THE CRITICAL CONSTANTS OF ORGANIC SUBSTANCES

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CONTENTS

I. INTRODUCTION

In 1953 Kobe and Lynn[1] published a review article in this journal under the title of "Critical Properties of Elements and Compounds" which over the past 15 years has become recognized as a definitive study of critical constants by workers in the area of physical and thermodynamic properties of pure substances.

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(1) K. A. Kobe and R. E. Lynn, *Chem. Rev.*, **52**, 117 (1953).

Since that time, however, great progress has occurred in this area due to the availability of purer substances and the development of new and more precise methods for measurement of properties in the critical state. Therefore, it is timely to analyze and evaluate the newer data and prepare a comprehensive compilation on the critical constants of substances. To keep this review within bounds, we have restricted ourselves primarily to organic substances, except for key substances such as O_2, H_2O, CO, and CO_2. Furthermore, a study on the elements and inorganic compounds is now being carried out by the National Bureau of Standards Section of Thermochemistry in conjunction with their revision of "Selected Values of Chemical Thermodynamic Properties, NBS Circular 500." The first two parts of the NBS study have already appeared as NBS Technical Note 270-1, 1965, and NBS Technical Note 270-2, 1966. Where overlapping occurs on the 1 carbon atom compounds found in the revised NBS Circular 500, decisions were made on a single set of selected values acceptable to both groups of investigators.

As a sequel to Kobe and Lynn's[1] article, this review thoroughly covers the literature published in the period 1951 through December 1967. A concise summary of the principal topics covered in this review is as follows.

1. Theory and measurement. The important investigations which led to the "correct" definition of the critical temperature are discussed. A comparison is made of the various existing experimental procedures together with recommendations as to the "best" method or methods for obtaining the most precise and accurate values of the critical temperature, the critical pressure, and the critical volume or the critical density.
2. Evaluation and selection procedures.
3. Critical evaluation of experimental data and selection of "best" values. Numerical tables of all the available values for the critical constants for each substance of any class or closely related group of compounds are arranged in the following standard order: (i) key substances, *i.e.*, O_2, H_2O, etc.; (ii) saturated hydrocarbons; (iii) unsaturated hydrocarbons; (iv) aromatic hydrocarbons; (v) compounds of C, H, and O; (vi) halogen-containing compounds; (vii) sulfur-containing compounds; (viii) nitrogen-containing compounds; (ix) miscellaneous compounds.

Discussion and selection of the "best" values.

4. Correlation procedures for the prediction of t_c, P_c, and d_c or V_c.
5. A summary of selected experimental critical constants (Table XXXV).
6. Estimated uncertainties of the critical constants (Table XXXVI).
7. Glossary.

The final results of this review and compilation study may be summarized briefly. New or revised values for the critical constants have been discussed, selected, and recorded for approximately 267 organic compounds. Kobe and Lynn's[1] selected values have been retained for 62 substances because of the nonavailability of any current or more precise measurements. For ease of reference, all the recommended selected values for the critical constants of organic substances are given in the final summary table (Table XXXV).

II. THEORY AND MEASUREMENT

Classical thermodynamics defines the critical temperature as the temperature at which the density and composition of the coexisting phases become identical. For a pure fluid, this definition is formulated in terms of the derivatives of the Helmholtz energy

$$\left(\frac{\partial A}{\partial V}\right)_{T_c} < 0 \qquad \left(\frac{\partial^2 A}{\partial V^2}\right)_{T_c} = \left(\frac{\partial^3 A}{\partial V^3}\right)_{T_c} = 0 \qquad (1)$$

which in practice are usually expressed as

$$P > 0 \qquad \left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \qquad (2)$$

The phenomenon of mutual liquid–vapor solubility was first observed by Traube in 1907[2] who foreshadowed the modern definition of the critical temperature as "that temperature at which the two solubility curves intersect, and in which the liquid and the gas phases are mutually soluble in all ratios." Smoluchowski[3] and Einstein[4] worked out a theory of light scattering according to which the opalescence of a fluid reaches a maximum at the critical point.

The extent to which critical-temperature determinations comply with the above definitions will be considered. A full discussion of the critical phenomenon is outside the scope of this article, and only points pertinent to this review will be covered. Firstly, it is necessary to distinguish the following two kinds of experimental studies: (i) measurements made for the purpose of studying the nature of the critical phenomena and of examining the existing theories of the critical state, and (ii) the measurements made to determine precise and accurate values of the critical constants. In this review, our discussion is limited to part ii dealing with the determination of critical constants only. Naturally, studies of the critical phenomena *per se* are important in giving directions for improving the measurements of the critical constants,[5] for example, such studies clarifying which temperature in the critical region of liquids is the "true" critical temperature. In this connection the investigations of

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(2) I. Traube, *Z. Physik. Chem.* (Leipzig), **58**, 475 (1907).

(3) M. Smoluchowski, *Ann. Physik*, **25**, 205 (1908).

(4) A. Einstein, *ibid.*, **33**, 1275 (1910).

(5) M. S. Green and J. V. Sengers, "Critical Phenomena," National Bureau of Standards Miscellaneous Publication 273, U. S. Government Printing Office, Washington, D. C., 1966.

Maass and coworkers[6,7] and of Schneider and coworkers[8-13] are both historic and outstanding.

Mason, Naldrett, and Maass[6] and Naldrett and Maass[7] studied the coexistence curves of ethane and ethylene, respectively, in the critical temperature region. They observed that the coexistence curve has the classical parabolic shape up to a temperature T_s, namely, the temperature associated with disappearance of the meniscus in a bomb of critical filling which is vigorously shaken and with the reappearance of the meniscus on cooling. Since they believe that at this temperature a dispersion of liquid and vapor occurs and that the liquid still persists above this temperature, they accordingly called it the "critical dispersion temperature." They further showed that the meniscus disappears at the same temperature in a stationary bomb provided that sufficient time is allowed for equilibrium. Their observations in infrared light showed that exactly at T_s ($\pm 0.0001°$) the opalescence reaches a maximum, and, therefore, in accordance with the Einstein–Smoluchowski theory, this temperature should correspond to the critical temperature. Such a definition of T_s is also consistent with the one defined by Traube.[2] However, at this critical temperature (T_s) they find that the densities of the coexisting phases are not equal and that the coexistence curve is approximately flat along the density axis. From a comparison of the sudden formation of the meniscus in the critical fillings with its gradual reappearance in the liquid and vapor fillings, it was contended that the coexistence curve is mathematically flat across a range of critical fillings. They showed that the critical temperature, as ordinarily determined in a stationary bomb, cannot be accurately determined, whereas the critical temperature, T_s, can be determined precisely and without ambiguity when the bomb is shaken. On this basis they suggested that each substance be assigned two characteristic critical temperatures, namely, their recommended empirical temperature, T_s, and a second formal one, T_c, which fulfills the thermodynamic condition (eq 2).

Experimental work of the ultimate possible precision of Schneider and coworkers[8-12] showed that the flat top observed by the earlier investigators was due to the effects of gravity, and showed conclusively that the two critical temperatures T_s and T_c are identical if the gravitational effects are properly taken into consideration. Weinberger and Schneider[13] used highly pure xenon to study the effect of gravity on the shape of the coexistence curve by using bombs of different vertical lengths of 1.2 and 19.5 cm. The temperature was maintained to ±0.001° for periods of several hours and to ±0.0005° for shorter periods of time. All observations were made visually. Their results are plotted in Figure 1 as temperature *vs.* density for xenon. The effect of gravity is minimized considerably in the shorter bomb as seen from the shape of the coexistence curve, whereas the curve for the longer bomb resembles the ones obtained for ethane and ethylene by Maass and coworkers.[6,7] To further verify Weinberger and Schneider's[13] findings made in a visual observation bomb, Habgood and Schneider[9] decided to carry out a precision P–V–T study of xenon in the critical region using the same sample as used in their earlier studies. To clearly observe the effect of gravity on the measurements, they used bombs of different heights, 1 and 25 cm, and corrected their P–V–T measurements for the effect of hydrostatic pressure of the fluid by a successive approximation procedure. The absolute accuracy claimed in their measurements was as follows: temperature, ±0.002°; pressure, ±0.005 atm; and density, ±0.2%. The results are given in Figure 2 as a pressure–density plot. From this plot, the minimum slopes of the pressure–density isotherms *vs.* temperature were obtained which showed that the maximum temperature at zero slope, *i.e.*, T_c, was essentially identical with the temperature of the disappearance of the meniscus (T_s). The pressure–density graph, however, clearly shows that it is very difficult even for very precise P–V–T measurements to determine exactly which of the isotherms corresponds to T_c, and, therefore, it is preferable to determine the critical temperature visually.

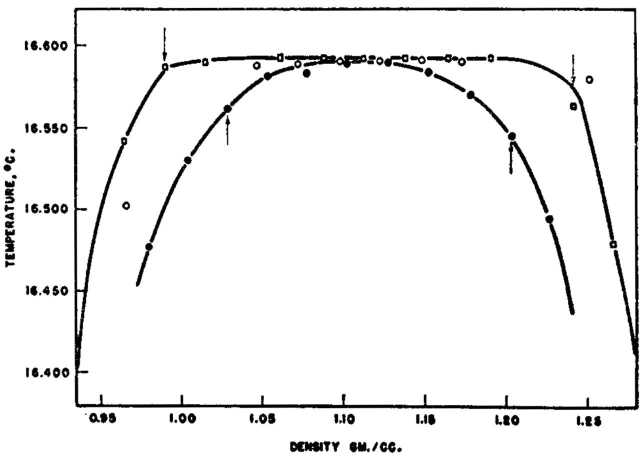

Figure 1.—Larger scale plot of coexistence curves of xenon: ○, □, vertical bomb; ●, horizontal bomb. Reproduced by permission of the National Research Council of Canada from *Can. J. Chem.*, **30,** 432 (1952).

