was distilled *in vacuo* five times, the center cuts being retained each time. They stated that the critical temperature was evaluated by the usual method (probably the method of the disappearing meniscus).

The ethylene used by Maass and Geddes was 99.95 per cent ethylene distilled three times. They reported values for the critical temperature of 9.39°C. depending upon the thermal history of the determination. The temperature of reappearance of the meniscus was always 9.36°C.

McIntosh and Maass followed the procedure of Maass and Geddes and attempted to show that liquid still existed above the classical temperature at which the meniscus disappeared.

McIntosh, Dacey, and Maass prepared ethylene in a manner similar to that of Maass and Geddes but evaluated the critical properties at the point where $(\partial P/\partial V)_T = 0$. The critical region as determined by them is shown in figure 12.

Naldrett and Maass purified 99.95 per cent ethylene by one fractionation in a Podbielniak column. The temperature of the disappearance of the meniscus was determined in a number of ways to evaluate the methods:

1. Large stationary bomb observed through a telescope 5 ft. away; 9.5₀°C.
2. Small stationary bomb observed directly from 1 foot away; 9.3₆°C.

3. Small bomb shaken well to insure equilibrium; 9.21°C.
4. This value (9.21°C.) was also obtained using stationary bombs, providing ample time had elapsed to insure equilibrium.
5. The temperature of reappearance of the meniscus was always at 9.21°C., regardless of the method used.

Kay used commercial ethylene of high purity and distilled an 80-ml. charge in a silvered, vacuum-jacketed column with Stedman packing of about one hundred theoretical plates. A 35-ml. sample was collected in a high-vacuum degassing apparatus and was alternately frozen and melted. The sample was thought to be very pure, because there was only 0.2 p.s.i. difference in the bubble-point and dew-point pressures at 32.17°F.

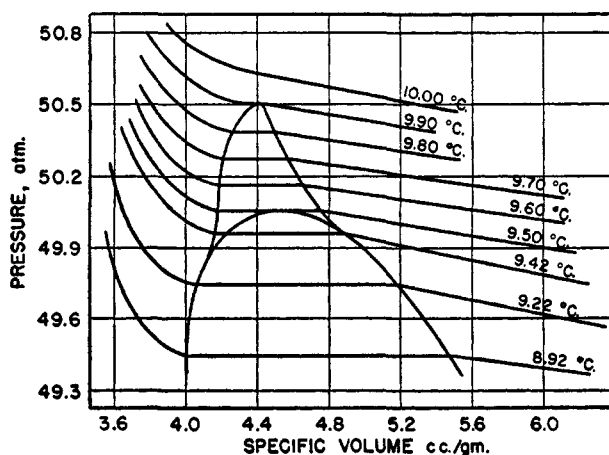


FIG. 12. Isothermals for ethylene near the critical point. The area enclosed by the dotted line is the critical region where $(\partial P/\partial V)_T = 0$ over a range of volume. The 9.50° isotherm is the temperature of disappearance of the meniscus.

In presenting the best values for the critical data, two sets of values are given: the true critical values $(\partial P/\partial V)_T = 0$ at one point only and the values corresponding to the disappearance of the meniscus in a shaken bomb. The de la Tour temperature (disappearance of the meniscus in a stationary bomb) is an indefinite point between the selected values and is dependent on the thermal history, the bomb size, and the method of observation.

(b) Propene

Siebert and Burrell prepared propene by the dehydration of propyl alcohol, using phosphorus pentoxide. It was collected over caustic potash and fractionated at low temperatures. The precision of the measurements was as follows: temperature, $\pm 0.1^\circ\text{C}$.; pressure, within 0.5 per cent.

Maass and Wright obtained propene by the dehydration of propyl alcohol over alumina at 350°C . The gas was collected over water, dried by phosphorus pentoxide, distilled several times, and finally distilled *in vacuo* five times, the middle portions being saved each time.

Winkler and Maass prepared propene in a manner very similar to that used by Maass and Wright. Constant vapor pressure indicated high sample purity. The precision in the temperature measurement was $\pm 0.03^\circ\text{C}$.

The propene used by Vaughan and Graves was prepared from 2-propanol by dehydration over alumina. The product was distilled at elevated pressure (180 p.s.i.g.) and twice fractionated in a Podbielniak column at atmospheric pressure. The change in pressure from the bubble point to the dew point was less than 2 p.s.i.

The data of Souders were reported along with the work of Vaughan and Graves (322). No information as to the purity of the sample or the methods of determination was given.

The propene used by Lee, Newitt, and Ruhemann was purchased from the Ohio Chemical Company and was found to be 99.5 per cent pure. It was fractionated without further treatment.

The sample of propene used by Marchman, Pringle, and Motard was obtained from the Phillips Petroleum Company (research grade). This was certified by the National Bureau of Standards to contain at least 99.7 per cent propene. The vapor pressure was constant from the bubble point to the dew point. The precision of the determinations was as follows: temperature, $\pm 0.015^\circ\text{C}$.; pressure, ± 0.02 atm.; volume, 1 per cent.

In selecting values for the critical temperature and pressure, the values of Marchman, Pringle, and Motard were chosen as being the most probable. The agreement between T_m and T_c is very good. The critical volume (density) is the hardest value to determine and the selected value is the one determined by the application of the law of rectilinear diameters.

(c) Butenes

Coffin and Maass prepared 1-butene by the action of alcoholic potash on *n*-butyl iodide, 2-butene by the action of glacial phosphoric acid (deposited on lump pumice) at 250–280°C. on 1-butanol, and isobutylene (2-methylpropene) by the dehydration of isobutyl alcohol over alumina at 250–300°C. The butylenes were collected over water, condensed by treatment with solid carbon dioxide and ether in an evacuated system, and separated from the water at -78°C ., the water remaining frozen to the sides of the container. The butylenes were then fractionated several times, the first and final portions being rejected. To check the purity, the dibromide derivatives were prepared and their melting points and vapor-pressure curves determined. The values checked well with the values in the literature.

The values cited by Doss were obtained from the M. W. Kellogg Company. No information regarding the preparation and purification of the sample or the method of determination is available.

The values given by Cragoe for t_c and p_c are estimated from experimental vapor-pressure data from three sources: (1) Natural Gasoline Association of America; (2) Royal Dutch-Shell Laboratory, Amsterdam; and (3) Petroleum Refining Laboratory, Pennsylvania State College. The critical densities were determined from these data by application of the law of rectilinear diameters.

Scheeline and Gilliland dehydrated *tert*-butyl alcohol to obtain isobutylene. The alcohol was distilled and repeatedly fractionally crystallized until there was a negligible melting-point range. The alcohol was then dehydrated in the presence of warm 35 per cent phosphoric acid. The isobutylene liberated was passed through water, dried over calcium chloride, and condensed by a kerosene–solid carbon dioxide mixture and stored in a steel cylinder. The material showed a 99.7 per cent absorption in bromine water, and the bulk impurity was thought to be residual air in the storage cylinder. The precision of the measurements was as follows: temperature, 1°C.; pressure, about 0.2 atm.

The 1-butene used by Olds, Sage, and Lacey was prepared by dehydration of 1-butanol over alumina. The product was purified by three fractionations. Three separately prepared and purified samples were used in the determinations. The results were smoothed graphically. The precision was stated to be: pressure, 0.1 per cent; temperature, 0.03°C.; critical density, 0.2 per cent.

Beattie and Marple obtained 1-butene from the Linde Air Products Company. The gas was cooled with liquid nitrogen and evacuated until one-tenth of the sample had evaporated. It was then distilled into a second receiver, the last one-tenth being discarded. The cycle was repeated seven times. Decreasing amounts of a white solid appeared on the first three cycles but disappeared completely on the fourth cycle. A slight increase in vapor pressure with decreasing vapor volume indicated the presence of a slight amount of impurity. The isotherms in the critical region also showed a slight slope, indicating impurities. For these reasons, the precision was given as follows: temperature, $\pm 0.3^\circ\text{C}$.; pressure, ± 0.3 atm.; density, 5 per cent.

Beattie, Ingersoll, and Stockmayer used a sample of isobutylene furnished by the M. W. Kellogg Company. It was prepared by the dehydration of isobutyl alcohol over alumina. The sample was distilled several times to remove non-condensable gases and then fractionated. The variation of vapor pressure with vapor volume indicated that the amount of permanent gases was negligible and that the amount of condensable impurity was slightly greater than the reproducibility of the measurements.

The values of Benedict were given by Beattie, Ingersoll, and Stockmayer without mention of the methods of determination. They merely confirmed the values obtained by Beattie *et al*.

In selecting the most probable values of the critical constants of 1-butene and isobutylene, the data of Beattie, Ingersoll, and Stockmayer were chosen except for critical densities. The value of Cragoe has been selected for the critical density of isobutylene and an average of the values of Cragoe (85), Olds, Sage, and Lacey (230), and Beattie and Marple (26) has been selected for the critical density of 1-butene.

(d) Pentenes

Kiyama, Suzuki, and Ikegami prepared 2-methyl-2-butene by the dehydration of isoamyl alcohol (b.p., 125–130°C.). The sample was then distilled through a Podbielniak column, and the portion which boiled at 37.8°C. at 760 mm. of

mercury was used. The literature value is 38.6°C. (A.P.I.). No mention was made of the uncertainties involved, but it was stated that the pressure was measured with a Bourdon-tube pressure gage.

Day stated that the critical temperature was within 1°C. of 201°C., but he could not reproduce the value because of polymerization of the sample.

(e) Hexene

The values given in table 4 are the only experimental data available for hexene. No information was given as to the preparation and purity of the sample.

TABLE 5
Aliphatic hydrocarbons: diolefins

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
(a). Propadiene						
1905	°C. 120.75	<i>atm.</i>	<i>g./cc.</i>	Lespieau and Chavanne	1	(180)
A.P.I.....	120.					
Value selected	120.					
(b). 1,3-Butadiene						
1942	163.2			Garner, Adams, and Stuchell	?	(113a)
1945	152.	42.7	0.245	Scott, Meyers, Rands, Brickwedde, and Bekkedahl	1	(298a)
A.P.I.....	152.	42.7	0.245			
Values selected....	152.	42.7	0.245			
(c). 1,5-Hexadiene						
1883	234.4			Pawlewski	1	(255)

(f) Octene

The data given in table 4 are the only experimental values available for octene. No information was given as to the preparation and purity of the sample used.

3. *Diolefins* (see table 5)

(a) Propadiene (allene)

The allene was prepared by the action of zinc on α -epidibromohydrin, $\text{CH}_2=\text{CHBrCH}_2\text{Br}$ (I), in alcohol solution. The melting point of I was 140-141°C.,

as compared with a literature value of 140°C. α -Epidibromohydrin was prepared from extremely pure tribromohydrin ($\text{CH}_2\text{BrCHBrCH}_2\text{Br}$). The allene obtained was washed, dried over calcium chloride, and passed through fused potash. It was then solidified and residual gases were removed by evacuation. A part of the allene was distilled into another tube and used for the determination. The melting point and normal boiling point were determined as -146°C . and -32°C ., respectively, for the best values. The sample was probably not pure; hence the value for the critical temperature is not accurate. Lespieau and Chavanne give another purity check involving explosion with oxygen and absorption of the carbon dioxide produced in potassium hydroxide. The method is not accurate and will not distinguish between allene and allylene.

(b) 1,3-Butadiene

The value for the critical temperature as reported by Gardner, Adams, and Stuchell was a private communication; hence no information as to the preparation or purification of the sample is available.

The 1,3-butadiene used by Scott, Meyers, Rands, Brickwedde, and Bekkedahl was furnished by the Dow Chemical Company. The workers prepared four samples, but the first two were too impure (by melting-point checks) to use for determination of critical values. The two samples used in the determinations were prepared as follows:

(I) 1,3-Butadiene was partially frozen by liquid air and was agitated by a magnetic stirrer to prevent aggregation. The liquid portion (approximately 50 ml.) was discarded and the solid portion was melted. The fractional crystallization was again repeated, about 75 ml. of liquid being discarded. The solid portion, 125 ml., was used as sample I.

(II) 400 ml. of butadiene was passed over activated silica gel, condensed, and fractionally crystallized three times. The purified portion was distilled twice and used as sample II.

(c) 1,5-Hexadiene (diallyl)

No information is available concerning the preparation and purification of the sample of diallyl used by Pawlewski.

4. Acetylenes (see table 6)

(a) Acetylene (ethyne)

The data prior to 1907 are presented for historical reasons only. In the investigations, all of the workers prepared acetylene from calcium carbide and water.

McIntosh purified acetylene by treatment with sodium hydroxide and chromic acid, and drying with concentrated sulfuric acid and phosphorus pentoxide. It was then solidified.

Mathias removed phosphine and stibine, dried the acetylene over calcium chloride, passed it through several tubes maintained at -79°C ., and solidified it by means of liquid air. The sample tubes were flushed seventeen times prior to filling and then evacuated (together with the solidified acetylene) to a frac-

tion of a millimeter of mercury. Five portions of the acetylene were evaporated and evacuated, and the sample tubes were filled by condensing the acetylene.

TABLE 6
Aliphatic hydrocarbons: acetylenes

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
(a). Acetylene (ethyne)						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1879	37.05	68.0	0.36	Ansdell	?	(11)
1880	37.			Dewar	?	(89)
1884	37.0	68.0		Dewar	?	(90)
1897	35.25	61.02		Kuenan	?	(170)
1907	36.5	61.6	0.314	McIntosh	1, 19	(204)
1909	37.05		0.2306	Mathias	?, 19	(194)
1912	35.4	61.65		Cardoso and Baume	3	(67)
1951	38.5	64.0		Kiyama, Ikegami, and Inoue	1	(164)
A.P.I.....	36.3	61.6	0.231			
Values selected...	36.	61.6	0.231			
(b). Propyne (allylene, methylacetylene)						
1905	129.5			Lespieau and Chavanne	1	(180)
1921	127.9			Maass and Wright	1	(187)
1931	121.6			Morehouse and Maass	13	(218)
1947	128.	52.8		Stull (Dow Chemical Co. files)	14	(304)
A.P.I.....	121.6					
Values selected...	128.	52.8				
(c). Higher acetylenes						
YEAR	COMPOUND	t_c	INVESTIGATORS	METHOD	REFERENCE	
		$^{\circ}\text{C.}$				
1934	Ethylacetylene	190.5	Morehouse and Maass	13	(219)	
1934	Dimethylacetylene	215.5	Morehouse and Maass	13	(219)	
1934	Propylacetylene	220.3	Morehouse and Maass	13	(219)	

Cardoso and Baume fractionally distilled (ten times) acetylene which had been bubbled through potassium permanganate and potassium hydroxide solutions and dried over phosphorus pentoxide.

Kiyama, Ikegami, and Inoue purified acetylene by absorption on ferric chlo-

ride, mercuric chloride, copper acetate, and acid clay. The gas was passed through dilute sodium hydroxide, dilute sulfuric acid, chromic acid, mercuric chloride in hydrochloric acid, alkaline sodium thiosulfate, and concentrated sodium hydroxide and dried over calcium chloride and phosphorus pentoxide. The acetylene as analyzed was said to be 98.7–99.4 per cent pure, with carbon monoxide, nitrogen, hydrogen, and methane as impurities. The acetylene reacted slightly with the mercury used as a pressure transmission fluid, but this effect was ignored because no pressure creep was found. These data are disregarded in the selection of the best values because of the deviation from other values.

The values of the critical pressure are in good agreement. However, the critical temperatures as determined by the various workers differ considerably; hence the average value of Cardoso and McIntosh is selected but no figure beyond the decimal point is believed warranted.

The value for the critical density as determined by Mathias is considered more reliable than that of McIntosh. Mathias used the law of rectilinear diameters, whereas McIntosh noted the volume at the critical point and weighed the amount of acetylene. From a series of tubes, an average density was calculated. If 309°K. is substituted into Mathias' equation for the rectilinear diameter, the value of 0.2313 is obtained for the critical density.

(b) Propyne

Lespieau and Chavanne prepared propyne from propylene bromide and sodium hydroxide in alcohol. The gas was passed through cuprous ammonium chloride, yielding a precipitate which was treated with dilute hydrochloric acid. The additional treatment of the propyne was identical to that for propadiene.

Maass and Wright prepared propyne as follows: A large tube was evacuated and filled with dry hydrogen. A small amount of freshly cut sodium was placed on a perforated plate in a side tube, heated, and forced through the plate by a stream of hydrogen. The side tube was then sealed off. Pure dry ammonia was condensed in the large tube (surrounded by a solid carbon dioxide-ether mixture). Pure dry acetylene was then passed into the large tube, which was warmed to remove unreacted acetylene. The calculated amount of methyl iodide was added, and the effluent gas was passed through numerous wash bottles to remove ammonia and collected over a saturated sodium chloride solution. The purity was checked by determinations of the density of the gas. The molecular weight under ideal conditions was calculated to be 40.05 as compared to a theoretical weight of 40.06. The propyne was then distilled five times *in vacuo*, the middle portion being retained. The precision of the temperature measurement was probably within 0.2°C.

Morehouse and Maass prepared propyne in the same manner as Maass and Wright, except that methyl iodide was added at reflux conditions. The propyne was distilled until a constant vapor pressure for different fractions was obtained. The value of the critical temperature was calculated from the Ramsay-Shields equation, and efforts to reproduce this value were in vain. The present authors calculated the critical temperature from the data of Morehouse and Maass

and obtained a value of 141.6°C. (not 121.6°C.). However, even though this value could not be duplicated, values for other compounds could be verified within a few tenths of a degree.

In view of this discrepancy, the experimental value of Maass and Wright has been selected as the most probable.

No information as to the critical pressure is available except the value reported by Stull. This value represents an extrapolation of the vapor-pressure curve (by Cox chart) to the critical temperature.

(c) Higher acetylenes

The data given in table 6 are from the work of Morehouse and Maass and have been calculated by the Ramsay-Shields equation. The methods used for the preparation and purification of the samples were similar to the procedures used for propyne. The values are probably within $\pm 5^\circ\text{C}$. of the true critical temperatures on the basis of a comparison of the selected values with those calculated by the Ramsay-Shields equation for two-carbon-atom and three-carbon-atom compounds.