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[6] J. G. Mason, S. N. Naldrett, and O. Maass, *Can. J. Res.*, **18B,** 103 (1940).

[7] S. N. Naldrett and O. Maass, *ibid.*, **18B,** 118 (1940).

[8] D. Atack and W. G. Schneider, *J. Phys. Chem.*, **55,** 532 (1951).

[9] H. W. Habgood and W. G. Schneider, *Can. J. Chem.*, **32,** 98, 164 (1954).

[10] K. E. MacCormack and W. G. Schneider, *ibid.*, **29,** 699 (1951).

[11] W. G. Schneider, "Changements de Phases," Compte rendu de la deuxième réunion annuele de la société de chimie physique, Paris, 1952, p 69.

[12] W. G. Schneider and H. W. Habgood, *J. Chem. Phys.*, **21,** 2080 (1953).

[13] M. A. Weinberger and W. G. Schneider, *Can. J. Chem.*, **30,** 422 (1952).

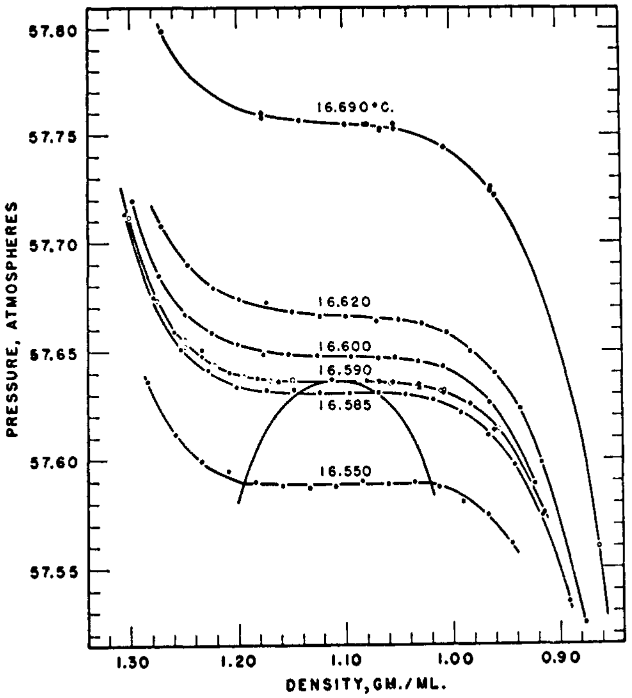

Figure 2.—Pressure-density isotherms of xenon in the immediate neighborhood of the critical point. Reproduced by permission of the National Research Council of Canada from *Can. J. Chem.*, **32**, 107 (1954).

On the basis of the above series of precise studies, the following comments and recommendations can be made regarding the determination of the critical constants T_c, P_c, and V_c or d_c.

A. CRITICAL TEMPERATURE, T_c

Whenever the vertical length of the bomb used is about 10 cm or larger, a flat portion on the coexistence curve as also on the P–V isotherm may appear, leading to a value for T_c which is too high when determined from the inflection on the P–V isotherm. In such cases the critical temperature, T_s, observed visually should be preferred over the critical temperature determined from the inflection of a P–V isotherm. If the precision of the T_c determination is low, *i.e.*, about ±0.1°, then it is immaterial how it is determined. In such less precise measurements there is also no need for very accurate filling of the tube in order to have the exact critical density, since the meniscus will move up or down and vanish at a height at which the local density is equal to the critical. However, for more precise measurements of T_c of the order of 0.01° or better, the following conditions must be met: the average density must be within 1% of the critical density; the tube must be short and well stirred; and the final heating must be carried out very slowly in an accurately controlled thermostat.

B. CRITICAL VOLUME, V_c

It has been well established by Schneider[11–13] and Rowlinson[14] that the law of rectilinear diameters of Cailletet and Mathias[15] is valid up to the nearest vicinity of T_c. This law can be applied with confidence to determine d_c even if the density measurements are a few degrees below T_c and have to be extrapolated up to the critical temperature. This procedure is recommended for all determinations of the critical density or critical volume.

C. CRITICAL PRESSURE, P_c

Once T_c is determined visually and the corresponding d_c calculated using the law of rectilinear diameters, then the P_c is obtained directly at the observed T, or from the P–V isotherm. However, in more precise determinations of P_c, *i.e.*, to ±0.02 atm, corrections for hydrostatic and gravitational effects must be made according to the procedures of Schneider, *et al.* Similar recommendations also apply to the determination of critical constants of mixtures.

A few additional comments may be appropriate regarding kinds of apparatus. Experimental methods which enable visual observation of T_c, the determination of d_c by the law of rectilinear diameters, and subsequently the direct determination of the corresponding P_c should be preferred over other methods for reasons mentioned earlier. The equipment should also be suitable for studies on mixtures since the determination of critical constants for mixtures is equally important.

The apparatus used by Ambrose and coworkers[16–19] fulfills most of the above conditions except that it is not suitable for measurements on mixtures. In this method only the upper part of the experimental tube is maintained at an elevated temperature, while the lower part of the tube is kept at lower temperatures. In this way, the liquid mercury is kept out of the heated area; however, part of the liquid under study is then at a lower temperature. This method, while perfectly acceptable for studies on pure liquids, is not suitable for mixtures since temperature gradients along the fluid cause concentration gradients to develop, and thus the critical pressures measured correspond to the wrong composition.

Douslin and coworkers at the U. S. Bureau of Mines have carried out highly precise P–V–T measurements using the Beattie-type apparatus.[20–24] The only disad-

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(14) J. S. Rowlinson, "Liquids and Liquid Mixtures," Academic Press Inc., New York, N. Y., 1959, pp 88–109.

(15) L. Cailletet and E. Mathias, *Compt. Rend.*, **102**, 1202 (1886).

(16) D. Ambrose, B. E. Broderick, and R. Townsend, *J. Chem. Soc.*, *A*, 663 (1967).

(17) D. Ambrose, J. D. Cox, and R. Townsend, *Trans. Faraday Soc.*, **56**, 1452 (1960).

(18) D. Ambrose and D. G. Grant, *ibid.*, **53**, 771 (1957).

(19) D. Ambrose and R. Townsend, *J. Chem. Soc.*, 3614 (1963).

(20) D. R. Douslin, R. H. Harrison, and R. T. Moore, *J. Phys. Chem.*, **71**, 3477 (1967).

(21) D. R. Douslin, R. H. Harrison, R. T. Moore, and J. P. McCullough, *J. Chem. Phys.*, **35**, 1357 (1961).

(22) D. R. Douslin, R. H. Harrison, R. T. Moore, and J. P. McCullough, *J. Chem. Eng. Data*, **9**, 358 (1964).

vantage of this method is that T_c cannot be observed visually and must be determined from the inflection in the P–V isotherm.

Of the variety of kinds of equipment used in study of critical constants, it appears that only Kay's equipment[25–28] seems to fulfill all the conditions mentioned earlier for precise measurements of the critical constants of the pure components and of mixtures and is to be preferred over other kinds of equipment used in current work.

Since liquid mercury is commonly used as a pressure-transmitting medium in P–V–T equipment designed for critical constant determinations, it has been customary to correct the critical pressure value for the presence of mercury by simply subtracting the vapor pressure of mercury. This is done whenever the mercury–sample interface is in a heated zone at a temperature of 100° or above, where the vapor pressure of Hg becomes significant. Jepson and Rowlinson[29] have questioned this ideal gas correction procedure for mercury on studies of low-boiling paraffins, such as propane and butane, indicating that the error increases as the temperature or molar density of the sample increases. To test this contention, Kay[30,31] has recently determined the t_c and P_c of a high-boiling and low-density paraffin, *n*-decane, with the Hg–hydrocarbon interface both at room temperature and in the heated zone at the critical t_c (344.3°) for both stirred and *not* stirred samples. The values of t_c for both samples were only 0.06° *higher* when the Hg–decane interface was in the heated zone. This seems to verify the fact that the mercury effect on the critical temperature may be negligible which is also supported by t_c values determined for hydrocarbons in a sealed bomb and in an expansion apparatus where the values agree within the accuracy of the measurements (±0.05°). For the P_c values, Kay found, after applying the ideal gas correction for the mercury vapor, that the values measured in the heated zone were 0.16 (stirred sample) to 0.29 atm (unstirred) *lower* than those at room temperature. This difference of 0.13 atm he ascribed to failure to reach true equilibrium. In a second study of the critical pressure of *o*-xylene, Kay found the difference in the P_c values, for the Hg–sample interface outside and inside the heated zone, to be equal to the vapor pressure of Hg at the given temperature (357.1°) to within the experimental error of ±0.03 atm. On the basis of these studies by Kay, it appears advisable to continue the usual practice of correcting for the mercury effect by substracting the vapor pressure of pure mercury vapor at the sample temperature from the observed critical pressure measurements.

III. EVALUATION AND SELECTION PROCEDURES

In spite of the experience of the authors in this area, we are not aware of any recognized sets of principles universally acceptable by qualified experts for the critical evaluation and selection of "best" numerical values for properties of substances, and hopefully, within limits, also the correct values. In the preparation of this review, we have closely adhered to the philosophy and recommendations set down by Rossini[32] and Bridgman.[33] Some of the more pertinent steps in our analysis, evaluation, and selection of values will be described.

At the onset we must take stock of the nature of the parameters to be analyzed, namely, the so-called critical constants or properties of the critical point. Certain physical constants or properties can be subjected to finer and almost indefinite precision of measurement subject only to the Heisenberg uncertainty relation, or some other such limitation of theory. Other properties, however, because of their nature and the conditions of measurement, are on the end of applicability of equilibrium thermodynamics so that certain parameters are not controllable, resulting in blurred-out averages and set limits on attainable precision. The critical constants of substances appear to fall into this category of properties. It is perhaps more proper to speak of a *critical region* instead of a *critical point* within which rapid fluctuations of small-scale density occur, characterized by a variety of relaxation times. It would appear possible on the basis of statistical theory to calculate at least upper limits on the precision of measurement of t_c and P_c values for certain kinds of simple and complex chemical substances.

The data reported in this review were obtained, in a large majority of the cases, from the original literature sources. Only in the case of obscure publications was it necessary to wholly depend on *Chemical Abstracts.*

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(23) D. R. Douslin, R. T. Moore, J. P. Dawson, and G. Waddington, *J. Am. Chem. Soc.*, **80**, 2031 (1958).

(24) D. R. Douslin, R. T. Moore, and G. Waddington, *J. Phys. Chem.*, **63**, 1959 (1959).

(25) W. B. Kay, *J. Am. Chem. Soc.*, **68**, 1336 (1946).

(26) W. B. Kay, *ibid.*, **69**, 1273 (1947).

(27) W. B. Kay and W. E. Donham, *Chem. Eng. Sci.*, **4**, 1 (1955).

(28) J. H. McMicking and W. B. Kay, *Proc. Am. Petrol. Inst.*, **45**, (III), 75 (1965).

(29) W. B. Jepson and J. S. Rowlinson, *J. Chem. Phys.*, **23**, 1599 (1955).

(30) W. B. Kay, The Ohio State University, personal communication, 1968.

(31) W. B. Kay and D. Hissong, API Annual Report on Critical Properties of Hydrocarbon Mixtures, The Ohio State University, Columbus, Ohio, Aug 1967.

(32) F. D. Rossini, "Preparation of Continuing Critical Tables of Physico-Chemical Data for Basic Research," Technical Report of the API Research Project 44 and the MCA Research Project, Thermodynamics Research Center, Texas A&M University, College Station, Texas, 1958.

(33) P. W. Bridgman, *Proc. Natl. Acad. Sci. U. S.*, **46**, 1394 (1960).

In such cases the details regarding purity of the sample and the equipment used in the investigation were seldom available. The precision of such data was primarily ascertained from the reputation of the investigators. In some instances the unpublished or prepublication data were obtained through personal communications.

In the analysis, the work of each investigator was carefully scrutinized as to the precision and accuracy of the actual measurements of the critical constants and to the identification of the units of measurement. Particular attention was given to the method of calibration of the measuring instruments. The source and/or method of synthesis of the sample as also the number and kinds of purification procedures employed were carefully noted in order to ascertain the purity of the substance.[33a] In many instances, especially in the case of older data, no mention of source or of purity of the sample was reported. Since the presence of impurities in a sample may make the measured value of the property either greater or smaller, the identification of the amount and kind of impurity, in some instances, simplifies the evaluation procedure. Estimations of purity of the sample were made in many cases by comparing their simple physical properties such as boiling point, refractive index, density, etc., with well-established selected literature values.[34-36] Close attention was also paid to the method of measurement of the critical constants, since entirely different results may be obtained on the same substance because of the differences in apparatus and in methods of observation, and in analysis of the empirical data.

For the more common substances, that is, simple inorganic and organic molecules, several sets of numerical values were always available. Initial screening on the basis of purity criteria usually eliminated some of the values. In turn, other values were given little or zero weight on the basis of inadequate reliability of the physical measurements themselves. Furthermore, the reliability of a specific set of values was enhanced if a certain investigator included in his studies a reference compound as a calibration standard for which quite accurate literature values were known. If the agreement proved satisfactory, this particular investigation was weighted more heavily than others.

In a few propitious cases, the selection of the "best" value for a given compound was made not for one individual compound alone but for a group of structurally related compounds. Through such a procedure, empirical and semiempirical correlation procedures developed for closely related chemical substances can be effectively employed as an additional criteria in the evaluation and final selection of the data. As examples, we can cite the analysis of data on *n*-alkanes, 1-alkenes, isomeric alkanes, and *n*-alkylbenzenes.

Throughout the main body of the review, specific examples of our selection and evaluation procedures are given in all detailed discussions for each compound or group of compounds. In view of the extensive and continuing work carried out by D. Ambrose and his colleagues at the National Physical Laboratory at Teddington, England, some additional comments, which demonstrate specific points regarding the reliability and selection of their values, are in order. During the past 12 years, Dr. Ambrose and his group have carried out an impressive number of highly reliable measurements of the critical temperatures of some 80 different organic compounds. In some instances, the values of P_c and d_c were also reported. The importance of such continuing measurements by the same group of highly qualified experts in the same laboratory over a period of years cannot be overemphasized. Another important facet of their work was to include t_c measurements on several important organic compounds whose values date back to 1927, or even earlier. These data are immeasurably important for comparison of change in the international practical temperature scale over a period of some 40–50 years, as also for a fruitful comparison of newer methods of purification. In general, we have preferred Ambrose's values whenever available, since critical temperatures determined visually, other things being equal, are to be preferred over values determined from the inflection of the P–V isotherm. In instances where no decisions could be made between two or more seemingly equally reliable and independent determinations, a mean of the values was selected as the "best" value.

IV. CRITICAL EVALUATION OF EXPERIMENTAL DATA AND SELECTION OF BEST VALUES

The available literature data on critical constants reported in the main body of this review have been obtained by a variety of experimental methods and procedures. To simplify the tabulation of these methods, we have elected to follow the same system used by Kobe and Lynn[1] based on a key for ease of reference as tabulated below.

(33a) A. Kreglewski, "The Characterization of Chemical Purity: Vapor Pressure and Boiling Point Measurements," Joint Report of Investigation of API Research Project 44 and MCA Research Project, Thermodynamics Research Center, Texas A&M University, College Station, Texas, May 1966.

(34) "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A&M University, College Station, Texas (loose-leaf data sheets, extant 1968).

(35) "Selected Values of Properties of Chemical Compounds," Thermodynamics Research Center Data Project, Thermodynamics Research Center, Texas A&M University, College Station, Texas (loose-leaf data sheets, extant 1968).

(36) J. Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950.

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: $(\partial P/\partial V)_T = 0$
6	Disturbance of a balanced tube
7	Method of Ipatieff and Monroe (rotating bomb)
8	Method of Cailletet and Colardeau
9	Plot of enthalpy *vs.* 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 *vs.* pressure
19	Law of rectilinear diameters

A. SOME KEY SUBSTANCES (TABLE I)[37–51]

1. *Oxygen*

Jones and Rowlinson[42] obtained oxygen of 99.5 mole % purity supplied by the British Oxygen Co. The gas was passed over tubes packed with phosphorus pentoxide. Mass spectrographic analysis showed the presence of 0.5% argon in the purified sample. The temperature was measured by a copper–constantan thermocouple with four pairs of junctions. The reference junctions were kept at 0° by means of frozen distilled water in a dewar vessel. The sensitivity of the thermocouples was 0.01°. They were calibrated at the triple points of purified carbon dioxide and of five hydrocarbons of high purity supplied by the National Chemical Laboratory, Teddington, U. K. The reproducibility of the measurements of the t_c was 0.05°.

Kobe and Lynn[1] selected Hoge's[41] values for the critical temperature and the critical pressure. An average of the values of Hoge,[41] of Mathias,[39] and of Mathias and Onnes[40] was selected for the critical density.

The difference between Hoge's value of t_c, determined from the P–V isotherm, and that of Jones and Rowlinson, observed visually, is about 0.23° with the latter value being the higher. The presence of 0.5% argon in the sample used by Jones and Rowlinson will make a difference of 0.03° in their value of 155.0°K (-118.1_5°C). Hence the corrected value for T_c is 155.03°K (-118.1_2°C). Hoge used a highly purified sample of O_2 with an estimated maximum impurity of 4×10^{-5}%. Hoge measured the temperature by a well-calibrated capsule-type Pt resistance thermometer. Measurement of P–V isotherms at 154.187_5, 154.580_3, and 154.759_8°K were made to determine the t_c, P_c, and the vapor pressures immediately below the critical point. The critical temperature was estimated by comparing the shapes of the P–V isotherms of O_2 with the accurate isotherms covering the critical region of CO_2 determined by Michels, Blaisse, and Michels.[37] From the comparison, 154.78 ± 0.03°K was estimated for the T_c of O_2. The critical pressure was obtained at 154.78°K from the vapor pressure data. The difference of about 0.2° in the t_c of Hoge and of Jones and Rowlinson is beyond the experimental uncertainty of both investigations and may be due to actual differences in the temperature measurement or to the purity of the sample of Jones and Rowlinson.

On the basis of purity of sample and precision of measurement, Hoge's values of t_c and P_c were selected with the t_c rounded off to four significant figures. This selection for t_c is the same as Kobe and Lynn's selection in 1953.[1]

Hoge[41] deduced the critical density from the isotherm measurements in the critical region. Hoge commented that by taking into account the uncertainty in the measurement of the volume containing the known mass of O_2, the computed critical density could be raised from 0.38 to about 0.44/cm.^{3} Since Mathias and Onnes determined the d_c by the application of the law of rectilinear diameters, this value is probably more accurate than the value of Hoge. For this reason, the d_c value of Mathias and Onnes,[40] rounded off to two significant figures because of the scatter of the literature values, was selected as the most probable value.

2. *Water*

Kobe and Lynn selected the critical constants of Osborne, Stimson, and Ginnings.[43] Since that time, at the Sixth International Conference on the Properties of Steam in Oct 1963, New York, N. Y., the new "International Skeleton Tables" of the thermodynamic properties of water were adopted. The following critical constants were recommended for water: $t_c = 374.15 \pm 0.1°$; $P_c = 221.2 \pm 0.1$ bars (218.3 ± 0.1 atm); and $V_c = 3.17 \pm 0.15$ cm^3/g ($d_c = 0.315 \pm 0.015$ g/cm^3); these values are also adopted for this review.