D. CYCLOPARAFFINS (SEE TABLE 7)

1. Cyclopentane and alkyl derivatives

The samples of cycloparaffins used by Kay were supplied by the National Bureau of Standards, American Petroleum Institute Projects No. 6 and No. 45. These compounds were used without further purification. The amounts of impurities were as follows: cyclopentane, 0.02 ± 0.01 mole per cent; ethylcyclopentane, 0.22 ± 0.10 mole per cent; methylcyclopentane, 0.16 ± 0.06 mole per cent. The accuracy of the determinations was as follows: temperature, $\pm 0.05^\circ\text{C}$.; pressure, 0.02 atm.

2. Cyclohexane

Young and Fortey fractionally distilled Galician crude petroleum to obtain a fraction of cyclohexane which boiled at 80.8°C . The freezing point was not constant, so the sample was further purified by fractional crystallization. Chemical analysis indicated that the sample was pure.

Rotinyanz and Nagornow (279) and Fischer and Reichel (109) did not state how they purified their samples.

The data of Young are selected as the most probable on the basis of sample purity and careful experimental technique.

3. Methylcyclohexane

The samples used by Kay were obtained from Project No. 45 of the American Petroleum Institute and the Barrett Division of the Allied Chemical and Dye Corporation. The impurities were stated to be 0.10 ± 0.08 mole per cent. The accuracy of the determinations was: temperature, $\pm 0.05^\circ\text{C}$.; pressure, 0.02 atm.

The data of Kay are selected as the most reliable values available for the critical constants.

E. AROMATIC HYDROCARBONS (SEE TABLE 8)

1. Benzene

The data on benzene prior to 1910 are presented only for their historical value. The benzene used by Young was distilled commercial benzene. After distillation it was frozen twice and then repeatedly shaken with concentrated sulfuric

TABLE 7
Cycloparaffins

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
1a. Cyclopentane						
	°C.	atm.	g./cc.			
1947	238.6	44.55	0.27	Kay	1, 19	(155)
1b. Methylcyclopentane						
1947	259.61	37.364	0.264	Kay	1, 19	(155)
1c. Ethylcyclopentane						
1947	296.3	33.526	0.262	Kay	1, 19	(155)
2. Cyclohexane						
1893	280.0	39.96	0.2735	Young and Fortey	1, 19	(351)
1910	280.	39.84	0.2735	Young	1, 19	(350)
1934	281.0	40.57	0.2725	Rotinyanz and Nagornow	1, 19	(279)
1943	280.7			Fischer and Reichel	4	(109)
Values selected . .	280.	40.0	0.273			
3. Methylcyclohexane						
1926	301.5			Nagornow and Rontinyanz	1	(226)
1947	299.13	34.322	0.285	Kay	1, 19	(155)
Values selected . .	299.1	34.32	0.285			

acid (to remove thiophene). The final purification was by fractional distillation. The melting point was determined as 5.58°C.; the specific gravity at 0°C. (against water at 4°) was 0.9006; the normal boiling point was 80.2°C. The value in parentheses is recalculated, using 289.5°C. as the critical temperature.

The benzene used by Harand was reported to have a normal boiling point of 80.1°C., and the critical temperature reported was the average of nine determinations.

The data from the Esso Laboratories were reported by Gornowski, Amick,

TABLE 8
Aromatic hydrocarbons

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
1. Benzene						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1878	280.6	49.5		Sajotschewsky	?	(285)
1881	291.7	60.4		Ramsay	1	(267)
1891	296.4			Schmidt	1	(294)
1893	290.5	50.1		Altschul	1	(4)
1899	288.1			Radice	?	(266)
1908	288.7	49.5		Schamhardt	?	(288)
1910	288.5	47.9	0.3045 (0.3040)	Young	2, 19	(350)
1934	290.8			Harand	1	(128)
1941	289.45	48.9		Esso Laboratories	?	(117)
1943	291.2			Fischer and Reichel	4	(109)
1947	289.5	48.7	0.297	Gornowski, Amick, and Hixson	1, 19	(117)
1952	288.94	48.34	0.308	Bender, Furukawa, and Hvndman	5	(31)
A.P.I.....	289.45	48.6	0.300			
Values selected	289.	48.6	0.300			
2. Toluene						
1892			0.287	Mathias	19	(192)
1893	320.6	41.6		Altschul	1	(4)
1930		41.6		Krase and Goodman	16	(167)
1943	320.8			Harand	1	(128)
1943	320.8			Fischer and Reichel	4	(109)
A.P.I.....	320.8	40	0.32			
Values selected	320.8	41.6	0.29			
3a. <i>o</i> -Xylene						
1893	358.3	36.9		Altschul	1	(4)
1906	362.9			Brown	1	(53)
1943	358.5			Fischer and Reichel	4	(109)
A.P.I.....	359.0	36.	0.28			
Values selected	358.4	36.9				
3b. <i>m</i> -Xylene						
1893	345.6	35.8		Altschul	1	(4)
1906	349.			Brown	1	(53)
A.P.I.....	346.0	35.	0.27			
Values selected	346.	36.				

TABLE 8—Continued

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
3c. <i>p</i> -Xylene						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1893	344.4	35.0		Altschul	1	(4)
1906	348.5			Brown	1	(53)
1943	345.0			Fischer and Reichel	4	(109)
A.P.I.....	345.0	34.	0.29			
Values selected	345.	35.				
4. Ethylbenzene						
1893	346.4	38.1		Altschul	1	(4)
A.P.I.....	346.4	37.	0.29			
Values selected	346.4	38.				
5a. 1,2,3-Trimethylbenzene						
A.P.I.....	395.	31.	0.28			
5b. 1,2,4-Trimethylbenzene						
1893	381.2	33.2		Altschul	1	(4)
A.P.I.....	381.5	32.	0.28			
Values selected	381.2	33.				
5c. 1,3,5-Trimethylbenzene						
1893	367.7	33.2		Altschul	1	(4)
1906	370.5			Brown	1	(53)
A.P.I.....	369.	32.	0.28			
Values selected	368.	33.				
5d. 1,2,3,5-Tetramethylbenzene						
1920	389.0			Prud'homme	13	(264)
5e. 1,2,4,5-Tetramethylbenzene						
1920	402.5	28.6		Guye and Mallet	1	(120)
5f. Pentamethylbenzene						
1920	418.0			Prud'homme	13	(264)

TABLE 8—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
5g. Hexamethylbenzene						
1902	°C. 478.	<i>atm.</i>	<i>g./cc.</i>	Guye and Mallet	1	(120)
1913	494.			Société Française de Physique	?	(10)
6. Ethylmethylbenzenes						
	t_c	p_c	d_c			
	°C.	<i>atm.</i>	<i>g./cc.</i>			
2-Ethyl-1-methylbenzene	380.	31.	0.28			
3-Ethyl-1-methylbenzene	363.	31.	0.28			
4-Ethyl-1-methylbenzene	363.	31.	0.28			
YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
7a. <i>n</i> -Propylbenzene						
1893	°C. 365.6	<i>atm.</i> 32.3	<i>g./cc.</i>	Altschul	1	(4)
A.P.I.	365.	31.	0.28		?	
Values selected	365.6	32.				
7b. Isopropylbenzene (cumene)						
1893	362.7	32.2		Altschul	1	(4)
A.P.I.	336.1	31.	0.28		?	
Values selected	362.7	32.				
8. Cymenes						
1893	378.6	28.6		Altschul	1	(4)
1906	385.5			Brown	1	(53)
9. Isobutylbenzene						
1893	377.1	31.1		Altschul	1	(4)

and Hixson. No information as to the method used, the preparation and purification of the sample, etc., is available.

Gornowski, Amick, and Hixson used Baker's c.p. thiophene-free benzene. It was agitated with concentrated sulfuric acid and washed twice with distilled

water. The sample was then treated with 0.1 *N* sodium hydroxide and again washed twice with distilled water. The benzene was cooled slowly until a certain fraction solidified, the supernatant liquid being discarded; the procedure was then repeated to insure removal of impurities such as cyclohexane.

Bender, Furukawa, and Hyndman used three samples of benzene in their determinations. The first was reagent-grade benzene, treated with sulfuric acid until it gave negative tests for thiophene, washed with water, and dried over calcium chloride and sodium wire. It was distilled over fresh sodium wire and fractionated. The second sample was Phillips Petroleum Company research-grade benzene certified by the National Bureau of Standards to be 99.93 ± 0.03 mole per cent benzene. The final sample was "thiophene-free" reagent-grade benzene, which was dried over sodium wire and then fractionated at a reflux ratio of 20:1 through an Oldershaw column. The constant-boiling fraction was used in the determinations. The various samples gave consistent checks. The uncertainties of the measurements were as follows: temperature, $\pm 0.05^\circ\text{C}$.; pressure, ± 0.03 atm.; volume (density), ± 1 per cent.

The data of Gornowski, of the Esso Laboratories, and of Bender, Furukawa, and Hyndman are averaged to give the selected data for the critical temperature and critical pressure. The critical density is taken to be the average of the data of Gornowski and those of Young, because it is believed that the method of rectilinear diameters gives more reliable values of the critical density.

2. Toluene

No information is available on the purification and preparation of the sample used by the investigators of the critical constants of toluene.

3. Xylenes

No information on the preparation or purification of the samples of the xylenes was given by the investigators. However, certain physical constants were given by Brown and by Fischer and Reichel. These are compared with values from A.P.I. Project No. 44 as follows:

XYLENE	NORMAL BOILING POINT		REFRACTIVE INDEX, n_D^{20}	
	Brown	A.P.I.	Fischer and Reichel	A.P.I.
<i>o</i> -Xylene.....	144.0	144.414	1.5037	1.50543
<i>m</i> -Xylene.....	139.0	139.102		
<i>p</i> -Xylene.....	138.5	138.348	1.4962	1.49581

From a comparison of these physical properties, it is seen that the samples used by Brown and by Fischer and Reichel were of reasonable purity. However, the values of Altschul and of Fischer and Reichel more nearly check and are given preference over Brown's values.

The values listed for the critical density were reported as a part of A.P.I. Project No. 44 (278a); hence no information is available.

4. Ethylbenzene

The sample used by Altschul was distilled from a flask containing a large quantity of ethylbenzene. No other information is available on the preparation and purification of the sample.

No other samples of ethylbenzene have been investigated.

5. Polymethylbenzenes

The only information on the purity of the polymethylbenzenes was the normal boiling point for 1,3,5-trimethylbenzene given by Brown: 165.4°C. (A.P.I. value, 164.711°C.).

The hexamethylbenzene used by Guye and Mallet decomposed; hence their value is incorrect.

6. Ethylmethylbenzenes

The only data available on these compounds were reported by Project No. 44 of the American Petroleum Institute (278a); hence no information other than the critical values is available.

7. Propylbenzenes

The only information available on the preparation of the samples is that Altschul used samples of *n*-propylbenzene and isopropylbenzene obtained from Landolt and Sahn, who had used them for determinations of the boiling point and density. Altschul simply distilled these samples into the experimental tube.

8. Cymenes

The only values known for the cymenes are those of Brown (53) and Altschul (4). Neither investigator states which isomer was used.

The sample used by Brown had a normal boiling point of 177.0°C., which compares favorably with the A.P.I. (278a) value of 177.10°C. for *p*-cymene; hence it may be assumed that he actually used *p*-cymene. There is no indication as to what Altschul's sample actually was. Doss gives these data for both *o*- and *p*-cymene. In all probability, Altschul used a mixture of the two isomers.

However, in view of the uncertainties involved, no selection is made of the most probable values.

9. Isobutylbenzene

No data other than those given in table 8 are available for butylbenzenes.

F. SUBSTITUTED AROMATIC COMPOUNDS (SEE TABLE 9)

1. Fluorobenzene

Fluorobenzene was prepared by the action of concentrated hydrofluoric acid on benzene diazopiperidine. The sample was fractionated until a constant boiling point was obtained.

TABLE 9
Substituted aromatic compounds

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
1. Fluorobenzene						
1910	°C. 286.55	atm. 44.6	g./cc. 0.354	Young	2, 19	(350)
2. Chlorobenzene						
1893	362.2			Altschul	1	(4)
1910	359.2	44.6	0.365	Young	2, 19	(350)
Values selected	359.2	44.6	0.365			
3. Bromobenzene						
1910	397.	44.6	0.4583	Young	13, 19	(350)
1943	397.7			Fischer and Reichel	4	(109)
Values selected	397.	44.6	0.458			
4. Iodobenzene						
1910	448.	44.6	0.581	Young	13, 19	(350)
5. Phenol						
1899	419.2			Radice	1	(120)
1923	419.2	60.5		Herz and Neukirch	1, 15	(135)
Values selected	419.2	60.5				
6a. <i>o</i> -Cresol						
1899	422.3			Radice	1	(120)
1923		49.4		Herz and Neukirch	15	(135)
Values selected	422.	49.4				
6b. <i>m</i> -Cresol						
1902	432.0	45.0	0.346	Guye and Mallet	1	(120)
Values selected	432.	45.0	0.35			

TABLE 9—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
6c. <i>p</i> -Cresol						
1899	°C. 426.0	<i>atm.</i>	<i>g./cc.</i>	Radice		(120)
1923		50.8		Herz and Neukirch	15	(135)
Values selected	426.	50.8				
7. Aniline						
1902	425.6	52.3	0.340	Guye and Mallet	1, 19	(120)
8. Methylaniline						
1923	428.4	51.3		Herz and Neukirch	1, 15	(135)
9. Dimethylaniline						
1902	414.7	35.8		Guye and Mallet	1, 15	(120)

2. Chlorobenzene

The chlorobenzene used by Young was obtained from Kahlbaum and was purified by fractional distillation. A comparison of density data with the data of Timmermans (314) showed that the sample was extremely pure. The precision of measurements was as follows: temperature, $\pm 0.05^\circ\text{C}.$; pressure, ± 0.1 atm.; density, 1 per cent.

*3. Bromobenzene**4. Iodobenzene*

The samples of bromobenzene and iodobenzene used by Young were obtained from Kahlbaum and were fractionally distilled until constant-boiling samples were obtained. Young found that bromobenzene and iodobenzene decomposed above $270^\circ\text{C}.$ even in the absence of light. If it is assumed that the closely related benzene derivatives were to obey van der Waals' equation, then the critical pressures should be equal at any given pressure. These ratios were calculated and found to be equal at a series of particular pressures; hence the ratios of the critical temperatures were established. The critical temperature and critical pressure of fluorobenzene were determined experimentally and the critical values for chlorobenzene, bromobenzene, and iodobenzene were calculated by knowing the ratios of the critical temperatures. Later the critical values for chlorobenzene were determined experimentally and substantiated the assumptions which had been made. Therefore, it is assumed that Young's values for the critical points of iodobenzene and bromobenzene are the most reliable data available.

5. Phenol

No information is available concerning Radice's work on phenol. Herz and Neukirch purified commercial-grade phenol by heating it to 150°C. in a distilling flask. Air was passed over sulfuric acid and calcium chloride and then through the hot phenol. The sample was fractionated twice and the fraction which boiled at 181.4–181.5°C. was used in the determination.

6. Cresols

There is no information available concerning the work of Radice on the values which were reported by Guye and Mallet.

Herz and Neukirch obtained their samples from Kahlbaum and purified them by distillation. The determinations of the critical pressure of *p*-cresol were accompanied by frequent explosions.

Guye and Mallet fractionally distilled cresol samples which were obtained from Kahlbaum. These workers found that *m*-cresol decomposed rapidly near the critical point. They stated, however, that the critical pressure was accurately determined within $\frac{1}{20}$ atm. The critical density was determined by the rule of Mathias and was stated to be accurate to 3 per cent.

7. Aniline

The values for aniline presented in table 9 are the only experimental determinations that have been made on the critical state of aniline. The aniline used by Guye and Mallet was prepared by reduction of nitrobenzene. The samples were purified by prolonged refluxing over lead oxide, by distillation, and then by redistilling over sodium.

Two samples were prepared and used in the determinations. Also, two calibrated thermometers were used to ascertain the temperature. The critical temperature varied between 425.4° and 425.9°C., depending on the sample used and the thermometer which was read. The selected value is an average value of these readings and is accurate to $\pm 0.2^\circ\text{C}$.

The critical pressure is also an average value and the precision is ± 0.1 atm.

8. Methylaniline

Herz and Neukirch obtained methylaniline from Kahlbaum. The sample was dried and distilled over sodium sulfate. The portion boiling at 193.8–194.0°C. was used for the determinations. The critical pressure was determined to ± 0.5 atm., but no information was given as to the probable accuracy of the critical temperature.

9. Dimethylaniline

Guye and Mallet purified Kahlbaum dimethylaniline by boiling it over lead oxide. The sample was then distilled three times. The viscosity and refractive index were constant after the second distillation. The critical pressure was determined to ± 0.2 atm., but no information was given as to the expected accuracy for the critical temperature.

G. ALCOHOLS (SEE TABLE 10)

1. *Methyl alcohol*

The data for methyl alcohol reported prior to 1904 are presented for historical value only.

Centnerszwer used a sample which had been purified by drying relatively pure methanol over calcium oxide for two months. The sample was then distilled, the center cut being used for the determinations.

Young prepared methanol by distilling crystalline methyl oxalate and ammonia. The distillate was rectified, distilled over quicklime, and finally redistilled over barium oxide. It was then allowed to stand over anhydrous calcium sulfate for a number of weeks, after which it was distilled six times to a constant boiling point.

Salzwedel purified his sample by letting it stand over chalk for a long time and then distilling it.

No information as to the preparation and purification of the sample is available for the work of Fischer and Reichel.

Because of the extreme care exercised by Young as to both sample preparation and experimental technique, the data as reported by him are selected as the most probable.

2. *Ethyl alcohol*

No information is available on the preparation of the sample used by Hannay and Hogarth. The probable error was estimated by these workers to be $\pm 2^\circ\text{C}$. for the critical temperature and 1 atm. for the critical pressure.

The ethanol used by Hannay was purified by fractionation, standing over burned lime and calcium chloride, and distillation. The probable error was estimated to be 0.2°C . for the critical temperature and 0.13 atm. for the critical pressure.

The critical temperature of Ramsay and Young was estimated to be within 0.5°C . of the true value. Moreover, Young's data (probable error $\pm 0.1^\circ\text{C}$.) verify this value.

The data of Fischer and Reichel somewhat temper the reliability of Young's data; hence the selected values are rounded to three significant figures.

The value of Prideaux for the critical temperature is disregarded in the final choice, even though it was determined in relatively recent years.

3. *n-Propyl alcohol*

The data prior to 1900 are presented for historical value only.

Young obtained *n*-propyl alcohol from Kahlbaum and purified it by fractional distillation. Potassium carbonate was added during the last part of each distillation to remove any water that might be present. The purified sample showed a normal boiling point of 97.20°C . and a specific gravity of 0.81923.

Fischer and Reichel stated that their sample was very pure but did not say how they purified it.

TABLE 10

Alcohols

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
1. Methyl alcohol						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1882	232.7	72.85		Hannay	?	(174)
1882	233.0	79.73		Nadejdine	6	(222)
1904	240.2		0.275	Centnerszwer	1, 19	(77)
1910	240.0	78.47	0.2722	Young	2, 19	(350)
1930	240.0	99.0	0.3587	Salzwedel	10	(286)
1943	240.6			Fischer and Reichel	4	(109)
Values selected . . .	240.0	78.5	0.272			
2. Ethyl alcohol						
1880	234.6	65.0		Hannay and Hogarth	1	(124)
1882	235.5	67.1	0.288	Hannay	1	(123)
1886	243.6	62.8	0.280	Ramsay and Young	2, 19	(270)
1910	243.1	63.0	0.2755	Young	2, 19	(350)
1911	249.0			Prideaux	1	(262)
1943	241.7			Fischer and Reichel	4	(109)
Values selected . . .	243.	63.0	0.276			
3. <i>n</i> -Propyl alcohol						
1882	256.0	53.26		Nadejdine	?	(221)
1883	254.2			Nadejdine	?	(222)
1888	261.0			de Heen	?	(174)
1891	265.8			Schmidt	1	(293)
1892			0.2778	Mathias	19	(192)
1910	263.7	50.16	0.2734	Young	2, 19	(350)
1943	264.1			Fischer and Reichel	4	(109)
Values selected . . .	264.	50.2	0.273			
4. Isopropyl alcohol						
1883	235.0	53.1		Nadejdine	1	(223)
1888	238.0			de Heen	?	(174)
1904			0.274	Mathias	19	(193)
1906	243.47			Brown	1	(53)
1943	235.6			Fischer and Reichel	4	(109)
Values selected . . .	235.6	53.	0.274			

TABLE 10—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
5a. <i>n</i> -Butyl alcohol						
	°C.	<i>atm.</i>	<i>g./cc.</i>			
1883	287.1			Pawlewski	?	(255)
1888	270.5			de Heen	?	(174)
1923	287.0	48.4		Herz and Neukirch	1	(135)
1943	288.0			Fischer and Reichel	4	(109)
Values selected . . .	288.	49.				
5b. <i>sec</i> -Butyl alcohol						
1906	265.			Brown	1	(53)
5c. <i>tert</i> -Butyl alcohol						
1883	235.			Pawlewski	1	(255)

On the basis of evidence presented, there is no reason to select either Young's value or the value of Fischer and Reichel as the most probable; hence the average value rounded to three significant figures is chosen as the most probable value for the critical temperature.

Young's value has been selected as the most probable for the critical pressure and density. All of Young's work was performed with great care and with very pure samples.

4. *Isopropyl alcohol*

There is no information available as to the preparation or purification of the samples of isopropyl alcohol used by the workers listed in table 10. On the basis of techniques, the value of Fischer and Reichel is selected as the most probable for the critical temperature.

The values selected for the critical pressure and density are the best available, but not too much reliance can be placed on their accuracy.

5. *Butyl alcohols*

No information is available as to sample preparation and purification for any of the data given in table 10 for the butyl alcohols. On the basis of technique and method, the value of Fischer and Reichel is selected as the most probable for the critical temperature.

H. ETHERS (SEE TABLE 11)

1. *Dimethyl ether*

The data prior to 1900 are presented for historical value only.

The sample used by Briner and Cardoso was purified by distillation, and evidence as to its degree of purity was given.

TABLE 11

Ethers

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
1. Dimethyl ether						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1883	129.6			Nadejdine	1	(223)
1897	129.6	57.		Leduc and Sacerdote	1	(179)
1907	123.	53.		Briner and Cardoso	1	(50)
1908	127.1	53.		Briner and Cardoso	1	(51)
1923	126.9	52.		Cardoso and Bruno	19	(69)
1923	126.9		0.2417	Cardoso and Coppola	19	(70)
1932	126.2	53.		Winkler and Maass	1	(337)
1932	126.5			Winkler and Maass	1	(338)
1933	126.9		0.2255	Tapp, Steacie, and Maass	1, 19	(309)
1933	126.2	53.		Winkler and Maass	1	(339)
1935	126.9	52.6	0.2465	Edwards and Maass	1, 19	(102)
1936	126.9			Pall and Maass	1	(251)
Values selected	126.9	53.	0.242			
2. Ethyl methyl ether						
1887	168.4	46.27	0.3070	Nadejdine	1	(225)
1924	164.7	43.40	0.2722	Berthoud and Brum	1, 19	(42)
Values selected	164.7	43.4	0.272			
3. Diethyl ether						
1878	190.0	36.9		Sajotschewsky	?	(285)
1881	195.5	40.0		Ramsay	?	(267)
1890	191.8			Galitzine	?	(113)
1891	193.7			Schmidt	?	(174)
1892	197.0	35.77	0.208	Battelli	?	(174)
1900	194.7			V. Hirsch	?	(174)
1901	193.61	36.28		Galitzine and Wilip	?	(174)
1904	194.4		0.258	Centnerszwer	?	(77)
1907	193.6			Travers and Usher	?	(320)
1908	193.04	36.90		Schamhardt	?	(288)
1910	193.8	35.61	0.2625	Young	2, 19	(350)
1929	193.4	34.98	0.265	Schroer	1, 19	(296)
1929	194.6	35.6	0.265	Schroer	5	(297)
1943	192.3			Fischer and Reichel	4	(109)
Values selected	194.	35.6	0.264			
4. Ethyl propyl ether						
1924	227.4	32.1	0.260	Berthoud and Brum	1, 19	(42)
5. Dioxane						
1946	312.	50.7	0.36	Hojendahl	1, 16, 19	(141)

Cardoso and Bruno (69) and Cardoso and Coppola (70) prepared dimethyl ether by the action of sulfuric acid on methanol. The gas was then passed over phosphorus pentoxide and triple-distilled.

Maass and coworkers prepared their samples by treatment of methanol with sulfuric acid. The gas was passed through concentrated sulfuric acid saturated with dimethyl ether and then over calcium chloride. It was redistilled, passed over phosphorus pentoxide, and triple-distilled.

The best value for the critical temperature is readily selected, since the agreement among the results of the various workers is excellent. However, the data for the pressure and the density are more erratic. The best value for the critical pressure appears to be 53 atm.

The critical density is in general best evaluated by extrapolation of the rectilinear diameter. The value of Cardoso and Coppola was so determined; hence it has been chosen as the most probable value.

2. Ethyl methyl ether

Berthoud and Brum prepared ethyl methyl ether by the action of ethyl iodide on sodium methoxide in absolute methanol. The ether was purified by distillation and by washing with water; it was dried by passing over metallic sodium. The ether was then fractionated prior to use. The accuracy of the determination of the critical temperature was $\pm 0.01^\circ\text{C}$.

The values of Berthoud and Brum are selected as being the most probable, because of the careful purification of the sample and because the work was done more recently.

3. Diethyl ether

The data prior to 1910 are included for historical value only.

Young prepared ether by heating absolute alcohol with sulfuric acid. The distillate was shaken with caustic soda and then redistilled. The ether was dried with calcium chloride and again distilled, after which it was stored over metallic sodium. The samples were distilled from the sodium.

Schroer used diethyl ether obtained from Kahlbaum which he distilled from sodium four times. The ether was then stored for several weeks over sodium, dried with phosphoric acid, and re-stored over sodium. The precision of the temperature measurements was $\pm 0.15^\circ\text{C}$. for the disappearing meniscus method and $\pm 0.3^\circ\text{C}$. for the P - V - T measurements. The precision of the measurements of pressure was ± 0.05 atm. and ± 0.2 atm. for the two methods, respectively. The value for the critical density was accurate to ± 0.004 .

Fischer and Reichel used the microtechnique which depended on the disappearance of droplets as the criterion of the critical temperature. Their work is not as precise as the work of Young and of Schroer.

The average values of Young and of Schroer are selected as the most probable.

4. Ethyl propyl ether

The ethyl propyl ether was prepared by the addition of propyl iodide to sodium ethoxide in absolute ethanol. The ether was washed with water, dried over metal-

lic sodium, and fractionated. The fraction which distilled at 60.2–60.3°C. under a pressure of 733 mm. of mercury was used in the determinations.

The work of Berthoud showed good agreement with the results obtained by other investigators for ammonia and the aliphatic amines; hence the values presented by Berthoud and Brum for ethyl propyl ether are considered to be reasonably accurate.

5. Dioxane

The only data available on the critical properties of dioxane are those of Hojendahl. The dioxane was frozen, dried over sodium, and distilled to give four

TABLE 12
Ketones

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
1. Acetone						
	°C.	atm.	g./cc.			
1878	232.8	52.2		Sajotschewsky	?	(174)
1878	237.5	60.0		Sajotschewsky	?	(174)
1884	232.6			Bartoliu-Stracciati	?	(174)
1890	234.4			Galitzine	?	(113)
1902	233.7	46.78		Kuenan and Robson	1	(172)
1923	235.6		0.252	Herz and Neukirch	1, 19	(135)
1943	235.8			Fischer and Reichel	4	(109)
1951	235.5	46.6	0.273	Rosenbaum	8	(278)
Values selected	235.5	46.6	0.273			
2. Ethyl methyl ketone						
1938	260.	43.3		Shell Chemical Co.	?	(300)
1951	260.5	39.46	0.252	Rosenbaum	8	(278)
Values selected	260	39.5	0.25			

fractions. The melting points of the fractions were 11.75°, 11.76°, 11.80°, and 11.55°C. Timmermans and Roland (315) give 11.80°C. as the melting point of dioxane.

The precision of the measurements was as follows: temperature, $\pm 2^\circ\text{C}$.; pressure, ± 3 atm. The precision of the density measurements is subject to the crude method used in determining the orthobaric densities and is probably of the order of 3 per cent.

I. KETONES (SEE TABLE 12)

1. Acetone

The data for acetone prior to 1900 are included for historical completeness only.

The acetone used by Kuenan and Robson was made from Kahlbaum's bisulfite compound and then dried over calcium chloride.

Herz and Neukirch prepared acetone from the bisulfite compound obtained from Kahlbaum. The acetone was dried over calcium chloride and then fractionated. The fraction which boiled at 56.0–56.1°C. was used in the determination.

No information was given by Fischer and Reichel as to the purification of their sample.

Rosenbaum used C.P. grade acetone which was treated with Drierite to remove water. The dried acetone was then distilled in a 30-plate packed column at a reflux ratio of 20:1. A 0.1°C. fraction was selected (600 ml. of a 2-l. charge), dried, and redistilled. A 350-ml. fraction having a boiling range of 0.01°C. was selected as the final purified sample. The sample had a refractive index at 20°C. of $n_D = 1.3590$ compared with a literature value of $n_D = 1.3591$; it boiled at 55.9°C. under 746 mm. of mercury (literature value, 56.5°C. at 760 mm. of mercury) (176). The uncertainties in the measurements were as follows: temperature, $\pm 1^\circ\text{C}.$; pressure, ± 0.6 atm.; density, ± 0.004 g./cc.

TABLE 13
Acetaldehyde

YEAR	t_c	INVESTIGATORS	METHOD	REFERENCE
1881	181.5	van der Waals	?	(174)
1903	188.0	Hollman	1	(143)
Values selected	188.			

The values of Rosenbaum are selected as the most probable because of the high purity of the samples.

2. Ethyl methyl ketone

No information on the purity of the sample of ethyl methyl ketone used is available for the values given by the Shell Chemical Company.

Rosenbaum used C.P. ethyl methyl ketone which had previously been purified. It was dried with Drierite and then distilled in a 30-plate packed column at a reflux ratio of 20:1. A fraction comprising half the charge was collected as the final purified sample. The refractive index of this sample at 20°C. was $n_D = 1.37865$, compared with a literature value of $n_D = 1.37881$ (84). The boiling point was 79.6°C. at 759 mm. of mercury (literature value, 79.6°C. at 760 mm. of mercury) (176). The uncertainties were as follows: temperature, $\pm 1^\circ\text{C}.$; pressure, ± 0.66 atm.; density, 0.004 g./cc.

J. ACETALDEHYDE (SEE TABLE 13)

There is no information available as to the methods employed by these investigators to produce the samples of acetaldehyde used.

Hollman noticed that each successive determination of the critical tempera-

ture which was made with the same sample gave increasing values for the critical temperature. He attributed this to paraldehyde formation; therefore the first determination was taken as the true critical temperature. In all probability the acetaldehyde was contaminated by paraldehyde even in this first determination.

K. ORGANIC ACIDS (SEE TABLE 14)

1. *Acetic acid*

Young purified acetic acid by repeated crystallizations. The recrystallized acetic acid was distilled, and the portion which showed no change in boiling point was used in the determinations.

Young's data are selected over Pawlewski's because Young exercised extreme care in his work and used extremely pure samples. Nothing is known concerning the purity of the samples used by Pawlewski.

2. *Acetic anhydride*

The acetic anhydride was obtained from Kahlbaum and was further purified to give a sample boiling at 136.5°C. at 760.6 mm. of mercury.

3. *Propionic acid*

Vespignani obtained his samples of propionic acid from Kahlbaum. The samples were used without further purification. No other information on sample purification is available. The data are in good agreement and an average value is selected as most probable.

4. *Butyric acids*

There is no information as to the purity of the samples used by Brown.

The critical pressure was determined by extrapolating the vapor-pressure data of Stull (304) to the critical temperature. The critical density was obtained by extrapolation of the density data of von Hirsch (138) by the method of rectilinear diameters.

5. *Valeric acids*

Only the data of Brown are available for the critical temperatures of the valeric acids. No information was given as to the preparation or purification of the samples. The data of Brown on isopropyl alcohol and the xylenes have been found to be inaccurate, but the values are probably precise within $\pm 3^\circ\text{C}$.

L. ESTERS (SEE TABLE 15)

1. *Methyl formate*

No information is available concerning the methods of preparation and purification of the samples of methyl formate used by Nadejdine and de Heen. Young and Thomas purified their sample by a procedure similar to that outlined under methyl acetate.

TABLE 14
Organic acids

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
1. Acetic acid						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1882	321.50			Pawlewski	1	(255)
1891	321.65	57.10		Young	2	(348)
1910	321.60	57.11	0.3506	Young	2, 19	(350)
Values selected...	321.6	57.1	0.351			
2. Acetic anhydride						
1903	296.	46.2		Vespignani	1	(323)
3. Propionic acid						
1883	339.9			Pawlewski	1	(255)
1891	337.6			Schmidt	?	(313)
1903	339.5	52.9		Vespignani	1	(323)
1928			0.315		19	(148)
Values selected...	339.	53.	0.32			
4a. <i>n</i> -Butyric acid						
1906	354.5-355.0			Brown	1	(53)
1951		52.	0.302	Hudel	17, 19	(145a)
Values selected...	355.	52.	0.302			
4b. Isobutyric acid						
1906	336.0-336.5			Brown	1	(53)
1951		40.	0.304	Hudel	17, 19	(145a)
Values selected...	336.	40	0.304			
5a. <i>n</i> -Valeric acid						
1907	377.5-380			Brown	1	(53)
Value selected...	378.					
5b. Isovaleric acid						
1907	360.5-361			Brown	1	(53)
Value selected...	361.					

TABLE 15

Esters

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
1. Methyl formate						
	°C.	atm.	g./cc.			
1887	212.	61.65		Nadejdine	1	(224)
1888	250.5			de Heen	?	(130)
1893	214.0	59.15	0.3489	Young and Thomas	2, 19	(352)
1910	214.0	59.25	0.3489	Young	2, 19	(350)
Values selected.....	214.0	59.2	0.349			
2. Ethyl formate						
1878	230.0	48.70		Sajotschewsky	1	(174)
1883	238.6			Pawlewski	1	(255)
1887	233.1	49.16		Nadejdine	1	(174)
1893	235.3	46.65	0.3232	Young and Thomas	2, 19	(352)
1910	235.3	46.76	0.3232	Young	2, 19	(350)
Values selected.....	235.3	46.8	0.323			
3. Propyl formate						
1882	267.40			Pawlewski	1	(255)
1887	260.80	42.7		Nadejdine	1	(224)
1888	260.50			de Heen	?	(130)
1893	264.85	40.08	0.3093	Young and Thomas	2, 19	(352)
1910	264.85	40.08	0.3093	Young	2, 19	(350)
Values selected.....	264.9	40.1	0.309			
4. Isobutyl formate						
1887	278.2	38.29		Nadejdine	1	(224)
5. Methyl acetate						
1893	229.8	57.60		Sajotschewsky	1	(285)
1893	232.9	42.54		Nadejdine	1	(224)
1893	233.7	46.33	0.3252	Young and Thomas	2, 19	(352)
Values selected.....	233.7	46.3	0.325			
6. Ethyl acetate						
1878	239.8	42.3		Sajotschewsky	1	(285)
1883	256.5			Pawlewski	1	(255)
1887	249.5	39.6	0.2993	Nadejdine	1	(224)
1888	275.7			de Heen	?	(174)
1893	250.1	38.0	0.3081	Young and Thomas	2, 19	(352)
1910	250.1	37.8	0.3077	Young	2, 19	(350)
Values selected.....	250.1	37.8	0.308			

TABLE 15—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
7. <i>n</i> -Propyl acetate						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1882	282.4			Pawlewski	1	(255)
1887	276.3	34.80		Nadejdine	1	(224)
1910	276.2	32.91	0.2957	Young	2, 19	(350)
Values selected.....	276.2	32.9	0.296			
8a. Methyl butyrate						
1910	281.30	34.28	0.3002	Young	2, 19	(350)
Values selected.....	281.3	34.3	0.300			
8b. Methyl isobutyrate						
1910	267.55	33.87	0.3012	Young	2, 19	(350)
Values selected.....	267.6	33.9	0.301			
8c. Ethyl isobutyrate						
	280.	30.	0.276	Nadejdine	1	(148)

2. Ethyl formate

For a discussion of results, see methyl acetate.