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(37) A. Michels, B. Blaisse, and C. Michels, *Proc. Roy. Soc.* (London), **A160**, 358 (1937).

(38) R. H. Wentorf, *J. Chem. Phys.*, **24**, 607 (1956).

(39) E. Mathias, "Le point critiques des corps purs," Paris, 1904.

(40) E. Mathias and H. Kamerlingh-Onnes, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **13**, 939 (1911).

(41) H. J. Hoge, *J. Res. Natl. Bur. Std.*, **44**, 321 (1950).

(42) L. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59**, 1702 (1963).

(43) N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Res. Natl. Bur. Std.*, **23**, 261 (1939).

(44) E. Mathias and C. A. Crommelin, *Ann. Phys.*, **5**, 137 (1936).

(45) H. T. Kennedy and C. H. Meyers, *Am. Soc. Heating, Refrig. Aircond. Engrs. J.*, **15**, 125 (1928).

(46) C. H. Meyers, and H. Van Dusen, *J. Res. Natl. Bur. Std.*, **10**, 381 (1933).

(47) D. Cook, *Trans. Faraday Soc.*, **49**, 716 (1953).

(48) H. L. Lorentzen, *Acta Chem. Scand.*, **7**, 1335 (1953).

(49) H. B. Palmer, *J. Chem. Phys.*, **22**, 625 (1954).

(50) E. Schmidt and W. Thomas, *Forsch. Gebiete Ingenieurw.*, **20B**, 161 (1954).

(51) D. Ambrose, *Trans. Faraday Soc.*, **52**, 772 (1956).

TABLE I
SOME KEY SUBSTANCES

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method[a]	Ref
1. Oxygen						
1904			0.400	Mathias	?	39
1911			0.4299	Mathias and Onnes	19	40
1950	−118.38	50.14	0.38	Hoge	5	41
1963	−118.15			Jones and Rowlinson	1	42
1953	−118.4	50.1	0.41	Kobe and Lynn		1
Selected value	−118.4	50.14	0.43			
2. Water						
1937	374.15	218.39	0.32	Osborne, Stimson, and Ginnings	5	43
1953	374.2	218.3	0.32	Kobe and Lynn		1
Selected value	374.15	218.3	0.315			
3. Carbon Monoxide						
1936	−140.23	34.53	0.3010	Mathias and Crommelin	1, 19	44
1963	−140.2			Jones and Rowlinson	1	42
1953	−140	34.5	0.301	Kobe and Lynn		1
Selected value	−140.23	34.53	0.301			
4. Carbon Dioxide						
1928	30.96			Kennedy and Meyers	1	45
1933	31.10	72.95		Meyers and Van Dusen	1, 16	46
1937	31.04	72.85	0.468	Michels, Blaisse, and Michels	5, 19	37
1953		72.6		Cook	16	47
1953	31.04			Lorentzen		48
1954	31.08			Palmer	1	49
1954	31.01	72.78	0.463	Schmidt and Thomas	1, 16	50
1956	31.01			Ambrose	1	51
1956	31.045	72.839	0.474	Wentorf	1	38
1953	31.0	72.9	0.468	Kobe and Lynn		1
Selected value	31.04	72.85	0.468			

[a] For key to method, see text, p 665.

3. Carbon Monoxide

Jones and Rowlinson obtained a 99 mole % pure sample from the Imperial Chemical Industries Ltd. The principal impurity, carbon dioxide, was removed by passing the gas over tubes packed with potassium hydroxide. Mass spectrographic analysis showed that the CO did not contain any of the main constituents of air as impurities greater than 0.1%. The details of the measurement technique are discussed under methane. The uncertainty in t_c was ±0.05°.

This recent value of Jones and Rowlinson for t_c agrees with the older value of Mathias and Crommelin[44] within the experimental uncertainty in the measurement of t_c. On this basis the critical constants of Mathias and Crommelin[44] were selected. The same values were recommended by Kobe and Lynn and more recently by Din.[52]

4. Carbon Dioxide

Michels, Blaisse, and Michels[37] purified their sample by a three-stage distillation and found that the vapor pressure during the condensation did not vary by more than 1/20,000, indicating only minute quantities of impurities. Temperatures were measured with mercury thermometers in units of 0.01° and calibrated by the Physikalisch-Technische-Reichsanstalt (PTR) at Berlin. The t_c value of 31.03 ± 0.01° was determined from the plot of $(\partial P/\partial V)_{T,\mathrm{minimum}}$ against temperature, T. The P_c value of 72.835 atm was obtained from the pressures of the inflection points plotted as a function of P. Extrapolation of the vapor pressure line yielded a value of 72.825 atm for P_c. The law of rectilinear diameters was used to calculate d_c which was reported in amagat units. This was converted to g/cm³ by multiplying by the density at 0° and at 1 atm, or 1.9770×10^{-3} g/cm³. The values of critical constants reported in the tables are slightly different from the experimental values and are those recommended by Michels, Blaisse, and Michels.

Cook prepared CO_2 from analytical grade $NaHCO_3$. After evacuation of $NaHCO_3$ for 24 hr with a mercury diffusion pump, the $NaHCO_3$ was gently heated and

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(52) F. Din, Ed., "Thermodynamic Functions of Gases," Vol. 1, Butterworth & Co. Ltd., London, 1956.

the CO_2 collected in a trap cooled in liquid nitrogen. The H_2O formed at the same time was removed by passing through a trap cooled by solid CO_2, then through a P_2O_5 drying tube, and finally through another trap cooled with Dry Ice. The increase in pressure on isothermal compression between the dew point and the bubble point was 0.03 atm at 25°. The vapor pressure of CO_2 thus prepared agreed within a few hundredths of an atmosphere with the results of Michels, Blaisse, and Michels. The P_c value was calculated by extrapolating the vapor pressure curve to T_c using a log P *vs.* $1/T$ plot.

Lorentzen[48] prepared CO_2 by dripping sulfuric acid into a solution of potassium bicarbonate. The gas was dried by passing through four U-tubes containing concentrated sulfuric acid and glass beads with the last tube kept at solid CO_2 temperatures. The purity of the sample was estimated to be better than 99.999 mole %. The thermostat temperature was adjusted to ±0.001°. The isotherms in the critical region were determined by observing the mass distribution in vertical glass tubes.

Palmer prepared CO_2 from reagent grade sulfuric acid and sodium carbonate. The liberated gas was bubbled through several sulfuric acid traps and passed over a Dry Ice trap before being collected. Analysis by absorption in 6 N KOH showed it to be about 99.997 mole % pure. The impurity of 0.003 was suspected to be air. Temperatures were measured by means of five copper–constantan thermocouples calibrated against a Leeds and Northrup Pt resistance thermometer in turn calibrated at the NBS. The absolute accuracy of measurement with the thermocouples was approximately ±0.01°. The t_c reported was the average of the disappearance and the reappearance temperatures of 31.08 and 31.09°. The uncertainty in t_c was ±0.02°.

Schmidt and Thomas[50] prepared CO_2 by reacting Na_2CO_3 with H_2SO_4. The gas was dried repeatedly by passing it through four columns packed with calcium chloride, silica gel, and phosphorus pentoxide. It was then cooled in liquid nitrogen. This treatment was repeatedly carried out to remove the noncondensable impurities. Temperature were measured with three manganin–constantan thermocouples, calibrated against a Pt resistance thermometer. The reproducibility of temperature measurement between 20 and 35° using the thermocouples was about ±0.015° on the International Practical Temperature Scale. The pressures were measured using a dead-weight gauge.

The carbon dioxide used by Wentorf[38] was generated from reagent grade sulfuric acid and boiled sodium bicarbonate solution, dried, and condensed into a steel storage cylinder. By absorbing 500 ml of the gas in 6 N KOH, the impurities were estimated to be 0.003%. This CO_2 gave a vapor pressure change of less than 1 mm between 10% liquid and 90% liquid at 16, 23, and 30°. Temperatures were measured with a Pt resistance thermometer. Pressures were measured with a relative error of 1 mm on a deadweight gauge. The gauge was calibrated using the vapor pressure data of carbon dioxide of Meyers and Van Dusen.[46] The critical constants calculated from the P–V plot with the conditions $(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0$ were $t_c = 31.06°$, $P_c = 72.870$ atm, and $d_c = 0.48$ g/cm^3.

Ambrose used commercial solid carbon dioxide of high purity as a starting material. This contained traces of air, water, and oil. The CO_2 gas was prepared from it by sublimation *in vacuo* several times after an initial passage through phosphorus pentoxide. Some of the product was passed into 10% potassium hydroxide solution. This treatment brought down the insolubles in the gas to about one part in 10,000 indicating that the resulting gas was of very high purity. The individual tubes filled with CO_2 gave values for the appearance and disappearance temperatures between 0.002 and 0.009°. There was a significant difference between the tubes depending on size of sample. The results covered a range of 0.07° with the largest tube giving the lowest value. The uncertainty in t_c was ±0.03°.

Kobe and Lynn[1] selected an average of Michels, Blaisse, and Michels[37] and Kennedy and Meyers'[45] values for t_c, Michels, Blaisse, and Michels and Meyers and Van Dusen's[46] value for P_c, and Michels, Blaisse, and Michels'[37] value for d_c.

It is significant to note that all the newer values for t_c differ from Michels' value by only ±0.04°. Such an agreement between the different investigators enables one to select the "best" value for t_c with much confidence. The value selected for t_c is the average of the values reported in Table I assigning zero weighting factors to the values of Kennedy and Meyers[45] and Meyers and Van Dusen.[46] Michels' values of P_c and d_c were selected as the most reliable, since P_c was obtained from the P–V–T measurements in the critical region and d_c was calculated using the law of rectilinear diameters. Cook's value for P_c is lower than the other literature values. Excellent agreement exists between Wentorf's values of t_c and P_c and those of Michels, Blaisse, and Michels; however, Wentorf's d_c value is considerably higher, since it was obtained from the P–V isotherm. Our selected values for t_c, P_c, and d_c agree satisfactorily with Prausnitz's[53] recommendations of $t_c = 31.04°$ and $P_c = 72.9$ atm and with Ambrose and McGlashan's[53a] recommendations of $t_c = 31.05°$, $P_c = 72.83$ atm, and $d_c = 0.468$ g/cm^3.

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(53) J. M. Prausnitz, "Solubility of Solids in Dense Gases," National Bureau of Standards Technical Note No. 316, U. S. Government Printing Office, Washington, D. C., 1965.

(53a) D. Ambrose and M. L. McGlashan, "Tables of Physical and Chemical Constants," 13th ed, G. W. C. Kaye and T. H. Laby, Ed., John Wiley and Sons, Inc., New York, N. Y., 1966, pp 151–152.

B. SATURATED HYDROCARBONS

1. *Alkanes* (*Paraffins*) (*Table II*)

a. Methane[54–59]

Bloomer and Parent[58] used "pure grade" (99 mole % minimum) methane obtained from the Phillips Petroleum Co. The sample was distilled in a Podbielniak low-temperature fractionating column, and the distillate was collected as a solid in a stainless-steel bomb immersed in liquid nitrogen. The difference between the bubble and the dew-point pressures of the sample was found to be of the order of 0.03 atm for 11 runs in the temperature range −150 to −80°. The mass spectrometric analysis showed that the sample was 99.97% methane and 0.03% nitrogen. Temperature was measured by a triple-junction copper–constantan thermocouple and a Type K-2 Leeds and Northrup potentiometer. The thermocouple was calibrated with a Pt resistance thermometer calibrated at the National Bureau of Standards. The calibration of the resistance thermometer was accurate to ±0.03° down to −150° and ±0.06° from −150 to −200°. The pressure was measured with a 70-atm capacity dead-weight gauge from the Refinery Supply Co. Pressure balance between the equilibrium cell and the gauge was through a mercury manometer. All pertinent corrections were made to the dead-weight gauge pressure readings. The uncertainties in t_c and P_c were ±0.06° and ±0.2 atm, respectively. The equipment used was checked by determining the vapor pressure data on methane which values were found to be in excellent agreement with reliable literature data.[34]

A NBS methane sample of 99.93 mole % was used by Hestermans and White[59] in their studies. This sample was redistilled to a final purity of 99.96 mole % with N_2 as the major impurity. Pressures above 2.5 atm were measured by a calibrated, modified MIT type, dead-weight gauge with a precision of 1 part in 30,000. Very precise measurements of vapor pressure–boiling point data were carried out in the temperature range of −160 to −83°. The critical pressure was obtained by extrapolation of the experimental vapor pressures over a 1° range to the critical temperature of −82.60° as recommended by Bloomer and Parent.[58]

Jones and Rowlinson[42] used methane of 99.98 mole % purity supplied in bulbs by the National Chemical Laboratory. Temperatures were measured with a four-junction copper–constantan thermocouple with a sensitivity of 0.01°. Calibrations carried out at the triple point of the purified carbon dioxide samples showed the depression of the freezing point was less than 0.02°, further confirming the high purity of the sample.

Kobe and Lynn[1] selected t_c and P_c of Keyes, Taylor, and Smith,[55] and their selected d_c value was taken as the mean of the values of Cardoso[54] and of Keyes, Taylor, and Smith.[55]

The literature values for the t_c of methane fall into three groups: −82.85° of Cardoso[54] and of Jones and Rowlinson;[42] −82.12° of Keyes, Taylor, and Smith[55] and of Wiebe and Brevoort;[56] −82.55° of Corcoran, Bowles, Sage, and Lacey[57] and of Bloomer and Parent.[58] It is extremely difficult in such cases to recommend the "best" value for the t_c. As Bloomer and Parent and Jones and Rowlinson carried out very precise work on samples of high purity, the difference between these two t_c values is difficult to understand. The difference of 0.25° may be due to variation in thermometry used by these investigators. The sample used by Keyes, Taylor, and Smith contained impurities of less than 1 part in 500. The melting point of methane used by Wiebe and Brevoort was −182.9° as compared to the literature value of −182.474°.[34] This depression in the freezing point amounts to 0.5% impurity.

Bloomer and Parents' value of −82.60° is selected, and an uncertainty of ±0.05° is assigned to this value. This value of −82.60° is substantiated by the value of −82.55° for t_c selected by Armstrong, Brickwedde, and Scott[59a] from the critical review of the literature. The agreement between the P_c values of Hestermans and White[59] and of Bloomer and Parent[58] is excellent. These two measurements represent very precise values for P_c of methane, and an average of these two values is selected. The available d_c values agree satisfactorily excepting that of Corcoran, Bowles, Sage, and Lacey.[57] Hence an average of the values of Cardoso, of Keyes, Taylor, and Smith, and of Bloomer and Parent is selected as the most reliable value.

b. Ethane[60–63]

Kay and Brice[62] used a sample furnished by the Phillips Petroleum Co. which was stated to be 99.9 mole % ethane. It was further purified by repeated distillation at low temperature and under high vacuum. The initial fraction and the residue was discarded and the middle fraction retained for each succeeding dis-

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(54) E. Cardoso, *Arch. Sci.* (Geneva), **36,** 97 (1913).

(55) F. G. Keyes, R. S. Taylor, and L. B. Smith, *J. Math. Phys.*, **1,** 211 (1922).

(56) R. Wiebe and M. J. Brevoort, *J. Am. Chem. Soc.*, **52,** 622 (1930).

(57) W. H. Corcoran, R. R. Bowles, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **37,** 825 (1945).

(58) O. T. Bloomer and J. D. Parent, *Inst. Gas Technol., Res. Bull.*, No. 17 (1952).

(59) P. Hestermans and D. White, *J. Phys. Chem.*, **65,** 362 (1961).

(59a) G. T. Armstrong, F. G. Brickwedde, and R. B. Scott, *J. Res. Natl. Bur. Std.*, **55,** 39 (1955).

(60) A. Prins, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **17,** 1095 (1915).

(61) J. A. Beattie, G. J. Su, and G. L. Simard, *J. Am. Chem. Soc.*, **61,** 924 (1939).

(62) W. B. Kay and D. B. Brice, *Ind. Eng. Chem.*, **45,** 615 (1953).

(63) S. G. Whiteway and S. G. Mason, *Can. J. Chem.*, **31,** 569 (1953).

tillation. High purity of the sample was indicated by the fact that the pressure change between the bubble and dew points at constant temperature amounted to only 0.012 atm. Kay and Brice studied the P–V–T–X behavior of ethane–hydrogen sulfide mixtures, but they did not describe the method for obtaining the critical constants of the pure components. We have assumed that the critical temperature was observed visually and the critical pressure determined simultaneously at this critical temperature.

Phillips Petroleum Co. Research Grade ethane of 99.75 mole % purity was used by Whiteway and Mason.[63] Temperatures were measured to a precision ±0.001° by a Beckmann thermometer calibrated against a Pt resistance thermometer to an absolute accuracy of ±0.01°. Using this system and the high-pressure filling method, a flat top at 32.23° was obtained over a considerable density range. Before the weight of the material could be determined, a leak developed in the metal tubing and the filling escaped. Although the procedure was repeated under the same conditions with a second filling, a flat top at 32.167° was obtained.

Palmer used Research Grade ethane of certified purity of 100%, obtained from the Phillips Petroleum Co. He studied the critical region using a Schlieren optical system. The temperature along the height of the cell was measured by means of five copper–constantan thermocouples located in wells which extended into the cell block to within $^3/_{16}$ in. of the cell wall. A Rubicon Type B potentiometer and a Rubicon wall galvanometer having high sensitivity were used to measure temperatures. Each of the thermocouples was calibrated against a Leeds and Northrup NBS calibrated Pt resistance thermometer. The absolute accuracy of measurement with the thermocouples was approximately ±0.01° with an available precision of about ±0.01° in the measurement of temperature differences. The cell temperature could be kept constant to about ±0.01° over periods of several hours. The criterion used for the existence of a meniscus was the ability to distinguish reflection of light from a surface within the fluid. The lowest temperature at which a reflection could no longer be distinguished was taken to be the temperature of meniscus disappearance. The meniscus disappearance temperature obtained was 32.315 ± 0.02° while the meniscus appearance temperature was 32.325 ± 0.02°. Thus, the temperatures of disappearance and reappearance of the meniscus coincided within the experimental uncertainty.

Schmidt and Thomas[50] obtained a cylinder of ethane gas from Badischen Anilin & Soda-Fabrik Co. The cell was initially purged with ethane many times. The test gas was passed through liquid nitrogen and then pumped into the cell. This procedure was repeatedly carried out to remove dissolved gases. The purity of the sample used was not stated. The temperature measurements were carried out by using three manganin–constantan thermocouples which were calibrated against a platinum resistance thermometer. The resistance thermometer was kept at 500° for 12 hr, and the resistances were checked at the ice point, steam point, and sulfur point. The reproducibility of temperature measurement between 20 and 35°, using the thermocouples, was about ±0.015° on the international scale. The pressure was measured using a dead-weight gauge.