3. Propyl formate

The data of Young for propyl formate are selected as the most probable values.

4. Isobutyl formate

For isobutyl formate only the data of Nadejdine are available. As can be seen by comparison with data of other investigators, the data of Nadejdine are in error by about 2 per cent (2°C.). This must be kept in mind when his data are used.

5. Methyl acetate

No information is available on the method used by Sajotschewsky for the preparation and purification of the sample. His work is disregarded because of this and because of the wide deviation from the values of Young and of Nadejdine.

Nadejdine (225) and Young and Thomas (352) used approximately the same method for the preparation of the ester. The methyl acetate was prepared by esterification of methanol with acetic anhydride under reflux. Excess acid was

removed by treatment with a concentrated potassium carbonate solution, followed by a water wash. The ester was then dried over phosphorus pentoxide, distilled, and fractionated twelve times. Nadejdine's sample was apparently contaminated with residual alcohol, whereas Young's sample was essentially pure.

Because of the careful work of Young and Thomas, their values are selected as the most accurate values of the critical constants of methyl acetate.

6. Ethyl acetate

No information is available on the preparation and purification of the sample except for the work of Young and Thomas.

The preparation of the ethyl acetate used by Young and Thomas is discussed under methyl acetate. Their data, as corrected by Young, are selected as the best values for the critical constants.

7. *n*-Propyl acetate

Pawlewski obtained *n*-propyl acetate from Kahlbaum. He did not purify the sample.

Nadejdine also obtained his samples from Kahlbaum but subjected the material to further purification. He mixed the ester with a solution of potassium carbonate and let the mixture stand for several days. The ester was distilled and then dried over anhydrous potassium carbonate and anhydrous copper sulfate until the copper sulfate did not change color on standing one week in the ester. The dehydrated ester was fractionated three times.

Young used samples from two sources. The first was prepared from acetic acid and *n*-propyl alcohol. The ester was neutralized with potassium carbonate, washed, and dried over potassium carbonate and phosphorus pentoxide. The sample was then fractionated twelve times. The second sample (from Kahlbaum) was treated with potassium carbonate and phosphorus pentoxide and then fractionated eighteen times. The two samples had the same normal boiling point (101.55°C.) and nearly the same specific gravities (0.91015 and 0.91017 at 0°C., respectively). The two samples gave the same values for the critical constants.

The data of Young are considered to be the most reliable on the basis of sample purity, the method used, and the general techniques employed in determining the critical state.

No data for isopropyl acetate have been found in the literature.

8. Butyrates

Young prepared these esters by the action of the appropriate acids and alcohols. Potassium carbonate was added to neutralize excess acid and the sample was then repeatedly washed with water and dried over phosphorus pentoxide. The samples were then distilled some twenty times.

Because of the care exercised by Young and his coworkers, their values are selected as the most probable, even though there are no other data for comparison purposes.

The data for ethyl isobutyrate were reported in the *International Critical Tables*. No information as to the preparation and purification of the sample is available.

M. NITROGEN COMPOUNDS (SEE TABLE 16)

1. Ammonia

The methods employed and the details of the preparation and purification of the samples used by Cragoe, McKelvy, and O'Connor (259), Postma (259), Estreicher and Schnerr (259), Jacquerod (259), Mathias (193), Vincent and Chappius (326), and Dewar (90) are unknown. However, it is believed that the samples were sufficiently pure so that one may include all data since 1900 in the final selection of values.

Centnerszwer prepared ammonia by heating ammonium chloride and marble. The gas was washed with concentrated caustic potash and absorbed in water at low temperature. More ammonia was passed through this wash water and then through soda lime, caustic potash, and potassium copper oxide.

Scheffer obtained his sample from pitch and purified it by several distillations. The gas was then passed over calcium oxide to insure complete dryness.

Cardoso and Giltay prepared ammonia by heating purified ammonium chloride with a very pure quicklime. The liberated gas was passed over caustic soda and sodium, after which it was distilled ten times. After each of the first four distillations, the gas was passed through barium oxide and sodium.

The ammonia used by Berthoud was prepared by heating a mixture of ammonium chloride and powdered caustic soda. The liberated gas was passed over pieces of sodium hydroxide and sodium, after which it was condensed and distilled into the sample tubes.

In selecting the best value for the critical temperature, all data since 1900 were considered and the mean value was selected as the most probable.

The data of Berthoud and of Cragoe, McKelvy, and O'Connor were averaged to give the most probable value for the critical density.

2. Hydrazine

The samples of hydrazine were prepared by two methods: (1) hydrazine hydrochloride ($\text{N}_2\text{H}_4 \cdot \text{HCl}$) was treated with sodium methoxide in methanol; (2) the hydrate of hydrazine was heated with barium oxide at 100°C . and distilled under reduced pressure to yield hydrazine. The distillation was performed in an atmosphere of hydrogen.

Decomposition of the sample started at about 350°C . but was very slight when the sample was heated at 360°C . for 8 hr. The critical pressure was actually determined by Boltwood but reported by de Bruyn. The critical pressure was reproducible within 0.3 atm.

3. Cyanogen

The cyanogen used by Cardoso and Baume was prepared from mercuric chloride and mercuric cyanide and was dried by passing it over phosphorus

TABLE 16
Nitrogen compounds

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
1. Ammonia						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1884	130.0	115.0		Dewar	?	(90)
1886	131.0	113.0		Vincent and Chappius	1	(326)
1903	132.53			Centnerszwer	1	(76)
1904			0.239	Mathias	19	(193)
1908	132.3			Jacquerod	1	(259)
1910	132.1	111.3		Scheffer	1	(290)
1912	132.9	112.3		Cardoso and Giltay	1	(73)
1913	132.2			Estreicher and Schnerr	1	(259)
1918	132.3		0.2364	Berthoud	1, 19	(40)
1918	132.3		0.2362	Berthoud	1, 19	(39)
1920	132.35	111.3		Postma	1	(259)
1923			0.234	Cragoe, McKelvy, and O'Connor	19	(259)
Values selected...	132.3	111.3	0.235			
2. Hydrazine						
1896	380.	145.		de Bruyn	1, 15	(54)
3. Cyanogen						
1884	124.0	61.7		Dewar	?	(90)
1910	128.3	59.6		Cardoso and Baume	3	(66)
1912	128.3	59.75		Cardoso and Baume	3	(67)
1916	126.55	58.20		Terwen	1	(311)
Values selected...	127.	59.				
4. Hydrogen cyanide						
1925	183.5	53.2	0.195	Bredig and Teichman	1, 15, 19	(47)
5a. Methylamine						
1886	155.0	72.0		Vincent and Chappius	1	(328)
1917	156.9	73.6		Berthoud	1	(38)
Values selected..	156.9	73.6				
5b. Dimethylamine						
1886	163.00	56.00		Vincent and Chappius	1	(328)
1917	164.55	52.35		Berthoud	1	(38)
Values selected...	164.5	52.4				
5c. Trimethylamine						
1886	160.50	41.00		Vincent and Chappius	1	(328)
1950	160.15	40.24	0.233	Day and Felsing	5, 19	(87)
Values selected...	160.1	40.2	0.233			

TABLE 16—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
6a. Ethylamine						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1886	177	66		Vincent and Chappius	1	(328)
1917	183.2	55.54		Berthoud	1	(38)
Values selected...	183	55.5				
6b. Diethylamine						
1878	220	38.7		Sajotschewsky	1	(174)
1886	216	40		Vincent and Chappius	1	(328)
1917	223.2	36.58		Berthoud	1	(38)
Values selected...	223	36.6				
6c. Triethylamine						
1886	259	30		Vincent and Chappius	1	(328)
7a. Propylamine						
1885	218.0	50.00		Vincent and Chappius	1	(328)
1917	223.8	46.76		Berthoud	1	(38)
Values selected...	223.8	46.8				
7b. Dipropylamine						
1885	277.	31.		Vincent and Chappius	1	(328)
8(a)(1). Acetonitrile						
1902	270.1	47.7		Guye and Mallet	1, 15	(120)
1906	274.7		0.237	Ter-Gazarian	1, 19	(310)
Values selected...	274.7	47.7	0.237			
8(a)(2). Propionitrile						
1902	285.7	41.3		Guye and Mallet	1, 15	(120)
1906	291.2		0.240	Ter-Gazarian	1, 19	(310)
Values selected...	291.2	41.3	0.240			
8(a)(3). Butyronitrile						
1902	309.1	37.4		Guye and Mallet	1, 15	(120)
8(a)(4). Capronitrile						
1902	348.8	32.1		Guye and Mallet	1, 15	(120)
8(b). Benzoinitrile						
1902	426.2	41.6		Guye and Mallet	1	(120)

pentoxide. The sample was then condensed by liquid air and fractionated nine times. The paracyanogen which formed was neglected as being too insoluble in liquid cyanogen to affect the critical determinations.

Terwen used the same method of preparation and drying. However, the dried cyanogen was fractionally sublimed and the vapor pressures of the various fractions were compared. The purest fractions were combined and repeatedly melted and solidified under vacuum to remove traces of nitrogen. Two fractions of the final sample showed less than 0.03 per cent difference in vapor pressure at 0°C.

There is little choice between the data of the investigators; hence the whole-numbered averages are selected as the most probable values.

4. *Hydrogen cyanide*

The hydrogen cyanide was prepared from potassium cyanide or potassium ferrocyanide and concentrated sulfuric acid. The gas was then dried over calcium chloride and phosphorus pentoxide, liquefied, and fractionally distilled over phosphorus pentoxide. The fraction which boiled at 21°C. at 500 mm. of mercury was used in the determinations. The tubes were made of Jena-V glass to prevent reaction with the hydrogen cyanide.

5. *Methylamines*

Vincent and Chappius stated that their samples were pure but did not state how they had purified them.

Berthoud's samples were prepared by Kahlbaum by the alkylation of ammonia. The samples were purified by fractional crystallization, followed by a number of fractional distillations over barium oxide. The fractions that were used in the determinations boiled over a range of 0.1°C.

Day and Felsing prepared trimethylamine from the hydrochloride obtained from the Eastman Kodak Company. The hydrochloride was purified by crystallization from chloroform and *n*-propyl alcohol. It was then treated with an excess of 50 per cent potassium hydroxide solution, and the liberated gas was passed through Drierite and into a cylinder containing sodium. The gas was condensed and the cylinder was evacuated to remove non-condensable gases. The amine was then distilled into the sample tubes. The accuracy of the data was as follows: temperature, $\pm 0.1^\circ\text{C}$.; pressure, ± 0.05 atm.; density, ± 0.002 g./cc.

The data of Berthoud and of Day and Felsing are selected as the most probable values of the critical constants of the various amines because of the care exercised in obtaining the data and in preparing the samples.

6. *Ethylamines*

There is no information concerning the purification of the samples used in the work of Vincent and Chappius and of Sajotschewsky.

Berthoud used material supplied by Kahlbaum. Several fractional distillations were made on the samples, and the fractions which boiled over a 0.1°C. range were used.

7. Propylamines

Vincent and Chappius stated that their samples were pure, but they did not describe the methods of preparation and purification.

The sample used by Berthoud was prepared by Kahlbaum by the alkylation of ammonia. It was then purified by fractional crystallization and distillation over barium oxide. The fraction which distilled over a 0.1°C. range was used in the determination.

The data of Berthoud are selected as the better data.

8. Nitriles

(a) Aliphatic nitriles

The samples of acetonitrile, propionitrile, butyronitrile, and capronitrile used by Guye and Mallet were obtained from the Kahlbaum Company. These samples were said to be "very pure" and were used without further purification. The samples polymerized slightly but did not decompose very rapidly, as was evidenced by repeated determinations.

The samples of acetonitrile and propionitrile used by Ter-Gazarian were obtained from Kahlbaum and were dried over phosphorus pentoxide and repeatedly distilled. The following cuts were used in the determinations: acetonitrile, 79.97–80.00°C. at 717.5 mm. of mercury; propionitrile, 96.00–96.04°C. at 730.7 mm. of mercury.

The fact that Ter-Gazarian subjected the nitriles to further purification leads one to select his values as the more probable.

(b) Aromatic nitriles: benzonitrile

The benzonitrile was obtained from Kahlbaum and was said to be remarkably pure. However, the sample was redistilled before it was used. The critical temperature increased with the length of time the sample was heated, a result which indicated that the sample decomposed. The following table shows the variation of critical temperature with time.

TIME OF HEATING AT 420–425°C.	t_c
hours	°C.
3	429.5
5	431.0
9	433.5

On this basis, the data for the sample which had been heated a minimum length of time were selected as the most probable values.

N. INORGANIC HALIDES (SEE TABLE 17)

1. Hydrogen fluoride

Bond and Williams prepared anhydrous hydrogen fluoride by the dry distillation of potassium hydrogen fluoride (KHF₂). Baker and Adamson's C.P. potassium bifluoride was fused, electrolyzed by a direct current of 18 v., and dis-

TABLE 17
Inorganic halides

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
1. Hydrogen fluoride						
1931	°C. 230.2	atm.	g./cc.	Bond and Williams	6	(43)
2. Hydrogen chloride						
1879	51.25	86.		Ansdell	1	(12)
1884	52.3	86.	0.610	Dewar	?	(90)
1886	51.5	96		Vincent and Chappius	?	(327)
1897	52.0	83.		Leduc and Sacerdote	?	(179)
1904			0.462	Mathias	19	(193)
1906	51.8	83.6		Briner	?	(49)
1908	51.0	81.5	0.423	Dorsman	1	(93)
1912	51.4	81.55		Cardoso and Germann	3	(72)
1913	51.4			Estreicher and Schnerr	1	(104)
1913	51.1	80.49		Drozdowski and Pietrzak	?	(96)
Values selected.....	51.4	81.5	0.42			
3. Hydrogen bromide						
1896	90.8			Estreicher	1	(103)
1913	91.07			Estreicher and Schnerr	1	(104)
1913	90.00	84.44		Drozdowski and Pietrzak	?	(96)
1919	89.80	84.00		Moles	3, 17	(217)
Values selected.....	90.0	84.0				
4. Hydrogen iodide						
1896	150.5			Estreicher	1	(103)
1913	150.8			Estreicher and Schnerr	1	(104)
1913	150.0	80.8		Drozdowski and Pietrzak	?	(96)
Values selected.....	150.	81.				
5a. Boron trifluoride						
1932	-12.3	49.2		Booth and Carter	1	(44)
5b. Boron trichloride						
1927	178.8			Parker and Robinson	1	(252)
1947		38.2		Stull	16	(304)
5c. Boron tribromide						
1946	300		0.90	Hojendahl	1, 19	(141)

TABLE 17—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
6. Phosgene						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1919	183.5			Hackspill and Mathieu	1	(121)
1926	182.	56.	0.52	Germann and Taylor	1, 19	(114)
Values selected.....	182.	56.	0.52			
7. Germanium tetrachloride						
1887	276.9	38		Nilson and Patterson	1	(229)
8a. Silicon tetrafluoride						
1906	-1.50	50.0		Moissan	1	(216)
1935	-14.15	36.66		Booth and Swinehart	1	(45)
Values selected.....	-14.1	36.7				
8b. Chlorotrifluorosilane						
1935	34.48	34.20		Booth and Swinehart	1	(45)
8c. Dichlorodifluorosilane						
1935	95.77	34.54		Booth and Swinehart	1	(45)
8d. Trichlorofluorosilane						
1935	165.26	35.33		Booth and Swinehart	1	(45)
8e. Silicon tetrachloride						
1861	230.0			Mendelejeff	1	(211)
1927	233.6			Parker and Robinson	1	(252)
Value selected.....	233.					
9. Stannic chloride						
1891	319.4	36.95		Young	1	(349)
1910	318.7	36.95	0.7419	Young	1, 19	(350)
Values selected.....	318.7	37.0	0.742			
10. Sulfur hexafluoride						
1951	45.555		0.7517	Atack and Schneider	5	(13)
1951	45.547	37.113		MacCormack and Schneider	1	(188)
Values selected.....	45.55	37.11	0.752			

tilled in a platinum still. The potassium fluoride was treated with aqueous hydrogen fluoride, evaporated, fused, and electrolyzed as before. The acid was distilled from the salt in the platinum still. The hydrogen fluoride so obtained was a clear limpid colorless liquid which contained less than 0.2 per cent of non-volatile solid.

2. Hydrogen chloride

The data prior to 1908 are presented for completeness only and were not considered in the final selection.

The hydrogen chloride used by Dorsman was prepared from sodium chloride and sulfuric acid and condensed by means of liquid air. The sample tube was evacuated and washed out several times with the hydrogen chloride.

Cardoso and Germann used concentrated sulfuric acid and pure precipitated sodium chloride to prepare hydrogen chloride. The evolved gas was passed through five bottles of concentrated sulfuric acid and then over phosphorus pentoxide. The sample was fractionated ten times and passed over phosphorus pentoxide after each of the first six fractionations.

Drozdowski and Pietrzak also prepared hydrogen chloride from sodium chloride and sulfuric acid and purified the sample by fractionation.

The data of Cardoso and Germann are selected for the critical temperature and pressure because of the elaborate preparation of the sample and the care with which the determinations were made. The choice is substantiated by the data of the other investigators.

The value for the critical density has been verified by the correlations of Fales (107), who obtained a value of 0.424. However, the third significant figure has been dropped because of the uncertainties involved in the determinations.

3. Hydrogen bromide

Estreicher prepared hydrogen bromide by the reaction of bromine and red phosphorus in water. The excess bromine vapor was removed by passing the gas through a water suspension of red phosphorus. The hydrogen bromide was condensed and distilled into the sample tubes.

Estreicher and Schnerr gave no information concerning the sample preparation. The critical temperature was an average of twenty determinations.

Drozdowski and Pietrzak obtained hydrogen bromide by the direct combination of hydrogen and bromine over heated platinized asbestos. The hydrogen bromide was then solidified and the excess hydrogen evacuated. The final purification consisted of treatment with activated charcoal and fractionation. Discrepancies (as much as 10 per cent) in vapor-pressure determinations above 4 atm. were due to the presence of impurities.