Kobe and Lynn[1] selected for the critical temperature an average of the values reported by Beattie, Su, and Simard,[61] Mason, Naldrett, and Maass,[6] and Prins.[60] The critical pressure and critical density values were taken from Beattie, Su, and Simard.[61]

The value of the critical temperature reported by Kay and Brice[62] is lower than most of the other experimental determinations. The difference between the two values reported by Whiteway and Mason[63] and that found by Palmer[49] and by Prins[60] seems too large to be accounted for by differences in the technique of observing the meniscus. Therefore, an average of the values reported by Prins,[60] Beattie, Su, and Simard,[61] Mason, Naldrett, and Maass,[6] Palmer,[49] and Schmidt and Thomas[50] is selected for the critical temperature. Kay and Brice did not say how their value of the critical pressure was obtained but it is believed to have been measured simultaneously at t_c. Therefore an average of Beattie, Su, and Simard's value and that of Kay and Brice is selected for P_c. The d_c of Beattie, Su, and Simard is selected.

c. Propane[64–68]

Kay and Rambosek[67] used propane furnished by the Phillips Petroleum Co. of stated purity of 99.99 mole %, the total detectable impurities being less than 0.01 mole %. A quantity of the gas was passed over P_2O_5, condensed, deaerated, and sealed in the glass bulbs by condensation of the vapor with liquid nitrogen. The pressure difference between the dew and bubble points was found to be 0.034 atm at 75.82° indicating the sample was of high purity.

Clegg and Rowlinson[68] obtained their sample from the National Chemical Laboratory which was certified to be 99.99% propane. This sample was found to have a mean vapor pressure of 30.98 atm at 80.00°. The difference between the dew and bubble points was 0.04 atm.

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(64) J. A. Beattie, N. Poffenberger, and C. J. Hadlock, *J. Chem. Phys.*, **3**, 96 (1935).

(65) C. H. Meyers, *J. Res. Natl. Bur. Std.*, **29**, 168 (1942).

(66) H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **41**, 482 (1949).

(67) W. B. Kay and G. M. Rambosek, *ibid.*, **45**, 221 (1953).

(68) H. P. Clegg and J. S. Rowlinson, *Trans. Faraday Soc.*, **51**, 1333 (1955).

Kobe and Lynn selected Beattie, Poffenberger, and Hadlock's[64] values of t_c and P_c, and an average of Meyers' value[65] and that of Reamer, Sage, and Lacey[66] for d_c. The agreement between Kay and Rambosek[67] and Clegg and Rowlinson[68] for both t_c and P_c is excellent, and these newer values are slightly lower than the earlier ones. These two pairs of investigators determined t_c visually; therefore averages of their values for t_c and P_c are selected. Clegg and Rowlinson[68] calculated d_c by the law of rectilinear diameters, and their value is slightly lower than that reported by Meyers[65] and by Reamer, Sage, and Lacey.[66] The latter authors recalculated d_c from Beattie, Poffenberger, and Hadlock's[64] results by the application of the law of rectilinear diameters. Since Clegg and Rowlinson[68] used a sample of high purity and measured both the densities of the vapor and the liquid very carefully, their value for d_c of propane is selected.

d. *n*-Butane[69,70]

No new data are available. Values selected are those recommended by Kobe and Lynn[1] but are reported to one more significant figure for t_c and P_c.

e. 2-Methylpropane (isobutane)[71]

No new data are available. Values selected are those recommended by Kobe and Lynn[1] but are reported to one more significant figure for t_c and P_c.

f. *n*-Pentane[72–75]

Beattie, Levine, and Douslin[74] used an American Petroleum Institute–National Bureau of Standards sample of *n*-pentane made available through the American Petroleum Institute Research Project 44. The impurities were stated to be 0.15 ± 0.07 mole %. The sample was further purified by repeated freezing, distillation, and pumping in the loading system to remove air. The vapor pressure was determined at 100°, while the vapor volume was varied from 95 to 0.26 ml. The increase in pressure of 0.009 atm during this process indicated a satisfactory purity of the sample.

Partington, Rowlinson, and Weston[75] used a sample of purity between 99.8 and 99.99 mole % supplied by the National Chemical Laboratory. The critical point was observed by twice raising and lowering the temperature at a speed not exceeding 0.2°/hr. The critical temperature was reproducible to 0.1°. The thermometers were calibrated to 0.1° by the National Physical Laboratory.

Ambrose, Cox, and Townsend[17] obtained a sample of 99.95 mole % purity from the National Chemical Laboratory. Two determinations of t_c were carried out and the range of observations, *i.e.*, the amount by which the temperature of disappearance exceeded that of reappearance, was 0.04°.

Kay [30] used Phillips Research Grade *n*-pentane without further purification.

The agreement between the visually observed t_c values of Partington, Rowlinson, and Weston[75] and of Ambrose, Cox, and Townsend[17] is very good. However, Beattie, Levine, and Douslin's[74] value for t_c, which was determined from P–V–T data, is about 0.3° higher than that of Ambrose but is in excellent agreement with Kay's unpublished value which was observed visually. As the older values for t_c of Young[72] and of Sage and Lacey[73] are considerably higher, they are not considered in the final selection. The variation in the experimental values of t_c is difficult to understand as all the other investigators made careful measurements on high-purity samples. Because of this variation in the t_c values, an average of the values of Beattie, *et al.*,[74] Partington, *et al.*,[75] Ambrose, *et al.*,[17] and Kay[30] is selected and rounded off to four significant figures. The critical pressure is calculated at this selected t_c using the P–V–T data of Beattie, Levine, and Douslin.[74]

The large difference between Beattie, Levine, and Douslin's value of d_c and those of Young[72] and of Sage and Lacey[73] made selection of the "best" d_c value again very frustrating. In general, Beattie and his coworkers[74] carried out their determinations with extreme care, resulting in high precision and accuracy. Young,[72] however, obtained the d_c from the law of rectilinear diameters, a preferred method for this determination. To select a value of d_c, the experimental vapor and liquid densities of Young and of Sage and Lacey were plotted. This plot was then superimposed on a large scale plot of the P–V–T data of Beattie, *et al.* Young's t_c of 197.2° was made to coincide with the selected t_c of 196.5°. The vapor–liquid envelope was then redrawn by weighting the data of Beattie, *et al.*, a bit more than that of Young and of Sage and Lacey. A value for d_c of 0.237 ±0.003 g/cm^3 obtained from the law of rectilinear diameters was selected.

Our selected value is considerably lower than that of Beattie, *et al.;* however, it is quite close to the average of the values of Beattie, *et al.*, and of Young.

g. 2-Methylbutane (isopentane)

Research Grade isopentane (2-methylbutane) obtained from Phillips Petroleum Co. was used by Vohra

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(69) J. A. Beattie, G. L. Simard, and G. J. Su, *J. Am. Chem. Soc.*, **61**, 24 (1939).

(70) W. B. Kay, *Ind. Eng. Chem.*, **32**, 358 (1940).

(71) J. A. Beattie, D. G. Edwards, and S. Marple, *J. Chem. Phys.*, **17**, 576 (1949).

(72) S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1909–10).

(73) B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **34**, 730 (1942).

(74) J. A. Beattie, S. W. Levine, and D. R. Douslin, *J. Am. Chem. Soc.*, **73**, 4431 (1951).

(75) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56**, 479 (1960).

and Kobe.[76] The purity based on a determination of the melting point was 100 mole %. The sample which was transferred back to the cylinder from the Burnett apparatus after the conclusion of Silberberg's work[77] might have contained some dissolved air during the process. Therefore, the sample was frozen with liquid nitrogen, and the permanent gases were removed by evacuation. The sample was melted, and the first 10% was evacuated and distilled into a second receiver, leaving the last 10% in the original flask. This operation was repeated several times to obtain the original purity. However, the behavior of the sample during experiments indicated that the isopentane was not as pure as desired.

Ambrose, Cox, and Townsend[17] obtained a sample of 100 mole % purity from Phillips Petroleum Co. Five determinations of t_c were carried out giving the range of observations of 0.06°.

Kobe and Lynn[1] selected Young's data[72] data which were determined in 1910. The difference of 0.56° in t_c between the value of Vohra and Kobe[76] and that of Ambrose, Cox, and Townsend[17] is probably due to the impure sample used by the former. The t_c value of Ambrose, Cox, and Townsend is selected, and P_c and d_c are interpolated at the selected t_c using Vohra and Kobe's $P-V-T$ data.

h. 2,2-Dimethylpropane (neopentane)

Partington, Rowlinson, and Weston[75] used a sample obtained from the National Chemical Laboratory with a purity in the range of 99.8–99.99 mole %. No exact purity for this sample was specified. Critical temperature was reproducible to 0.1°.

Kobe and Lynn[1] selected values of Beattie, Douslin, and Levine.[78]

As the new value for critical temperature determined by Partington, Rowlinson, and Weston[75] is identical with that of Beattie and his coworkers, the final selection for the critical constants of neopentane are the same as those selected by Kobe and Lynn.

i. *n*-Hexane

Glaser and Rüland[79] determined the critical temperatures and the critical pressures of a number of technically important organic substances. However, they did not mention the source or the purity of their samples. Temperatures were measured with a Pt|Pt-Rh thermocouple and a precision millivoltmeter. Pressures from 0 to 100 atm were measured with a precision manometer. The calibration curves of seven substances were determined, and on comparison with the "best" literature values it was concluded that this equipment yielded satisfactory results. t_c and P_c were obtained graphically from the cooling and the heating curves. The precision of measurement by this method is not very high.

Nichols, Reamer, and Sage[80] obtained Research Grade *n*-hexane from the Phillips Petroleum Co., which was reported to contain not more than 0.003 mole fraction of material other than *n*-hexane. The hydrocarbon was dried over metallic sodium and solidified at liquid nitrogen temperatures. It was maintained at a relatively high vacuum in the solid state for an extended period to complete the removal of noncondensable gases. The index of refraction relative to the D-line of sodium at 25° was 1.37225 as compared with 1.37226 for air-saturated *n*-hexane.[34] The authors suggest that the impurity was less than 0.001 mole fraction. The temperature was measured using a platinum resistance thermometer through a modulating electronic circuit. The temperature of the contents of the pressure vessel was known within 0.01° of the international platinum scale throughout the temperature interval between 4 and 238°. Pressures were measured by means of a balance utilizing a piston–cylinder combination which was calibrated against the vapor pressure of CO_2. The pressures at the ice point were known within 0.01% of that of CO_2.