Moles found that hydrogen bromide, prepared according to the method of Estreicher, contained impurities. The sample used by Moles was prepared by the action of metaphosphoric acid on potassium bromide. The gas was liquefied and distilled into the sample tubes. The critical pressure was calculated by five empirical relations. The extremes were 71 and 99 atm.

The values selected are the means of the last three entries in the table. The general agreement is good, but the data of no single investigator can be selected as the most probable.

4. *Hydrogen iodide*

Estreicher prepared hydrogen iodide by the action of red phosphorus on a mixture of water and pulverized iodine. The iodine vapor was removed with water and the sample was dried over phosphorus pentoxide. It was solidified by means of a mixture of solid carbon dioxide and ether and then distilled to remove traces of iodine.

Drozdowski and Pietrzak prepared hydrogen iodide in a manner similar to that used for the preparation of hydrogen bromide. The vapor pressure was measured to 147°C.

There is little basis for making an accurate selection of the most probable values; hence an average value is selected for the critical temperature and the critical pressure is rounded to the whole-numbered value.

5. *Boron trihalides*

Booth and Carter prepared boron trifluoride by fusing boric acid and then dissolved the boric oxide in sulfuric acid. Fluorspar was added and the mixture was heated. The gas which was evolved was passed through a reflux condenser and then through a wash solution containing boric oxide and hydrochloric acid, condensed, and fractionally distilled. The sample was stored for six months and then fractionally distilled eight times.

The boron trichloride used by Parker and Robinson was prepared by Briscoe and Robinson (52). Boric oxide glass was ground and reduced by magnesium in the presence of carbon. The material was then converted into boron trichloride by the action of chlorine gas. The crude sample was fractionated and stored over sodium amalgam for several months, after which it was distilled a number of times. The boron trichloride gave reproducible results for the atomic weight of boron and was judged to be very pure.

Stull extrapolated vapor-pressure data to the critical temperature determined by Parker and Robinson.

Boron tribromide was twice distilled in a stream of pure hydrogen. The melting point was determined to be $-47^{\circ}\text{C}.$, as compared to a value of $-46^{\circ}\text{C}.$ found by Stock and Kuss. Twice-distilled and thrice-distilled boron tribromide yielded the same value for the refractive index. Rather crude methods for obtaining the orthobaric densities were used; hence little faith may be placed on the value for the critical density. At best, it should be considered as an approximate value only. The critical temperature is probably within $2^{\circ}\text{C}.$ of the true value.

6. *Phosgene*

Hackspill and Mathieu purified industrial phosgene by fractional distillation to remove contaminants consisting of sulfur compounds. Chlorine was removed by contact with mercury for 24 hr.

Germann and Taylor repeatedly fractionated commercial phosgene to obtain a relatively pure sample. The fact that it was not entirely pure was evidenced by the inability of the workers to condense the sample completely at constant pressure. A thermometer of the Anschutz type, calibrated by the Bureau of Standards to tenths of a degree, was used. The temperature of disappearance of the meniscus was found to be 181.8°C. and of reappearance, 181.6°C. The observed critical pressure was found to be 55.3 atm., whereas by extrapolation of the vapor-pressure curve, it was found to be 55.6 atm. These authors, therefore, reported 182°C. and 56 atm. for the critical temperature and pressure, respectively. For the determination of the critical density, they used the density data of Paternò and Mazzucchelli (253), derived the mean density equation, $d_T = 0.715 - 0.0010t$ (where t is °C.), and extrapolated to 182°C.

7. Germanium tetrachloride

No information was given concerning the preparation and purification of the sample, which was said to be sufficiently pure for molecular weight determinations.

8. Silicon halides

The data of Moissan and Mendelejeff are not considered in the selection of the best values, as their samples were not sufficiently pure.

Booth and Swinehart prepared chlorofluorosilanes from pure silicon tetrachloride. The silicon tetrachloride was purified by fractional distillation and the other samples were made from it by the action of antimony trifluoride and antimony pentachloride. The fractions were then purified by fractionation. The purity of the samples was established by qualitative analysis and molecular weight determinations.

Parker and Robinson prepared silicon tetrachloride by chlorinating ferrosilicon. The sample was distilled and stored over sodium amalgam for two months and then fractionally distilled under vacuum. The center fraction of the last distillation was considered sufficiently pure for determinations of critical constants.

9. Stannic chloride

Young obtained stannic chloride from Kahlbaum. The sample was distilled and the first fractions were hydrated. After the hydrates were removed, the sample boiled at a constant temperature. The samples were stored over phosphorus pentoxide to prevent hydrate formation.

10. Sulfur hexafluoride

A spectrogram analysis showed that the sulfur hexafluoride contained no water, air, or sulfuryl fluoride. The sample had been purified by repeated fractionation. Schneider and coworkers made the following observations: (1) There was no evidence of the teapot dome in the critical region. (2) Some opalescence was noted. (3) The horizontal line below T_m was good evidence that the sample

was pure. (4) No effect was observed due to the thermal history of length of heating.

The uncertainties were said to be $\pm 0.003^\circ\text{C}$. in the temperature and 0.003 atm. in the pressure.

O. ORGANIC HALIDES: ALIPHATIC (SEE TABLE 18)

1. *Methyl fluoride*

Collie prepared methyl fluoride by heating tetramethylammonium fluoride. The products were trimethylamine and methyl fluoride. The amine was removed from the mixture by adsorption on pumice moistened with concentrated sulfuric acid. Collie pointed out that the temperature may be in error by 0.2°C . and the pressure by 2 atm. because of air in the sample.

Cawood and Patterson prepared methyl fluoride by two methods and found that the determinations of critical constants were identical regardless of the method used. In one method, the methyl fluoride was prepared by heating methylammonium fluoride, whereas in the second method the methyl fluoride was produced by the action of potassium fluoride on potassium methyl sulfate. The methyl fluoride was passed through concentrated sulfuric acid, solid and liquid potassium hydroxide, and cooled by a solid carbon dioxide-acetone mixture. The gas was then dried over phosphorus pentoxide and solidified by liquid air. The vessel was evacuated to remove non-condensable gases. The resulting gas was fractionated three times and passed through its own liquid.

On the basis of the purity of the sample, the data of Cawood and Patterson are selected as the most probable values for the critical constants of methyl fluoride.

2. *Methyl chloride*

Only data since 1900 are considered in the final selection.

Centnerszwer purified his sample of methyl chloride by passing the gas over soda lime, calcium chloride, and sulfuric acid. The sample was then distilled into the experimental tubes. The accuracy in the determination of the critical temperature was $\pm 0.2^\circ\text{C}$.

No information is available as to the method of sample preparation used by Brinkmann.

Baume passed methyl chloride over sulfuric acid and distilled it five or six times.

Harand did not discuss the preparation of the sample. In view of the fact that he used such small samples (0.05–0.1 mg.), it is felt that little reliance can be placed in his data.

For critical temperature and pressure, the data of Brinkmann (313), Baume (16), and Centnerszwer (77) on the critical density varied from 0.3397 to 0.3790 within 0.01°C . of the critical temperature. This wide variation introduces doubt that the value selected is accurate even to the second figure. The data of Brinkmann are therefore selected for the best value of the critical density.

TABLE 18
Aliphatic organic halides

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
1. Methyl fluoride						
	°C.	atm.	g./cc.			
1889	44.9	62.		Collie	1	(82)
1932	44.55	58.0	0.300	Cawood and Patterson	1, 19	(75)
Values selected...	44.6	58.0	0.300			
2. Methyl chloride						
1886	141.5	73.		Vincent and Chappius	1	(327)
1893	143.0	65.0		Kuenan	1	(259)
1904			0.354	Mathias	13	(193)
1904	143.0		0.370	Centnerszwer	1, 19	(77)
1904	143.12	65.93	0.353	Brinkman	1, 19	(313)
1906	143.2	65.85		Baume	1	(16)
1935	141.5			Harand	1	(128)
Values selected...	143.1	65.9	0.353			
3. Methyl bromide						
1920	191(?)			Prud'homme	13	(264)
4. Methyl iodide						
1916	255(?)			Herz	13	(134)
1919	255			Moles	13	(217)
5. Methylene chloride						
1882	245.			Nadejdine	1	(222)
1927	215.7			Perry	13	(258)
1934	237.5			Harand	1	(128)
1934	216.1	108.0		Sugawara	1	(305)
1942	239.0			Seger	14	(299)
1946	237.0	59.97		Dzung	1, 16	(97)
Values selected...	237.	60.				
6. Chloroform						
1878	260.0	54.9		Sajotschewsky	1	(174)
1895	258.8			Pictet and Altschul	1	(260)
1902	262.9	53.8		Kuenan and Robson	1	(172)
1923	262.5		0.496	Herz and Neukirch	1, 19	(135)
1934	263.4			Harand	1	(128)
1943	263.5			Fischer and Reichel	4	(109)
Values selected...	263.4	54.	0.50			

TABLE 18—Continued

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
7. Carbon tetrachloride						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1879	277.9	58.1		Hannay and Hogarth	1	(124)
1882	285.3			Pawlewski	?	(255)
1882	282.5	57.57		Hannay	1	(123)
1891	284.9			Schmidt	1	(294)
1902	259.5	39.50		Vespignani	1	(323)
1910	283.15	44.97	0.5576	Young	2, 19	(350)
1935	282.60			Harand	1	(128)
1943	283.2			Fischer and Reichel	4	(109)
Values selected...	283.2	45.0	0.558			
8. Ethyl fluoride						
1935	102.16	46.62		Booth and Swinehart	1	(45)
9. Ethyl chloride						
1859	184.1			Drion	?	(259)
1878	182.7	52.6		Sajotschewsky	?	(259)
1884	189.9			Djatschewsky	?	(259)
1886	182.5	54.0		Vincent and Chappius	1	(328)
1895	181.0			Pictet	1	(259)
1895	181.8			Pictet and Altschul	1	(260)
1902	189.5			Eversheim	11	(106)
1917	187.2	51.72		Berthoud	1	(38)
Values selected...	187.2	52.				
10. Ethyl bromide						
1883	236.0			Pawlewski	13	(255)
1923	230.7	61.5	0.507	Herz and Neukirch	1, 19	(135)
Values selected...	230.7	61.5	0.507			
11a. 1,1-Dichloroethane						
1883	254.5			Pawlewski	1	(256)
1887	250.0	50.0		Nadejdine	1	(224)
Values selected...	250.	50.				
11b. 1,2-Dichloroethane						
1883	283.			Pawlewski	1	(256)
1887	288.4	53.0		Nadejdine	1	(224)
1932	290 \pm 2		0.44	Hojendahl	1, 19	(141)
Values selected...	288.	53.	0.44			

TABLE 18—*Continued*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
12. Dibromoethane						
1903	°C. 309.8	atm. 70.6	$g./cc.$	Vespignani	1, 15	(323)
13(a)(1). Chlorodifluoromethane						
1935	96.4	48.48		Booth and Swinehart	1	(45)
1939	96.0	48.70	0.525	Benning and McHarness	1, 16, 19	(37)
Values selected...	96.4	48.5	0.525			
13(a)(2). Dichlorofluoromethane						
1940	178.5	51.0	0.522	Benning and McHarness	1, 16, 19	(37)
13(a)(3). Chlorotrifluoromethane						
1941	28.8	39.4	0.581	Riedel	1, 16, 19	(276)
1952	28.86	38.2	0.578	Albright and Martin	1, 16, 19	(3)
Values selected...	28.8	39.	0.58			
13(a)(4). Dichlorodifluoromethane						
1931	111.5	39.56	0.555	Gilkey, Gerardi, and Bixler	1, 19	(115)
1940	111.5	39.6	0.555	Benning and Machwood	1, 16, 19	(34)
Values selected...	111.5	39.6	0.555			
13(a)(5). Trichlorofluoromethane						
1940	198.0	43.2	0.554	Benning and McHarness	1, 16, 19	(37)
13(b)(1). Chlorotrifluoroethylene						
1935	107.0	39.0		Booth and Swinehart	1	(45)
1951	105.8	40.1	0.55	Oliver, Grisard, and Cunningham	1	(232)
Values selected...	106.	40.	0.55			
13(b)(2). Dichlorotetrafluoroethane						
1932	146.1	37.4		Yant, Schunk, and Patty	?	(347)
1944	145.7	32.3		Benning and McHarness	1, 16	(36)
Values selected...	145.7	32.3				

TABLE 18—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
13(b)(3). Trichlorotrifluoroethane						
	°C.	atm.	g./cc.			
1933	187.6			Hovorka and Geiger	1	(145)
1938	214.1	33.7	0.576	Beuning and McHarness	1, 16, 19	(35)
Values selected...	214.1	33.7	0.576			
14a. Perfluoro- <i>n</i> -butane						
1947	113.3	23(?)	0.63	Fowler <i>et al.</i>	1, 16, 19	(110)
14b. Perfluoro- <i>n</i> -heptane						
1947	202.5	19(?)		Fowler <i>et al.</i>	1, 16	(110)
1951	201.7	16.0	0.584	Oliver, Blumkin, and Cunningham	1, 19	(231)
1952	201.5	15.9 ₆		Milton and Oliver	5	(215a)
Values selected...	201.6	16.0	0.584			
14c. Perfluoromethylcyclohexane						
1947	213.4	24(?)		Fowler <i>et al.</i>	1, 16	(110)

3. Methyl bromide

4. Methyl iodide

No experimental data for methyl bromide and methyl iodide are available.

5. Methylene chloride

Perry stated that the sample used by Nadejdine was not sufficiently pure; hence this value is excluded.

Perry's work was carefully done on a sample of methylene chloride supplied by the Eastman Kodak Company. The sample was further purified by shaking with sulfuric acid and then was fractionated four times. Change of vapor pressure with ratio of vapor volume to liquid volume was less than 1 mm. of mercury. However, since the critical temperature was calculated using Prud'homme's equation, its accuracy is no better than that of the equation.

Harand purified methylene chloride by distillation but no further information was given concerning the purity of the sample. His data on other methane derivatives give good checks with those of other investigations.

The sample used by Sugawara was supplied by Kahlbaum. Sugawara claims an accuracy of 2 per cent, but because of the wide discrepancy between his data and those of Harand and of Dzung, his data are ignored in the final selection.

Dzung does not state how he purified his sample except that he used "purified and distilled" methylene chloride. The critical pressure was obtained by extrapolation of the vapor-pressure curve to the critical temperature.

6. Chloroform

The data prior to 1900 are included for historical completeness. Kuenan and Robson prepared chloroform from chloral but did not state how they purified it.

Herz and Neukirch did not state how they purified the chloroform which they used. The accuracy of the determination was said to be $\pm 0.2^\circ\text{C}$.

Harand (128) and Fischer and Reichel (109) did not mention sample purity, but since both had done careful work their values are selected as the most probable value for the critical temperature.

The critical pressure and density are not known to any great degree of accuracy; hence they are reported to only two figures.

7. Carbon tetrachloride

The data prior to 1900 are presented for historical value only.

Vespignani did not mention the method of preparation of the sample. Since his values deviated widely from those of the other investigators, they are disregarded in the final selection.

Young (350), Harand (128), and Fischer and Reichel (109) all failed to mention the method of preparation of the sample, although they stated that their samples were very pure.

Since the data of Young and those of Fischer and Reichel agree, their values are selected as the most probable.

8. Ethyl fluoride

Ethyl fluoride was prepared according to Frem's synthesis. It was fractionated ten times for the first sample and five times more for the second sample. The two samples gave identical results for the determinations.

9. Ethyl chloride

Only Berthoud discussed the purification of the sample. It was obtained from Kahlbaum and was purified by fractional distillation. The fraction used in his determinations boiled at $12.5\text{--}12.6^\circ\text{C}$. at 725 mm. of mercury. The manometer which he used was calibrated by the use of Amagat's vapor-pressure data for carbon dioxide; hence the results of Berthoud's pressure data were 0.2–0.3 atm. too low.

Eversheim measured the dielectric constant of ethyl chloride at various temperatures. The temperature at which the dielectric constant did not change was said to be the critical temperature. The agreement is good, but this is not a generally accepted method of determining critical constants and the results are therefore disregarded.

The data of Berthoud are selected as the best values for the critical constants.

10. Ethyl bromide

Pawlewski investigated the critical temperatures and boiling points for a number of alkyl halides and concluded that the difference was equal to a constant for a homologous series. On this basis, the critical temperature of ethyl bromide was calculated.

The sample used by Herz and Neukirch was prepared from ethyl alcohol and potassium bromide in the presence of a potassium sulfate catalyst. Multiple steam distillations were made, and the product was washed with dilute caustic solutions and with water. The bromide was dried over calcium chloride and then fractionated. The fraction boiling at 38.3–38.5°C. was again dried over calcium chloride and fractionated. The fraction boiling at 38.4°C. was used as the sample.

The data of Herz and Neukirch are selected as the most probable values of the critical constants of ethyl bromide.

All values for ethyl iodide are calculated.

11. *Dichloroethanes*

Pawlewski obtained his samples from Kahlbaum but did not say how they were purified. It was stated that the purity was checked by checking the boiling point, the specific gravity, and the vapor density.

Nadejdine prepared ethylidene dichloride (1,1-dichloroethane) from paraldehyde. The sample was washed with dilute sodium hydroxide and dried with caustic lime. The 1,2-dichloroethane was obtained from Kahlbaum and was washed with dilute sodium hydroxide and dried over calcium chloride. Both compounds were then fractionally distilled as the final step in the purification.

Hojendahl passed ethylene dichloride through silica gel to remove strong dipoles and then fractionated the sample in a tall Raschig-ring-packed column operated adiabatically. The fraction boiling at 83.50–83.62°C. was used in the determinations.

The data of Nadejdine are selected as the most reliable.

12. *Dibromoethane*

No information was given as to the preparation and purification of the sample.

13. *Freons*

(a) Freons containing one carbon atom

Benning and McHarness fractionated their samples three times in a column packed with silicon carbide. No more than 3 per cent of the material boiling 0.05°C. higher or lower than the main body was retained. No changes in boiling point during the second and third fractionations were detectable. The middle cuts of the third fractionations were dried over phosphorus pentoxide. The purity of the sample was checked by fractional freezing and by evaporating slowly at constant temperature. In the latter case the sample was evaporated almost to dryness without perceptible change in vapor pressure.

Booth and Swinehart prepared chlorodifluoromethane by the fluorination of chloroform with an antimony trifluoride–pentachloride mixture. The sample was fractionated twelve times until the critical constants were not changed by further fractionation.

The chlorotrifluoromethane used by Riedel was fractionated several times, the middle three-fifths being used each time as the charge for the next fractionation. The procedure was repeated until no change in the vapor pressure of the fractions was noted.

The sample used by Albright and Martin was obtained from E. I. du Pont de Nemours and Company and was said to be 99.9 per cent pure. No further purification was made. The vapor pressures were measured by a Bourdon-tube gage which had been calibrated against a dead-weight tester. The gage was accurate to 0.1 per cent of the indicated pressure. The critical pressure was determined by an extrapolation of the vapor-pressure equation to the critical temperature.

The data of Riedel and of Albright are in close agreement; averages of their values have been selected as the most probable values for the critical constants of chlorotrifluoromethane.

The data of Booth and Swinehart were selected as the more reliable data for chlorodifluoromethane because their sample was pure, whereas the sample used by Benning and McHarness contained some impurities.

(b) Freons containing two carbon atoms

Booth and Swinehart obtained chlorotrifluoroethylene from other workers in the laboratory and further purified it by fractionating it eleven times.

Oliver and coworkers obtained their sample by the dichlorination of Freon-113 with zinc in an alcohol solution. The sample was cooled to -75°C . to inhibit polymerization. The top vapors were pumped off before a sample was taken. The purity was checked by the freezing-point depression method and the sample was found to be 99.84 per cent pure. The critical density was determined by a volume measurement at the point where the meniscus was made to disappear by a very slight increase in pressure.

The data of Oliver *et al.* are selected over those of Booth and Swinehart because of the known high purity of their sample. No information is available concerning the data which were given to Oliver by A. L. Henne of the Midgley Foundation of Ohio State University.

Benning and McHarness purified their samples by repeated fractionation and checked the purity by melting point, limiting vapor density, and change in vapor pressure during distillation.

Hovorka and Geiger distilled trichlorotrifluoroethane from barium oxide, condensed the distillate with carbon dioxide snow, and then fractionally distilled the product until the boiling point was constant to 0.04°C .

The data of Booth and Swinehart and of Benning and McHarness are selected as the most reliable values.

14. Perfluoro compounds

Fowler and coworkers prepared fluoro compounds by the action of cobalt trifluoride on the vaporized hydrocarbon at elevated temperatures. The samples were purified by fractionation. The critical temperature was determined to within 0.2°C . The critical pressure was estimated from vapor-pressure data with the assumption that the latent heat of vaporization was constant. The critical pressures, therefore, are probably not very accurate.

Oliver and coworkers prepared their samples in the same manner as Fowler. The purification procedure is to be published, but the sample was said to have

a purity of 99.92 ± 0.02 mole per cent. The uncertainties were $\pm 0.05^\circ\text{C}$. in the temperature and ± 0.02 atm. in the pressure. The sample used by Milton and Oliver was said to be 99.97 mole per cent pure, as determined from a time-temperature curve for the temperature and pressure, respectively. The data of Oliver and coworkers are selected on the basis of the purity of the sample.

P. OXIDES (SEE TABLE 19)

1. Carbon dioxide

The presentation of data prior to 1924 has been adequately covered by S. F. Pickering (259); hence only the data obtained since then will be discussed here.

Meyers and Van Dusen prepared carbon dioxide by the action of pure sodium bicarbonate and sulfuric acid. The resultant gas was dried by passing over calcium chloride and phosphorus pentoxide and purified by fractional sublimation. However, the test equipment leaked during the determinations and later results were published by Kennedy and Meyers. The latter authors used a platinum resistance thermometer calibrated to 0.003°C . Their samples were prepared by a method analogous to that of Meyers and Van Dusen.

Lowry and Erickson determined orthobaric densities by the method of Young (350). Together with their own data, they used data of Amagat (5), Cailletet and Mathias (60), Behn (30), Keyes and Kennedy (160), and Jenkin (151) and determined the critical density by the method of rectilinear diameters.

Michels, Blaisse, and Michels purified their sample by a three-stage distillation. It was believed that the sample was very pure.

It is significant to note that the two latest determinations differ by only 0.08° in the value for the critical temperature. The former value was obtained by the method of meniscus disappearance, whereas the latter was fixed by P - V - T measurements. Because of the very slight difference, the average values are selected as the most probable values.

2. Carbon monoxide

Only the data presented since 1913 have been considered in the selection of the most probable values.

Cardoso prepared carbon monoxide by the treatment of formic acid with sulfuric acid. The gas was then passed through a potassium hydroxide solution and dried over phosphorus pentoxide. Cardoso checked the purity of the sample by observing the vapor pressure during isothermal condensation. The precision was given as follows: temperature, $\pm 0.1^\circ\text{C}$.; pressure, 0.1 atm.

Mathias and Crommelin prepared carbon monoxide by the action of sulfuric acid on sodium formate. The sample was solidified so that carbon dioxide and water were removed. The impurities were determined to be within 1 part in 2000 to 1 part in 5000.

The data of Mathias and Crommelin are selected as being the most probable because of the purity of the sample and the techniques used in the experimental determinations.

TABLE 19
Oxides

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
1. Carbon dioxide						
	°C.	atm.	g./cc.			
1869	31.1	73.0		Andrews	5	(7)
1879	30.92	77.0	0.3	Andrews	5	(8)
1881	31.0			Hautefeuille and Cailletet	?	(129)
1882	32.0	77.0	0.4395	Sarrau	13	(287)
1884	31.9	77.0	0.65	Dewar	?	(90)
1886			0.46	Cailletet and Mathias	19	(60)
1892	31.35	72.9	0.464	Amagat	5	(5)
1894	31.4			Chappius	?	(78)
1894	31.7			Villard	1	(324)
1896	31.0			Verschaffelt	?	(259)
1897	31.1			Keunan	1	(170)
1903	30.98	72.93	0.469	Keesom	1, 19	(157)
1904	31.12			Brinkman	?	(248)
1906	30.985		0.460	Onnes and Fabius	1	(247)
1908	31.10	73.00	0.459	Dorsman	?	(259)
1908	31.26			Bradley, Brown, and Hale	1	(46)
1912	31.0	72.85		Cardoso and Bell	3	(68)
1913	30.97			Hein	1	(131)
1917			0.4597	Keyes and Kennedy	19	(160)
1926	31.10	72.95		Meyers and Van Dusen	1, 16	(214)
1927			0.4683	Lowry and Erickson	19	(183)
1928	30.96			Kennedy and Meyers	1	(159)
1937	31.04	72.85	0.468	Michels, Blaise, and Michels	5	(215)
Values selected....	31.0	72.9	0.468			
2. Carbon monoxide						
1883	-141.1	34.6-35.2		Wroblewski	1	(343)
1884	-139.5	35.5		Olzewski	1	(235)
1913	-141.1	35.9		Onnes, Mathias, and Crommelin	1	(259a)
1915	-138.7	34.60	0.3110	Cardoso	1, 19	(63)
1936	-140.2	34.529	0.3010	Mathias and Crommelin	1, 19	(196)
Values selected....	-140.	34.5	0.301			
3. Ethylene oxide						
1922	192.0			Maass and Boomer	1	(185)
1950			0.32	Post	19	(261)
1950	195.8	70.97		Hess and Tilton	?	(137)
Values selected....	195.	71.0	0.32			

TABLE 19—Continued

YEAR	t_c	P_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
4. Nitrous oxide						
	°C.	atm.	g./cc.			
1878	36.4	73.07		Janssen	?	(150)
1884	35.4	75.		Dewar	?	(90)
1886			0.41	Cailletet and Mathias	19	(60)
1894	38.8	77.5	0.454	Villard	?	(325)
1897	36.	71.9		Kuenan	1	(170)
1912	36.5	71.65		Cordoso and Arni	3	(65)
1929			0.459	Quinn and Wernimont	19	(265)
Values selected....	36.5	71.7	0.457			
5. Nitric oxide						
1885	-93.5	71.2		Olszewski	1	(236)
1895			0.524(?)	Natanson	13	(259)
1908	-96	64.0		Olszewski	1	(259)
1910	-92.9	64.6		Adwentowski	1	(259)
Values selected....	-93.	64.	0.52(?)			
6. Nitrogen peroxide						
1885	171.2			Nadejdine	1	(291)
1913	158.2	100		Scheffer and Treub	1	(291)
1919	158.0	99		Baume and Robert	1	(17)
1933			0.570	Bennewitz and Windisch	19	(33)
1952		100	0.550	Reamer and Sage	16, 19	(273)
Values selected....	158.	100.	0.56			
7. Sulfur dioxide						
1859	157.0			Drion	1	(95)
1878	157-161			Ladenburg	1	(173)
1879	155.4	78.9		Sajotschewsky	?	(285)
1882	155.0			Schuch	?	(298)
1884	155.4	78.9		Dewar	?	(90)
1887	156.0		0.52	Cailletet and Mathias	1, 19	(61)
1903	157.26			Centnerszwer	1	(76)
1906	157.2	77.95		Briner	1	(49)
1907	157.3			Travers and Usher	1	(320)
1912	157.15	77.65		Cardoso and Bell	1	(68)
1912	157.6			Niggli	1	(228)
1913	157.14			Hein	1	(132)
1926	157.5	77.79		Cardoso and Fiorentino	1	(71)
1927			0.524	Cardoso and Sorrentino	19	(74)
Values selected....	157.5	77.8	0.524			

TABLE 19—*Concluded*

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFER- ENCE
8. Sulfur trioxide						
	°C.	atm.	g./cc.			
1922	218.2	83.8	0.633	Berthoud	1, 19	(41)
9. Water						
1869	362			de la Tour	1	(224)
1885	358.1		0.429	Nadejdine	1	(224)
1890	364.3	194.6	0.2078	Battelli	1	(295)
1891	365.0	200.5		Cailletet and Colardeau	5	(295)
1900	359	205		Knipp	5	(92)
1904	374			Traube and Teichner	1	(319)
1910	374.07	218		Holborn and Baumann	5	(142)
1927	374.2			Schroer	1	(225)
1931	374.11	218.53	0.3242	Keyes and Smith	5	(161)
1934	374.11	218.167		Keyes, Smith, and Gerey	5	(92)
1935	374.20		0.329	Reichenfield and Chany	1	(275)
1936	374.			Chitaron and Iwonow	1	(79)
1937	374.2	218.26	0.3265	Eck	1	(98)
1937	374.15	218.39	0.32	Osborne, Stimson, and Ginnings	5	(250)
Values selected....	374.2	218.3	0.32			

3. Ethylene oxide

Maass and Boomer prepared ethylene oxide by the action of sodium hydroxide on chlorohydrin. The sample was purified by low-temperature vacuum distillation. The purity was checked by measuring the vapor pressure of the distillate and residue at 0°C. After the third distillation, the vapor pressure for each portion was constant, but two additional distillations were made to insure high purity. The purity was also checked by (1) molecular weight determination, (2) reactivity with metallic sodium, and (3) conductivity. All tests indicated a product of high purity.

The value for the critical density was determined by Post by application of the law of rectilinear diameters. The data of Maass and Boomer for liquid density were used, and the gas densities were calculated from the perfect gas equation. The data were extrapolated over 180° and the uncertainty in the value is at least 5 per cent.

The data reported by Hess and Tilton are from the files of the Carbon and Carbide Chemicals Division of the Union Carbide and Carbon Corporation. No information as to the preparation of the sample or the methods of determination is available.

4. Nitrous oxide

Only the data since 1890 were considered in the final selection of the most probable values for nitrous oxide.

Villard used nitrous oxide from two sources: (1) decomposition of the hydrate and (2) commercial cylinder gas. The gas was treated with special absorbents, liquefied, and then distilled. The behavior of the sample in the neighborhood of the critical point was normal, indicating a pure sample.

Kuenan purified commercial nitrous oxide by passing it over calcium chloride, caustic potash, and phosphorus pentoxide. He then liquefied and distilled the gas. An increase in pressure of 0.3 per cent on isothermal condensation indicated a trace of impurity.

Cardoso and Arni prepared nitrous oxide by the action of sodium nitrite on hydroxylamine hydrochloride. The gas was treated with sulfuric acid and phosphorus pentoxide and then was fractionally distilled ten times. The vapor pressure changed less than 0.05 atm. when the sample was isothermally condensed. The sample of nitrous oxide used by Quinn was commercial-grade gas purified by repeated fractional distillation. Analysis prior to distillation showed the gas to be free from other oxides of nitrogen, halogens, carbon dioxide, sulfur compounds, and ammonia. Water and air were removed by fractional distillation.

The data of Cardoso and Arni are selected for the most probable values for the critical temperature and pressure, whereas the values of Quinn and Wernimont and those of Villard are averaged to give the selected value for the critical density.

5. Nitric oxide

Olszewski did not observe the critical state in 1885 but merely noted that the meniscus was still visible at -93.5°C . In 1908, he reported the values for the critical constants given in table 19 but did not give any details.

Adwentowski did not state how his samples were purified but indicated that the maximum amount of impurities was 0.25 per cent.

There is little basis for selecting the most probable values for the critical constants. More weight has been given the data of Adwentowski but only whole-numbered values are reported.

6. Nitrogen peroxide

No information is available as to the preparation and purification of the samples used by the workers indicated, except for Reamer and Sage (273).

The sample used by Reamer and Sage was obtained from the Allied Chemical and Dye Corporation. It was fractionated in a 16-plate glass column at a reflux ratio of 12:1. The initial and final 10 per cent were discarded and the balance was dried over phosphorus pentoxide, frozen at liquid-air temperatures, and evacuated to 0.1 mm. mercury.

The data are in good agreement and later values are averaged to give the selected values.

7. Sulfur dioxide

A survey of the critical constants of sulfur dioxide was made by Pickering (259) covering the data prior to 1924. The values as reported by Cardoso and coworkers represent more accurate data; hence they are selected as the most probable.

Cardoso and Fiorentino purified commercial sulfur dioxide by passing it through concentrated sulfuric acid and phosphorus pentoxide; they then distilled the sample ten times.

8. Sulfur trioxide

The data of Berthoud are the only data available at the present time. It is fortunate that he used extreme care and a good technique in making his determinations. The precautions were such that the amount of water was less than 1 mole per 1000 moles of sulfur trioxide gas.

9. Water

The data prior to 1900 are presented for historical value only.

All of the samples were purified by distillation, but the samples used by the latest investigators were distilled under vacuum to remove air.

The data are in excellent agreement. The selected values are those of Osborne and coworkers, which are approximately the average values of all data after 1900. The agreement between values obtained by the disappearing meniscus method and the P - V - T method should be carefully noted. Water is a highly associated substance and should exhibit a maximum difference between T_m and T_c . Actually, the difference is negligible.

Q. SULFUR AND SULFUR COMPOUNDS (SEE TABLE 20)

1. Sulfur

The value reported by Rassow for the critical temperature of sulfur is the only experimental value available. No information was given as to the purity of the sample.

The value reported by West for the critical pressure was calculated by means of Duhring plots, with water and ammonia as reference substances, by application of the vapor-pressure equation, and by Othmer plots with water, sulfur dioxide, and ammonia as reference substances. These values were averaged to give the value of 116 atm. The use of this value is recommended until experimental data are available.

2. Carbonyl sulfide

Ilosvay prepared carbonyl sulfide by treating an aqueous solution of potassium butyl thiocarbonate with dilute sulfuric acid. The sample was purified by passing through concentrated sodium hydroxide, sulfuric acid, and triethylphosphine.

The sample used by Hempel was prepared by the action of dilute sulfuric acid on ammonium thiocyanate. The purification was performed in a manner similar

to that of Ilosvay, except that the final treatment consisted in passing the gas through a mixture of triethylphosphine, pyridine, and nitrobenzene.

The sample used by Hempel was rather impure as compared to the samples of Stock and Kuss (303) and of Kemp and Giaque (158). Also, the type of Bourdon gage used by Hempel is accurate to only ± 5 per cent; hence the value of 61 atm. for the critical pressure is selected as more probable. This value is estimated from the vapor-pressure data of Stock and Kuss (303) and is reported in the *International Critical Tables* (148).

3. Carbon disulfide

Hannay purified carbon disulfide as follows: The sample was digested over sodium and distilled from quicklime into a small flask and stored over sulfuric acid under a bell-jar. The thermometers were calibrated daily and the mean probable error was fixed at 0.16°C . Hydrogen was used as a reference gas in the pressure measurements. The mean probable error in the pressure measurement was 0.07 atm.

The value of Fischer and Reichel is selected as the most probable value and is in good agreement with the data of Hannay and Galitzine. The value of Hannay for the critical pressure is probably the most reliable. Since Mathias used the rectilinear diameter in determining the critical density, this value is selected.

4. Hydrogen selenide

Since no information is available concerning the preparation and purification of the sample, there is no basis for selecting the more probable values. Because of the later date of the work of Bruylants and Dondeyne, their data are probably more accurate.

5. Hydrogen sulfide

Only the data reported since 1900 are discussed and considered in the final selection.

Scheffer prepared hydrogen sulfide by the action of dilute sulfuric acid on sodium hydrosulfide. The solution contained barium sulfide. Purification was accomplished by fractional distillation.

Estreicher and Schnerr did not mention the method used for the purification of their sample. They made twenty observations wherein the temperature of meniscus appearance and disappearance varied from 100.03° to 100.84°C .

The hydrogen sulfide used by Cardoso and Arni was prepared by the action of hydrochloric acid on precipitated ferrous sulfide. The sample was then passed through water, and over calcium chloride and phosphorus pentoxide. The gas was then fractionated fourteen times. Extreme care was taken to insure complete dryness throughout, in order to prevent decomposition. The accuracy was stated to be $\pm 0.1^{\circ}\text{C}$. and ± 0.1 atm.