Partington, Rowlinson, and Weston[75] used a sample supplied by the National Chemical Laboratory which was of purity between 99.8 and 99.99 mole %. The transfer of the sample into the experimental tube under vacuum ensured against contamination by air. The critical point was observed by twice raising and lowering the temperature at a speed not exceeding 0.2°/hr. The temperatures were measured by a set of mercury-in-glass thermometers calibrated at the National Physical Laboratory to 0.1° within the 2 years prior to the experimental determinations. The critical temperature was reproducible to 0.1°.

Ambrose, Cox, and Townsend[17] used a Research Grade sample of *n*-hexane obtained from the Phillips Petroleum Co. The purity of 99.81 mole % was determined by an appropriate cryoscopic technique. Five determinations were carried out with a range of observation of 0.02°.

Kay and Hissong[31] used highly purified sample made available by the Phillips Petroleum Co. Values listed by them were for the air-saturated sample.

There is a large variation in the critical temperature values available in literature. Kay carefully purified the sample of *n*-hexane used in his work and determined t_c visually. Nichols, Reamer, and Sage[80] obtained their value from $P-V-T$ determinations, and the

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(76) S. P. Vohra and K. A. Kobe, *J. Chem. Eng. Data*, **4**, 329 (1959).

(77) I. H. Silberberg, J. J. McKetta, and K. A. Kobe, *ibid.*, **4**, 323 (1959).

(78) J. A. Beattie, D. R. Douslin, and S. W. Levine, *J. Chem. Phys.*, **19**, 948 (1951).

(79) F. Glaser and H. Rüland, *Chem. Ingr.-Tech.*, **29**, 772 (1957).

(80) W. B. Nichols, H. H. Reamer, and B. H. Sage, *A.I.Ch.E. J.*, **3**, 262 (1957).

agreement with the older value of Kay is good. They also agree satisfactorily with Glaser and Rüland[79] in both the t_c and P_c values. However, the newer value of Ambrose, Cox, and Townsend is considerably lower than all of the previous values. This difference cannot be accounted for on the basis of the method used by various investigators. Partington, Rowlinson, and Weston's[75] value falls between that of Ambrose, Cox, and Townsend[17] and all of the other investigators. Kobe and Lynn[1] recommended Kay's values because they were the most reliable values available at that time. Ambrose, Cox, and Townsend used a high-purity sample and exercised extreme care in their measurements; therefore, their value for t_c is selected. Because of the variation in the experimental values, the selected t_c is rounded off to four significant figures.

Critical pressure and critical density values which are selected were calculated at the selected t_c using equations recommended by Kay.

j. 2-Methylpentane

The sample used by Kay[25] was obtained from close-boiling fractions of petroleum naphthas by distillation using a 100-plate distilling column with a reflux ratio of 50:1. The maximum difference in pressure between the bubble and the dew points amounted to about 0.04 atm. The normal boiling point of the sample was 60.13° as compared with the literature value of 60.271°.[34]

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.98 mole % purity. Four determinations of t_c were carried out with a range of observation of 0.06°.

Kobe and Lynn selected Kay's values as most reliable. The disparity of about 0.6° between the values of t_c of these two investigators may be due to the difference in the purities of their samples. It appears that Ambrose's sample was purer than the one used by Kay. On this basis, Ambrose, Cox, and Townsend's value for t_c is selected. P_c and d_c values are calculated at the selected t_c from the vapor pressure equation and the density equation given by Kay.

k. 2,2-Dimethylbutane

Kay obtained a "pure" grade sample from the Phillips Petroleum Co. It was further purified by sulfuric acid treatment and distillation in a 60-plate column. The density of the sample used was 0.6503 g/cm³ at 20° as compared to the literature value of 0.64916 g/cm³.[34]

Ambrose, Cox, and Townsend[17] used a Phillips Petroleum Co. sample of 99.99 mole % purity. Five determinations of t_c were carried out with a range of observation of 0.03°.

Kobe and Lynn selected Kay's values. The newer value of Ambrose, Cox, and Townsend for t_c differs considerably from that of Kay. As Ambrose and coworkers used a very pure sample, their value is assumed to be more reliable and is selected. The recommended P_c and d_c values are calculated at the selected t_c using equations given by Kay.

l. 2,3-Dimethylbutane

The sample used by Kay[25] was prepared by the catalytic alkylation of isobutane and ethylene. The product was purified by distillation in a 15-plate column using a high reflux ratio.

Ambrose, Cox, and Townsend[17] used a sample of 99.87 mole % purity supplied by Phillips Petroleum Co. Five determinations of t_c were carried out with a range of observation of 0.03°.

Kobe and Lynn[1] selected Kay's values of t_c, P_c, and d_c. The older t_c values of Young[72] and Kay[25] are higher than the most recent value of Ambrose, Cox, and Townsend. In general, Kay's values of t_c for all hexanes are much higher than those reported by Ambrose, *et al.* As previously mentioned, this systematic difference may be due to impurities in Kay's samples or due to thermometry. All of the samples used by Ambrose, Cox, and Townsend were of very high purity, and their value of t_c for 2,3-dimethylbutane is selected. The selected P_c and d_c are calculated values at t_c = 226.78° using equations recommended by Kay.

m. *n*-Heptane[81–83]

Kobe, Crawford, and Stephenson[83] used Research Grade *n*-heptane of 99.94 mole% purity supplied by Phillips Petroleum Co. The critical temperature was taken as the highest point of deviation from the smooth vapor pressure curve when either of the one-phase regions was entered. The precision of the temperature measurement was 0.03°. The error in pressure was 0.04 atm, and the error in critical density was 0.040 g/cm³.

Ambrose, Cox, and Townsend[17] used a sample of 99.94 mole % purity from the Phillips Petroleum Co. Three determinations of t_c were carried out with a range of observation of 0.02°.

McMicking and Kay[28] also used a sample supplied by Phillips Petroleum Co. of 99.92 mole % purity.

Kobe and Lynn[1] selected the values of Beattie and Kay for the critical temperature and the critical pressure and the value of Kay for the critical density.

Kay and Hissong[31] used a highly purified sample obtained from the Phillips Petroleum Co. The values listed by them were for the air-saturated sample.

The limiting factor in the value of the critical temperature of Kobe, Crawford, and Stephenson[83] was the closeness with which the break at the phase boundary could be determined. Some uncertainty exists as to the

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(81) J. A. Beattie and W. C. Kay, *J. Am. Chem. Soc.*, **59**, 1586 (1937).

(82) W. B. Kay, *Ind. Eng. Chem.*, **30**, 459 (1938).

(83) K. A. Kobe, H. R. Crawford, and R. W. Stephenson, *ibid.*, **47**, 1767 (1955).

point of intersection, and as a result the critical temperature was determined no closer than ±0.33°. In spite of this, the agreement between Kobe's value and that of Ambrose, Cox, and Townsend is excellent. The values of Ambrose, Cox, and Townsend and that of McMicking and Kay differ by 0.28°. Both of these investigations represent precise and accurate work on very pure samples. Beattie and Kay's value of t_c and that of Kay and Hissong fall between these two newer values. The critical temperature value selected is an average of the values of Ambrose, Cox, and Townsend,[17] of McMicking and Kay,[28] and of Beattie and Kay[61] and is rounded off to four significant figures because of the variation in the experimental values. The critical pressure is calculated at selected critical temperature using the vapor pressure equation given by McMicking and Kay. McMicking and Kay's value of the critical density is selected because it was calculated using the law of rectilinear diameters.

n. 2-Methylhexane

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.91 mole % purity. Four determinations of t_c with range of observation of 0.02° were made.

McMicking and Kay[28] used an American Petroleum Research hydrocarbon of 99.91 ± 0.07 mole % purity. The agreement between these newer values of t_c is excellent. Kobe and Lynn[1] selected unpublished results of Keyes. The value selected for critical temperature is the mean of the recent values of Ambrose, Cox, and Townsend and of McMicking and Kay. The critical pressure and critical density values selected are those of McMicking and Kay.

o. Other isomers of heptane

The remaining isomers of heptane are reported in Table IIo. Accurate data are available from McMicking and Kay[28] on these highly pure American Petroleum Institute Research hydrocarbons. The critical constants, along with the purities of the compounds, are listed. For 2,3-dimethylpentane and 2,4-dimethylpentane, additional t_c values by Francis are available. No details regarding the source or the purity of the samples used by Francis were given. The agreement between the two sets of values for 2,3-dimethylpentane is good. The values recommended by Kobe and Lynn[1] were obtained from the unpublished work of Keyes and from the American Petroleum Institute Research Project 44.[34] The values of McMicking and Kay for t_c, P_c, and d_c for these isomers are selected.

p. *n*-Octane

Kreglewski[84] prepared *n*-octane by Würtz synthesis from carefully rectified *n*-butyl bromide and the product was shaken with concentrated sulfuric acid to remove traces of olefins formed during the synthesis. It was then rectified in presence of metallic sodium. The normal boiling point of the sample used in the measurement agreed within ±0.02° with the American Petroleum Institute Research Project 44 value.[34]

Ambrose, Cox, and Townsend used a sample of 99.63 mole % purity from the National Chemical Laboratory. Three determinations of t_c were carried out with a range of observation of 0.02°.

McMicking and Kay used an American Petroleum Institute Research hydrocarbon with a certified purity of 99.95 ± 0.04 mole %.

An American Petroleum Institute Standard sample was used by Connolly and Kandalic[85] with stated purity of 99.94 mole %. The sample arrived with magnetic break-off tips and was not exposed to air during handling. No further purification was attempted, except to remove any traces of air by distillation *in vacuo*. The pressure rise on going from the dew point to the bubble point was 0.01 atm at 200°. Temperatures were measured with a platinum resistance thermometer calibrated at the National Bureau of Standards, and pressures were measured with a dead-weight gauge.