Cardoso used additional precautions to insure the complete removal of hydrogen and polysulfides of hydrogen. The sample was absorbed in a magnesium hydroxide suspension which was heated to liberate the gas. The sample was then

TABLE 20
Sulfur and sulfides

YEAR	t_c	p_c	d_c	INVESTIGATORS	METHOD	REFERENCE
1. Sulfur						
	$^{\circ}\text{C.}$	<i>atm.</i>	<i>g./cc.</i>			
1920	1040			Rassow	1	(272)
1950		116		West	17	(332)
2. Carbonyl sulfide						
1881	105			Ilosvay	1	(146)
1901	105	65		Hempel	?	(133)
Values selected....	105	61				
3. Carbon disulfide						
1821	275	77.8		de la Tour	1	(316)
1874	276			Avenarius	1	(14)
1878	271.8	74.7		Sajotschewsky	?	(285)
1880	272.96	77.9		Hannay and Hogarth	1	(124)
1882	277.68	78.14		Hannay	1	(123)
1890	273.0	72.87	0.377	Battelli	?	(15)
1890	279.6			Galitzine	?	(113)
1898			0.441	Mathias	19	(195)
1943	279.			Fischer and Reichel	4	(109)
Values selected....	279.	78.	0.44			
4. Hydrogen selenide						
1890	138.0	91.0		Olszewski	1	(237)
1922	138.	88		Bruylants and Dondeyne	1	(55)
5. Hydrogen sulfide						
1884	100.2	92.0		Dewar	?	(90)
1890	100.0	88.7		Olszewski	1	(259)
1897	100.0	90.0		Leduc and Sacerdote	1	(179)
1910	99.6	88.3		Scheffer	1	(290)
1910	100.43			Estreicher and Schnerr	1	(259)
1912	100.43	89.05		Cardoso and Arni	3	(65)
1921	100.4	88.90		Cardoso	3	(64)
1950	100.4	88.9	0.3488	Reamer, Sage, and Lacey	5	(274a)
Values selected....	100.4	88.9	0.349			
6. Methyl sulfide						
?	231.2			Ferreto	?	(108)
1903	231.29	54.16		Vespignani	1	(323)
1923	229.0		0.301	Herz and Neukirch	19	(135)
1924	229.9	54.6	0.3089	Berthoud and Brum	1, 19	(42)
Values selected....	229.9	54.6	0.309			

TABLE 20—*Concluded*

YEAR	t_c	p_c	ρ_c	INVESTIGATORS	METHOD	REFERENCE
7. Ethyl mercaptan						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1900	228.0			Ferreto	1	(108)
1903	228.3	63.5		Vespignani	1	(323)
1924	225.5	54.2	0.300	Berthoud and Brum	1, 19	(42)
Values selected....	226.	54.2	0.300			
8. Ethyl sulfide						
	$^{\circ}\text{C.}$	atm.	g./cc.			
1900	284.67			Ferreto	1	(108)
1903	284.60	47.1		Vespignani	1	(323)
1924	283.80	39.1	0.279	Berthoud and Brum	1, 19	(42)
Values selected....	284.	39.1	0.279			

passed over phosphorus pentoxide. At this point there were still evidences of high-boiling impurities, which were removed by cooling and evaporating the hydrogen sulfide.

The hydrogen sulfide used by Reamer, Sage, and Lacey was prepared from chemically pure aluminum sulfide and distilled water. The evolved gas was dried over calcium chloride and calcium sulfate and collected under vacuum at liquid-air temperature. It was found that the vapor pressure at 100°F. (38°C.) changed less than 0.01 atm. upon a change in the fraction vaporized from 0.05 to 0.85.

The data of Cardoso and of Reamer, Sage, and Lacey are in exact agreement; hence they are selected as the most probable values for the critical points.

6. Methyl sulfide

No information is available concerning the preparation and purification of the samples used by Ferreto, Vespignani, or Herz and Neukirch.

Berthoud and Brum washed methyl sulfide with water to remove metallic salts and dried it over calcium chloride. The sample was then fractionated and the fraction boiling at 35.1–35.2°C. was used as the sample. These investigators were careful workers and their data are selected as the most probable values.

7. Ethyl mercaptan

8. Ethyl sulfide

No information is available concerning the purity of the samples used by Ferreto and Vespignani.

Berthoud and Brum prepared ethyl sulfide by the action of sodium ethyl sulfate on sodium hydrosulfide in aqueous solution. The solution was treated with sodium hydroxide to remove hydrogen sulfide. A layer of ethyl sulfide was formed below the basic solution and was treated with lead acetate after removal.

The mercaptan was liberated from the caustic solution. Both samples were dried and fractionally distilled.

TABLE 21
Miscellaneous compounds

YEAR	t_c	p_c	INVESTIGATORS	METHOD	REFERENCE
1. Phosphine					
	°C.	atm.			
1887	54.0	70.5	Skinner	1	(302)
1898	52.8	64.0	Leduc and Sacerdote	1	(178)
1906	51.3	64.5	Briner	1	(49)
Values selected.....	51.3	64.5			
2. Phosponium chloride					
1887	48.0	95.0	Skinner	1	(302)
1903	48.8	74.2	Tammann	1	(308)
1906	49.1	72.7	Briner	1	(49)
Values selected.....	49.1	72.7			
3. Pyridine					
1898	344.2		Radice	1	(120)
1923		60.0	Herz and Neukirch	15	(135)
4. Silane (SiH ₄)					
1911	-3.5?	47.8?	Adwentowski and Drozdowski	1	(2)
5. Thiophene					
1885	302.7	55.0	Shift	?	(255)
1888	317.3	47.7	Pawlewski	1	(255)
Values selected.....	317.	48.			
6. Nitromethane					
t_c	p_c	d_c	INVESTIGATOR	METHOD	REFERENCE
°C.	atm.	g./cc.			
315	62.3	0.352	Griffin	8	(117a)

The data of Berthoud and Brum are selected as the best values in spite of the apparent agreement between the data of the other two workers. The later performance of the work, together with the fact that the critical temperature as determined by two methods gave very good agreement, is the basis for the selection.

R. MISCELLANEOUS COMPOUNDS (SEE TABLE 21)

1. *Phosphine*2. *Phosphonium chloride*

Skinner prepared phosphine by the action of concentrated potash solution on phosphonium iodide. The sample was dried over calcium chloride and phosphorus pentoxide. The hydrogen chloride was prepared by the action of concentrated sulfuric acid on ammonium chloride. Equal volumes of phosphine and hydrogen chloride were used in the phosphonium chloride determinations.

Leduc and Sacerdote liberated phosphine from a cuprosodiphosphonium chloride solution by gentle heating. The liberated phosphine was passed over potassium hydroxide, crushed potash, and phosphorus pentoxide.

Tammann prepared phosphine from potassium hydroxide and phosphonium iodide. The phosphine and hydrogen chloride were condensed in the form of phosphonium chloride at the temperature of solid carbon dioxide. The exact ratio of phosphine to hydrogen chloride is practically impossible to maintain, but the sample was considered to be pure because at a pressure of 748 kg./sq. cm. and a temperature of 50.08°C., one-twentieth of the substance was liquid, while a pressure increase of 2 kg./sq. cm. caused over one-half of the vapor to liquefy.

Briner used low-temperature fractionation (liquid-air temperature) to purify both the phosphine and hydrogen chloride. The accuracy of Briner's work was stated as $\pm 0.2^\circ\text{C}$. for the critical temperature and ± 0.4 atm. for the critical pressure.

The data of Briner are selected as the most probable, since these data are in good agreement with those of Leduc and Tammann and were established with purer samples.

3. *Pyridine*

The critical temperature of pyridine as found by Radice was given by Guye and Mallet. No information is available concerning the purity of the sample.

Herz and Neukirch used the method of Altschul to determine the critical pressure. Again no information concerning the techniques used and the sample is available.

4. *Silane*

Adwentowski and Drozdowski prepared silane by shaking a magnesium silicon compound, Mg_2Si , with concentrated hydrochloric acid. The liberated gas was condensed with liquid air, and the condensate was distilled. The fraction boiling at -116°C . was used as the sample. At the present time, the boiling point of silane is generally accepted to be -112°C . Therefore the data of these workers may not be entirely reliable, but they are the only data available.

5. *Thiophene*

No information was given by either worker concerning the preparation and purification of their samples. The work of Pawlewski is, in general, fairly accurate; hence his values are selected as the better of the two sets of data.

TABLE 22
Summary of critical values*

SUBSTANCE	MOLECULAR WEIGHT	CRITICAL TEMPERATURE				CRITICAL PRESSURE		CRITICAL DENSITY		CRITICAL VOLUME	
		°C.	°K.	°R.	°F.	atm.	p.s.i.a.	g./cc.	lb./cu.ft.	cc./g.-mole	cu.ft./lb.-mole
<i>A. Inert gases:</i>											
Helium.....	4.003	-267.9	5.3	9.5	-450.2	2.26	33.2	0.0693	4.33	57.8	0.926
Helium ³	3.00	-269.82	3.34	6.01	-453.7	1.15	16.9				
Neon.....	20.183	-228.7	44.5	80.1	-379.6	26.9	395.	0.484	30.2	41.7	0.668
Argon.....	39.944	-122.	151.	272.	-188.	48.0	705.	0.531	33.2	75.2	1.20
Krypton.....	83.7	-63.8	209.4	376.9	-82.8	54.3	798.	0.908	56.7	92.2	1.48
Xenon.....	131.3	16.59	289.75	521.55	61.86	58.0	852.	1.105	68.99	118.8	1.903
<i>B. Elementary gases:</i>											
Chlorine.....	70.914	144.	417.	751.	291.	76.1	1120.	0.573	35.8	124.	1.99
Bromine.....	159.832	311.	584.	1052.	592.	102.	1500.	1.18	73.7	144.	2.31
Iodine.....		512.	785.	1414.	954.						
		553.		1487.	1027.						
Hydrogen (normal).....	2.016	-239.9	33.3	59.9	-399.8	12.80	188.1	0.0310	1.94	65.0	1.04
Hydrogen (equilibrium).....	2.016	-240.2	33.0	59.3	-400.4	12.8	188.	0.0326	2.04	61.8	0.990
Hydrogen deuteride.....	3.000	-237.2	36.0	64.7	-395.0	14.6	215.	0.0209	1.30	144.	2.31
Deuterium (equilibrium).....	4.00	-234.9	38.3	68.9	-390.8	16.3	240.	0.0151	0.943	265.	4.24
Deuterium (normal).....	4.00	-234.8	38.4	69.1	-390.6	16.4	241.				
Nitrogen.....	28.016	-147.0	126.2	227.1	-232.6	33.5	492.	0.311	19.4	90.1	1.44
Oxygen.....	32.000	-118.4	154.8	278.6	-181.1	50.1	736.	0.41	26.	78.	1.2
Ozone.....	48.00	-5.	268.	483.	+23.	67.	980.	0.537	33.5	89.4	1.43
<i>C. Aliphatic hydrocarbons:</i>											
<i>1. Paraffins:</i>											
Methane.....	16.042	-82.1	191.1	343.9	-115.8	45.8	673.	0.162	10.1	99.0	1.59
Ethane.....	30.068	32.3	305.5	549.8	90.1	48.2	708.	0.203	12.7	148.	2.37
Propane.....	44.094	96.8	370.0	665.9	206.2	42.0	617.	0.220	13.7	200.	3.20
<i>n</i> -Butane.....	58.120	152.0	425.2	765.2	305.5	37.5	551.	0.228	14.2	255.	4.08
Isobutane.....	58.120	134.9	408.1	734.5	274.8	36.0	529.	0.221	13.8	263.	4.21
<i>n</i> -Pentane.....	72.146	196.6	469.8	845.6	385.9	33.3	489.	0.232	14.5	311.	4.98
Isopentane.....	72.146	187.8	461.0	829.7	370.0	32.9	483.	0.234	14.6	308.	4.93
Neopentane.....	72.146	160.6	433.8	780.8	321.1	31.6	464.	0.238	14.9	303.	4.85
<i>n</i> -Hexane.....	86.172	234.7	507.9	914.2	454.5	29.9	439.	0.234	14.6	368.	5.89

2-Methylpentane.....	86.172	224.7	497.9	896.2	436.5	29.9	439.	0.235	14.7	367.	5.88
3-Methylpentane.....	86.172	231.5	504.7	908.4	448.7	30.8	453.	0.235	14.7	367.	5.88
2,2-Dimethylbutane.....	86.172	216.2	489.4	880.9	421.2	30.7	451.	0.240	15.0	359.	5.75
2,3-Dimethylbutane.....	86.172	227.1	500.3	900.5	440.8	30.9	454.	0.241	15.0	358.	5.73
n-Heptane.....	100.198	267.0	540.2	972.3	512.6	27.0	397.	0.235	14.7	426.	6.82
2-Methylhexane.....	100.198	257.9	531.1	955.9	496.2	27.2	400.	0.234	14.6	428.	6.86
3-Methylhexane.....	100.198	262.4	535.6	964.0	504.3	28.1	413.	0.240	15.0	417.	6.68
3-Ethylpentane.....	100.198	267.6	540.8 ^{3*}	973.4	513.7	28.6	420.	0.241	15.0	416.	6.66
2,2-Dimethylpentane.....	100.198	247.7	520.9	937.6	477.9	28.4	417.	0.248	15.5	404.	6.47
2,3-Dimethylpentane.....	100.198	264.6	537.8	968.0	508.3	29.2	429.	0.247	15.4	406.	6.50
2,4-Dimethylpentane.....	100.198	247.1	520.3	936.5	476.8	27.4	403.	0.239	14.9	419.	6.71
3,3-Dimethylpentane.....	100.198	263.	536.	965.	505.	30.	440.				
2,2,3-Trimethylbutane.....	100.198	258.3	531.5	956.6	496.9	29.75	437.2	0.254	15.9	394.	6.31
n-Octane.....	114.224	296.7	569.4	1024.9	565.2	24.6	362.	0.233	14.5	490.	7.85
2-Methylheptane.....	114.224	288.	561.	1010.	550.	24.8	364.	0.234	14.6	488.	7.82
3-Methylheptane.....	114.224	292.	565.	1018.	558.	25.6	376.	0.239	14.9	478.	7.66
4-Methylheptane.....	114.224	290.	563.	1014.	554.	25.6	376.	0.240	15.0	476.	7.63
3-Ethylhexane.....	114.224	294.	567.	1021.	561.	26.4	388.	0.245	15.3	466.	7.47
2,2-Dimethylhexane.....	114.224	279.	552.	994.	534.	25.6	376.	0.245	15.3	466.	7.47
2,3-Dimethylhexane.....	114.224	293.	566.	1019.	559.	26.6	391.	0.248	15.5	460.	7.37
2,4-Dimethylhexane.....	114.224	282.	555.	1000.	540.	25.8	379.	0.245	15.3	466.	7.47
2,5-Dimethylhexane.....	114.224	276.8	550.0	989.9	530.2	24.6	362.	0.237	14.8	482.	7.72
3,3-Dimethylhexane.....	114.224	291.	564.	1016.	556.	27.2	400.	0.254	15.9	450.	7.21
3,4-Dimethylhexane.....	114.224	298.	571.	1028.	568.	27.4	403.	0.253	15.8	451.	7.23
3-Ethyl-2-methylpentane.....	114.224	295.	568.	1023.	563.	27.4	403.	0.254	15.9	450.	7.21
3-Ethyl-3-methylpentane.....	114.224	305.	578.	1041.	581.	28.9	425.	0.263	16.4	434.	6.95
2,2,3-Trimethylpentane.....	114.224	303.	576.	1037.	577.	29.0	426.	0.264	16.5	433.	6.94
2,2,4-Trimethylpentane.....	114.224	270.9	544.1	979.3	519.6	25.4	373.	0.243	15.2	470.	7.53
2,3,4-Trimethylpentane.....	114.224	295.	568.	1023.	563.	27.6	406.	0.256	16.0	446.	7.14
2,2,3,3-Tetramethylbutane.....	114.224	270.8	544.0	979.1	519.4	24.5	360.	0.238	14.9	480.	7.69
2. Olefins:											
Ethylene.....	28.052	9.2	282.4	508.3	48.6	50.0	735.	0.227	14.2	124.	1.99
Propene.....	42.078	91.8	365.0	656.9	197.2	45.6	670.	0.233	14.5	181.	2.90
1-Butene.....	56.104	146.4	419.6	755.2	295.5	39.7	583.	0.234	14.6	240.	3.84
2-Butene.....	56.104	157.	430.	775.	315.	41.	600.	0.238	14.9	236.	3.78

TABLE 22—Continued

SUBSTANCE	MOLECULAR WEIGHT	CRITICAL TEMPERATURE				CRITICAL PRESSURE		CRITICAL DENSITY		CRITICAL VOLUME	
		°C.	°K.	°R.	°F.	atm.	p.s.i.a.	g./cc.	lb./cu.ft.	cc./g.-mole	cu. ft./lb.-mole
Isobutylene (2-methylpropene).....	56.104	144.7	417.9	752.2	292.5	39.5	580.	0.235	14.8	239.	3.83
1-Pentene.....	70.130	201.	474.	854.	394.	40.	588.				
2-Pentene.....	70.130	202.4	475.6	856.0	396.3	40.4	594.				
Isoamylene.....	70.130	191.6	464.8	836.6	376.9	33.9	498.				
2-Methyl-2-butene.....	70.130	197.	470.	847.	387.	34.	500.				
Hexene.....	84.156	243.5	516.7	930.0	470.3						
Octene.....	112.208	304.8	578.0	1040.3	580.6						
3. Diolefins:											
Propadiene.....	40.062	120.	393.	708.	248.						
1,3-Butadiene.....	54.088	152.	425.	766.	306.	42.7	628.	0.245	15.3	221.	3.54
1,5-Hexadiene.....	82.140	234.4	507.6	913.6	453.9						
4. Acetylenes:											
Ethyne.....	26.036	36.	309.	557.	97.	61.6	905.	0.231	14.4	113.	1.81
Propyne.....	40.062	128.	401.	722.	262.	52.8	776.				
Ethylacetylene.....	54.088	190.5	463.7	834.6	374.9						
Dimethylacetylene.....	54.088	215.5	488.7	879.6	419.9						
Propylacetylene.....	68.114	220.3	493.5	888.2	428.5						
D. Cycloparaffins:											
Cyclopentane.....	70.130	238.6	511.8	921.2	461.5	44.6	655.	0.27	17.	260.	4.2
Methylcyclopentane.....	84.156	259.6	532.8	959.0	499.3	37.4	550.	0.264	16.5	319.	5.11
Ethylcyclopentane.....	98.182	296.3	569.5	1025.0	565.3	33.5	492.	0.262	16.4	375.	6.01
Cyclohexane.....	84.156	280.	553.	996.	536.	40.0	588.	0.273	17.0	308.	4.93
Methylcyclohexane.....	98.182	299.1	572.3	1030.1	570.4	34.32	504.4	0.285	17.8	344.	5.51
E. Aromatic hydrocarbons:											
Benzene.....	78.11	289.	562.	1012.	552.	48.6	714.	0.300	18.7	260.	4.17
Toluene.....	92.13	320.8	594.0	1069.1	609.4	41.6	611.	0.29	18.	320.	5.1
o-Xylene.....	106.16	358.4	631.6	1136.8	677.1	36.9	542.				
m-Xylene.....	106.16	346.	619.	1115.	655.	36.	529.				
p-Xylene.....	106.16	345.	618.	1113.	653.	35.	514.				
Ethylbenzene.....	106.16	346.4	619.6	1115.2	655.5	38.	558.				
1,2,3-Trimethylbenzene.....	120.19	395.	668.	1203.	743.	31.	456.	0.28	17.	430.	6.9

1,2,4-Trimethylbenzene	120.19	381.2	654.4	1177.9	718.2	33.	485.	0.28	17.	430.	6.9
1,3,5-Trimethylbenzene	120.19	368.	641.	1154.	694.	33.	485.	0.28	17.	430.	6.9
2-Ethyl-1-methylbenzene	120.19	380.	653.	1176.	716.	31.	456.	0.28	17.	430.	6.9
3-Ethyl-1-methylbenzene	120.19	363.	636.	1145.	685.	31.	456.	0.28	17.	430.	6.9
4-Ethyl-1-methylbenzene	120.19	363.	636.	1145.	685.	31.	456.	0.28	17.	430.	6.9
<i>n</i> -Propylbenzene	120.19	365.6	638.8	1149.8	690.1	32.	470.	0.28	17.	430.	6.9
Isopropylbenzene	120.19	362.7	635.9	1144.6	684.9	32.	470.	0.28	17.	430.	6.9
Cymene	134.21	385.	658.	1185.	725.						
Isobutylbenzene	134.21	377.	650.	1171.	711.	31.	456.				
<i>F. Substituted aromatic compounds:</i>											
Fluorobenzene	96.10	286.6	559.8	1007.6	547.9	44.6	655.	0.354	22.1	271.	4.34
Chlorobenzene	112.56	359.2	632.4	1138.3	678.6	44.6	655.	0.365	22.8	308.	4.93
Bromobenzene	157.02	397.	670.	1207.	747.	44.6	655.	0.458	28.6	343.	5.49
Iodobenzene	204.02	448.	721.	1298.	838.	44.6	655.	0.581	36.3	351.	5.62
Phenol	94.11	419.2	692.4	1246.3	786.6	60.5	889.				
<i>o</i> -Cresol	108.13	422.	695.	1252.	792.	49.4	726.				
<i>m</i> -Cresol	108.13	432.	705.	1270.	810.	45.0	661.	0.35	22.	310.	5.0
<i>p</i> -Cresol	108.13	426.	699.	1259.	799.	50.8	747.				
Aniline	93.12	425.6	698.8	1257.8	798.1	52.3	769.	0.340	21.2	274.	4.39
Methylaniline	107.15	428.4	701.6	1262.8	803.1	51.3	754.				
Dimethylaniline	121.18	414.7	687.9	1238.2	778.5	35.8	526.				
<i>G. Alcohols:</i>											
Methyl alcohol	32.04	240.0	513.2	923.7	464.0	78.5	1154.	0.272	17.0	118.	1.89
Ethyl alcohol	46.07	243.	516.	929.	469.	63.0	926.	0.276	17.2	167.	2.68
<i>n</i> -Propyl alcohol	60.09	264.	537.	967.	507.	50.2	738.	0.273	17.0	220.	3.52
Isopropyl alcohol	60.09	235.6	508.8	915.8	456.1	53.	779.	0.274	17.1	219.	3.51
<i>n</i> -Butyl alcohol	74.12	288.	561.	1010.	550.	49.	720.				
<i>sec</i> -Butyl alcohol	74.12	265.	538.	969.	509.						
<i>tert</i> -Butyl alcohol	74.12	235.	508.	915.	455.						
<i>H. Ethers:</i>											
Dimethyl ether	46.07	126.9	400.1	720.1	260.4	53.	779.	0.242	15.1	190.	3.04
Ethyl methyl ether	60.09	164.7	437.9	788.2	328.5	43.4	638.	0.272	17.0	221.	3.54
Diethyl ether	74.12	194.	467.	841.	381.	35.6	523.	0.264	16.5	281.	4.50
Ethyl propyl ether	88.15	227.4	500.6	901.0	441.3	32.1	472.	0.260	16.2	339.	5.43
Dioxane	88.10	312.	585.	1054.	594.	50.7	745.	0.36	22.	240.	3.9

TABLE 22—Continued

SUBSTANCE	MOLECULAR WEIGHT	CRITICAL TEMPERATURE				CRITICAL PRESSURE		CRITICAL DENSITY		CRITICAL VOLUME	
		°C.	°K.	°R.	°F.	atm.	p.s.i.a.	g./cc.	lb./cu. ft.	cc./g.-mole	cu. ft./lb.-mole
<i>I. Ketones:</i>											
Acetone.....	58.08	235.5	508.7	915.6	455.9	46.6	685.	0.273	17.0	213.	3.41
Ethyl methyl ketone.....	72.10	260.	533.	960.	500.	39.5	580.	0.25	16.	290.	4.6
<i>J. Acetaldehyde</i>											
Acetaldehyde.....	44.05	188.	461.	830.	370.						
<i>K. Organic acids:</i>											
Acetic acid.....	60.05	321.6	594.8	1070.6	610.9	57.1	839.	0.351	21.9	171.	2.74
Acetic anhydride.....	102.09	296.	569.	1025.	565.	46.2	679.				
Propionic acid.....	74.08	339.	612.	1102.	642.	53.	779.	0.32	20.	230.	3.7
<i>n</i> -Butyric acid.....	88.10	355.	628.	1131.	671.	52.	764.	0.304	19.0	290.	4.65
Isobutyric acid.....	88.10	336.	609.	1097.	637.	40.	588.	0.302	18.9	292.	4.68
<i>n</i> -Valeric acid.....	102.13	378.	651.	1172.	712.						
Isovaleric acid.....	102.13	361.	634.	1142.	682.						
<i>L. Esters:</i>											
Methyl formate.....	60.05	214.0	487.2	867.9	417.2	59.2	870.	0.349	21.8	172.	2.76
Ethyl formate.....	74.08	235.3	508.5	915.2	455.5	46.8	688.	0.323	20.2	229.	3.67
Propyl formate.....	88.10	264.9	538.1	968.5	508.8	40.1	589.	0.309	19.3	285.	4.57
Isobutyl formate.....	102.13	278.2	551.4	992.5	532.8	38.3	563.				
Methyl acetate.....	74.08	233.7	506.9	912.4	452.7	46.3	680.	0.325	20.3	228.	3.65
Ethyl acetate.....	88.10	250.1	523.3	941.9	482.2	37.8	556.	0.308	19.2	286.	4.58
<i>n</i> -Propyl acetate.....	102.13	276.2	549.4	988.9	529.2	32.9	483.	0.296	18.5	345.	5.53
Methyl butyrate.....	102.13	281.3	554.5	998.0	538.3	34.3	504.	0.300	18.7	340.	5.45
Methyl isobutyrate.....	102.13	267.6	540.8	973.4	513.7	33.9	498.	0.301	18.8	339.	5.43
Ethyl isobutyrate.....	116.16	280.	553.	996.	536.	30.	441.	0.276	17.2	421.	6.74
<i>M. Nitrogen compounds:</i>											
Ammonia.....	17.03	132.3	405.5	729.8	270.1	111.3	1636.	0.235	14.7	72.5	1.16
Hydrazine.....	32.05	380.	653.	1176.	716.	145.	2130.				
Cyanogen.....	52.02	127.	400.	721.	261.	59.	867.				
Hydrogen cyanide.....	27.03	183.5	456.7	822.0	362.3	53.2	782.	0.195	12.2	139.	2.23
Methylamine.....	31.06	156.9	430.1	774.1	314.4	73.6	1082.				

Dimethylamine.....	45.08	164.5	437.7	787.8	328.1	52.4	770.				
Trimethylamine.....	59.11	160.1	433.3	779.9	320.2	40.2	591.	0.233	14.5	254.	4.07
Ethylamine.....	45.08	183.	456.	821.	361.	55.5	816.				
Diethylamine.....	73.14	223.	496.	893.	433.	36.6	538.				
Triethylamine.....	101.19	259.	532.	958.	498.	30.	441.				
Propylamine.....	59.11	233.8	507.0	912.5	452.8	46.8	688.				
Dipropylamine.....	101.19	277.	550.	991.	531.	31.	456.				
Acetonitrile.....	41.05	274.7	547.9	986.2	526.5	47.7	701.	0.237	14.8	173.	2.77
Propionitrile.....	55.08	291.2	564.4	1015.9	556.2	41.3	607.	0.240	15.0	230.	3.68
Butyronitrile.....	69.10	309.1	582.3	1048.1	588.4	37.4	550.				
Capronitrile.....	125.21	348.8	622.0	1119.5	659.8	32.1	472.				
Benzonitrile.....	103.12	426.2	699.4	1258.9	799.2	41.6	611.				
<i>N. Inorganic halides:</i>											
Hydrogen fluoride.....	20.01	230.2	503.4	906.1	446.4						
Hydrogen chloride.....	36.47	51.4	324.6	584.2	124.5	81.5	1198.	0.42	26.	48.	0.76
Hydrogen bromide.....	80.92	90.0	363.2	653.7	194.0	84.0	1235.				
Hydrogen iodide.....	127.93	150.	423.	762.	302.	81.	1190.				
Boron trifluoride.....	67.82	-12.3	260.9	469.6	9.9	49.2	723.				
Boron trichloride.....	117.19	178.8	452.0	813.5	353.8	38.2	561.				
Boron tribromide.....	250.57	300.	573.	1032.	572.			0.90	56.	280.	4.45
Phosgene.....	98.92	182.	455.	820.	360.	56.	823.	0.52	32.	190.	3.0
Germanium tetrachloride.....	214.43	276.9	550.1	990.1	530.4	38.	558.				
Silicon tetrafluoride.....	104.06	-14.1	259.1	466.3	6.6	36.7	539.				
Chlorotrifluorosilane.....	120.52	34.5	307.7	553.8	94.1	34.2	503.				
Dichlorodifluorosilane.....	136.97	95.8	369.0	664.1	204.4	34.5	507.				
Trichlorofluorosilane.....	153.43	165.3	438.5	789.2	329.5	35.3	579.				
Silicon tetrachloride.....	169.89	233.	506.	911.	451.						
Stannic chloride.....	260.53	318.7	591.9	1065.4	605.7	37.0	544.	0.742	46.3	351.	5.62
Sulfur hexafluoride.....	146.06	45.55	318.71	573.68	113.99	37.11	545.4	0.752	46.9	194.	3.11
<i>O. Aliphatic organic halides:</i>											
Methyl fluoride.....	34.03	44.6	317.8	572.0	112.0	58.0	852.	0.300	18.7	113.	1.81
Methyl chloride.....	50.49	143.1	416.3	749.3	289.6	65.9	968.	0.353	22.0	143.	2.29
Methyl bromide.....	94.95	191.	464.	836.	376.						
Methyl iodide.....	141.95	255.	528.	951.	491.						

TABLE 22—Concluded

SUBSTANCE	MOLE- CULAR WEIGHT	CRITICAL TEMPERATURE				CRITICAL PRESSURE		CRITICAL DENSITY		CRITICAL VOLUME	
		°C.	°K.	°R.	°F.	atm.	p.s.i.a.	g./cc.	lb./cu. ft.	cc./g.- mole	cu. ft./ lb.-mole
<i>O. Aliphatic organic halides:—(Cont.)</i>											
Methylene chloride.....	84.94	237.	510.	919.	459.	60.	882.				
Chloroform.....	119.39	263.4	536.6	965.8	506.1	54.	794.	0.50	31.	240.	3.8
Carbon tetrachloride.....	153.84	283.2	556.4	1001.5	541.8	45.0	661.	0.558	34.8	276.	4.42
Ethyl fluoride.....	48.06	102.2	375.4	675.7	216.0	46.6	685.				
Ethyl chloride.....	64.52	187.2	460.4	828.7	369.0	52.	764.				
Ethyl bromide.....	108.98	230.7	503.9	907.0	447.3	61.5	904.	0.507	31.7	215.	3.44
1,1-Dichloroethane.....	98.97	250.	523.	942.	482.	50.	735.				
1,2-Dichloroethane.....	98.97	288.	561.	1010.	550.	53.	779.	0.44	27.	220.	3.6
Dibromomethane.....	173.86	309.8	583.0	1049.3	589.6	70.6	1038.				
Chlorodifluoromethane.....	86.48	96.4	369.6	665.2	205.5	48.5	713.	0.525	32.8	165.	2.64
Dichlorofluoromethane.....	102.93	178.5	451.7	813.0	353.3	51.0	749.	0.522	32.6	197.	3.16
Chlorotrifluoromethane.....	104.47	28.8	302.0	543.5	83.8	39.	573.	0.58	36.	180.	2.9
Dichlorodifluoromethane (Freon 12).....	120.92	111.5	384.7	692.4	232.7	39.6	582.	0.555	34.6	218.	3.49
Trichlorofluoromethane (Freon 11).....	137.38	198.0	471.2	848.1	388.4	43.2	635.	0.554	34.6	248.	3.97
Chlorotrifluoroethylene.....	116.48	106.	379.	683.	223.	40.	588.	0.55	34.	210.	3.4
Dichlorotetrafluoroethane.....	170.93	145.7	418.9	754.0	294.3	32.3	475.				
Trichlorotrifluoroethane (Freon 113).....	187.39	214.1	487.3	877.1	417.4	33.7	495.	0.576	36.0	325.	5.21
Perfluoro- <i>n</i> -butane.....	238.04	113.3	386.5	695.6	235.9	23.	338.				
Perfluoro- <i>n</i> -heptane.....	388.07	201.6	474.8	854.6	394.9	16.0	235.	0.584	36.5	664.	10.6
Perfluoromethylcyclohexane.....	350.07	213.4	486.6	875.8	416.1	24.	353.				
<i>P. Oxides:</i>											
Carbon dioxide.....	44.01	31.0	304.2	547.5	87.8	72.9	1071.	0.468	29.2	94.0	1.51
Carbon monoxide.....	28.01	-140.	133.	240.	-220.	34.5	507.	0.301	18.8	93.1	1.49
Ethylene oxide.....	44.05	195.	468.	843.	383.	71.0	1043.	0.32	20.	138.	2.2
Nitrous oxide.....	44.02	36.5	309.7	557.4	97.7	71.7	1054.	0.457	28.5	96.3	1.54
Nitric oxide.....	30.01	-93.	180.	325.	-135.	64.	940.	0.52	32.	58.	0.93
Nitrogen peroxide.....	46.01	158.	431.	776.	316.	100.	1470.	0.56	35.	82.	1.3
Sulfur dioxide.....	64.06	157.5	430.7	775.2	315.5	77.8	1143.	0.524	32.7	122.	1.95

Sulfur trioxide.....	80.06	218.2	491.4	884.5	424.8	83.8	1232.	0.633	39.5	126.	2.02
Water.....	18.016	374.2	647.4	1165.3	705.6	218.3	3208.	0.32	20.	56.	0.90
<i>Q. Sulfur and sulfides:</i>											
Sulfur.....	32.06	1040.	1313.	2364.	1904.	116.	1705.				
Carbonyl sulfide.....	60.07	105.	378.	681.	221.	61.	896.				
Carbon disulfide.....	76.13	279.	552.	994.	534.	78.	1146.	0.44	27.	170.	2.8
Hydrogen selenide.....	81.22	138.	411.	740.	280.	88.	1293.				
Hydrogen sulfide.....	34.08	100.4	373.6	672.4	212.7	88.9	1306.	0.349	21.8	97.7	1.57
Methyl sulfide.....	62.13	229.9	503.1	905.5	445.8	54.6	802.	0.309	19.3	201.	3.22
Ethyl mercaptan.....	62.13	226.	499.	899.	439.	54.2	779.	0.300	18.7	207.	3.32
Ethyl sulfide.....	90.18	284.	557.	1003.	543.	39.1	575.	0.279	17.4	323.	5.17
<i>R. Miscellaneous compounds:</i>											
Phosphine.....	34.00	51.3	324.5	584.0	124.3	64.5	948.				
Phosphonium chloride.....	70.47	49.1	322.3	580.1	120.4	72.7	1068.				
Pyridine.....	79.10	344.2	617.4	1111.3	651.6	60.0	882.				
Silane.....	32.09	-3.5	269.7	485.4	25.7	47.8	702.				
Thiophene.....	84.13	317.	590.	1063.	603.	48.	705.				
Nitromethane.....	61.04	315.	588.	1059.	599.	62.3	915.	0.352	22.0	173.	2.77

* °K. = °C. + 273.16°.

°F. = (1.8)°C. + 32°.

°R. = °F. + 459.69°.

1 atm. = 14.69 p.s.i.a.

1 g./cc. = 62.43 lb./cu. ft.

6. Nitromethane

Griffin states that he used samples of "purified" nitromethane for the determinations. His results are reported as $315^{\circ}\text{C.} \pm 1^{\circ}$, 915 ± 15 p.s.i.a., 0.352 ± 0.004 g./cc.

VI. SUMMARY OF SELECTED VALUES

Table 22 summarizes the selected values for the critical temperature, critical pressure, critical density, and critical volume of the substances included in this review.

Undoubtedly omissions have occurred. The ever-growing chemical literature continues to record new and more accurate critical values for old compounds, as well as produce initial values for many compounds which have become of scientific and industrial importance. The authors will appreciate having omissions called to their attention and receiving reprints of papers reporting new critical data, in the hope that a later supplemental list can report all data known at that time.

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THE SPREADING OF LIQUID METALS ON SOLID SURFACES. THE SURFACE CHEMISTRY OF HIGH-ENERGY SUBSTANCES—*A. Bondi*, Shell Development Company, Emeryville, California.

THE REACTIONS OF ALIPHATIC ACID CHLORIDES—*Norman O. V. Sonntag*, Colgate-Palmolive-Peet Company, Jersey City, New Jersey.