Kay and Hissong[31] used a Phillips Petroleum Co. highly purified sample. The values reported by them were for air-saturated sample.

The agreement between the critical temperature values of Kreglewski,[84] McMicking and Kay,[28] and Connolly and Kandalic[85] is excellent. Kreglewski's synthetic sample appears to be of very high purity. Kay and Hissong's value for air-saturated sample falls within the experimental uncertainty of McMicking and Kay. The samples used by these different investigators are of similar purity. However, the value of Ambrose, Cox, and Townsend differs by about 0.2° probably because of a slightly impurity in their sample. Based on the purity of the samples used and the good agreement between the values obtained by these investigators, an average value of Kreglewski, McMicking and Kay, and Connolly and Kandalic is selected for the critical temperature. On the same basis, the selected value for the critical pressure is an average of those of McMicking and Kay and Connolly and Kandalic. Using saturated liquid and vapor densities reported by Connolly and Kandalic, $d_c = 0.232$ g/cm^3 was calculated by the law of rectilinear diameters. This value is in exact agreement with that of McMicking and Kay and is selected.

q. 2-Methylheptane

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.994

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[84] A. Kreglewski, *Roczniki Chem.*, 29, 754 (1955).

[85] J. F. Connolly and G. A. Kandalic, *J. Chem. Eng. Data*, 7, 137 (1962).

TABLE II

ALKANES (PARAFFINS)

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
				a. Methane		
1913	−82.85	45.6	0.1623	Cardoso	1, 19	54
1922	−82.11	45.79	0.1613	Keyes, Taylor, and Smith	1, 19	55
1930	−82.13			Wiebe and Brevoort	9	56
1945	−82.5	45.8	0.1381	Corcoran, Bowles, Sage, and Lacey	5, 9, 18	57
1952	−82.60	45.47	0.1625	Bloomer and Parent	1, 19	58
1962		45.41		Hestermans and White	17	59
1963	−82.85			Jones and Rowlinson	1	42
1953	−82.1	45.8	0.162	Kobe and Lynn		1
Selected value	−82.60	45.44	0.162			
				b. Ethane		
1915	32.32	48.13		Prins	1	60
1939	32.27	48.20	0.203	Beattie, Su, and Simard	5	61
1940	32.23			Mason, Naldrett, and Maass	10	6
1953	31.97	48.12		Kay and Brice	1	62
1953	32.23 32.167			Whiteway and Mason	1	63
1954	32.32			Palmer	4	49
1954	32.19	49.78		Schmidt and Thomas	1, 16	50
1953	32.3	48.2	0.203	Kobe and Lynn		1
Selected value	32.28	48.16	0.203			
				c. Propane		
1935	96.81	42.01	0.226	Beattie, Poffenberger, and Hadlock	5	64
1942			0.2194	Meyers	19	65
1949			0.220	Reamer, Sage, and Lacey	19	66
1953	96.67	41.94		Kay and Rambosek	1	67
1955	96.66	41.93	0.217	Clegg and Rowlinson	1, 16, 19	68
1953	96.8	42.0	0.220	Kobe and Lynn		1
Selected value	96.67	41.94	0.217			
				d. *n*-Butane		
1939	152.01	37.47	0.225	Beattie, Simard, and Su	5	69
1940	152.2	37.46	0.228	Kay	1, 19	70
1953	152.0	37.5	0.228	Kobe and Lynn		1
Selected value	152.01	37.47	0.228			
				e. 2-Methylpropane (Isobutane)		
1949	134.98	36.00	0.221	Beattie, Edwards, and Marple	5	71
1953	134.9	36.0	0.221	Kobe and Lynn		1
Selected value	134.98	36.00	0.221			
				f. *n*-Pentane		
1910	197.2	33.03	0.2323	Young	2, 19	72
1942	197.2	33.6	0.229	Sage and Lacey	5	73
1951	196.62	33.31	0.204	Beattie, Levine, and Douslin	5	74
1960	196.4			Partington, Rowlinson, and Weston	1	75
1960	196.34			Ambrose, Cox, and Townsend	1	17
	196.63	33.29		Kay	1	30
1953	196.6	33.3	0.232	Kobe and Lynn		1
Selected value	196.5	33.25	0.237			
				g. 2-Methylbutane (Isopentane)		
1910	187.8	32.9	0.2343	Young	2, 19	72
1959	187.8	33.66	0.236	Vohra and Kobe	5	76
1960	187.24			Ambrose, Cox, and Townsend	1	17
1953	187.8	32.9	0.234	Kobe and Lynn		1
Selected value	187.24	33.37	0.236			
				h. 2,2-Dimethylpropane (Neopentane)		
1951	160.60	31.57	0.238	Beattie, Douslin, and Levine	5	78
1960	160.6			Partington, Rowlinson, and Weston	1	75

TABLE II (*Continued*)

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
1953	160.60	31.57	0.238	Kobe and Lynn		1
Selected value	160.60	31.57	0.238			
				i. *n*-Hexane		
1946	234.7	29.94	0.234	Kay	1, 19	25
1957	234.8	29.6		Glaser and Rüland		79
1957	234.8	29.53		Nichols, Reamer, and Sage	5	80
1960	234.5			Partington, Rowlinson, and Weston	1	75
1960	234.15			Ambrose, Cox, and Townsend	1	17
1967	234.8	30.10		Kay and Hissong	1	31
1953	234.7	29.9	0.234	Kobe and Lynn		1
Selected value	234.2	29.73	0.233			
				j. 2-Methylpentane		
1946	224.9	29.95	0.235	Kay	1, 19	25
1960	224.30			Ambrose, Cox, and Townsend	1	17
1953	224.7	29.9	0.235	Kobe and Lynn		1
Selected value	224.30	29.71	0.235			
				k. 2,2-Dimethylbutane		
1946	216.2	30.67	0.240	Kay	1, 19	25
1960	215.58			Ambrose, Cox, and Townsend	1	17
1953	216.2	30.67	0.240	Kobe and Lynn		1
Selected value	215.58	30.40	0.240			
				l. 2,3-Dimethylbutane		
1910	227.35	30.74	0.2411	Young	2, 19	72
1946	227.1	30.99	0.241	Kay	1, 19	25
1960	226.78			Ambrose, Cox, and Townsend	1	17
1953	227.1	30.9	0.241	Kobe and Lynn		1
Selected value	226.78	30.86	0.241			
				m. *n*-Heptane		
1937	267.01	27.00	0.241	Beattie and Kay	5	81
1938	267.4	27.0	0.235	Kay	1, 19	82
1955	267.2	27.1	0.241	Kobe, Crawford, and Stephenson	5	83
1960	267.13			Ambrose, Cox, and Townsend	1	17
1965	266.85	27.002	0.232	McMicking and Kay	1, 19	28
1967	267.0	27.22		Kay and Hissong	1	31
1953	267.0	27.0	0.235	Kobe and Lynn		1
Selected value	267.0	27.00	0.232			
				n. 2-Methylhexane		
1960	257.18			Ambrose, Cox, and Townsend	1	17
1965	257.15	26.971	0.238	McMicking and Kay	1, 19	28
1953	257.9	27.2	0.234	Kobe and Lynn		1
Selected value	257.16	26.98	0.238			

o. Other Isomers of Heptane (McMicking and Kay, 1965)

Compound	t_c, °C	P_c, atm	d_c, g/cm³	Purity, mole %	Source^a	Ref
2-Methylhexane	262.04^b	27.77^b	0.248^b	99.80 ± 0.15	A	28
3-Ethylpentane	267.42^b	28.53^b	0.241^b	99.94 ± 0.03	A	28
2,2-Dimethylpentane	247.29^b	27.37^b	0.241^b	99.81 ± 0.06	A	28
2,3-Dimethylpentane	264.14^b	27.70^b	0.255^b	99.85 ± 0.10	A	28
	264					28
2,4-Dimethylpentane	246.58^b	27.01^b	0.240^b	99.88 ± 0.05	A	28
	248.5					28
3,3-Dimethylpentane	263.19^b	29.07^b	0.242^b	99.96 ± 0.04	A	28
2,2,3-Trimethylbutane	257.96^b	29.15^b	0.252^b	99.991 ± 0.008	A	28

p. *n*-Octane

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
1910	296.2	24.64	0.2327	Young	2, 19	72
1955	295.62			Kreglewski	1	84
1960	295.41			Ambrose, Cox, and Townsend	1	17
1962	295.62	24.55		Connolly and Kandalic	1	85
1965	295.59	24.537	0.232	McMicking and Kay	1, 19	28

TABLE II (*Continued*)

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
1967	295.7	24.72		Kay and Hissong	1	31
1953	296.2	24.6	0.233	Kobe and Lynn		1
Selected value	295.61	24.54	0.232			
				q. 2-Methylheptane		
1960	286.42			Ambrose, Cox, and Townsend	1	17
1965	286.41	24.517	0.234	McMicking and Kay	1.19	28
1953	288	24.8	0.234	Kobe and Lynn		1
Selected value	286.42	24.52	0.234			
				r. 2,2,4-Trimethylpentane		
1948	271.2	25.5	0.237	Beattie and Edwards	5	86
1951	270.676	25.308	0.243	Kay and Warzel	1, 19	87
1960	270.46			Ambrose, Cox, and Townsend	1	17
1965	270.74	25.340	0.244	McMicking and Kay	1, 19	28
1953	270.9	25.4	0.243	Kobe and Lynn		1
Selected value	270.74	25.34	0.244			

s. Other Isomers of Octane—Selected Values

Compound	t_c °C	P_c, atm	d_c, g/cm^3	Investigators, year	Purity, mole %, and source[c]	Ref
3-Methylheptane	290.45	25.127	0.246	McMicking and Kay, 1965	99.62 ± 0.23, A	28
4-Methylheptane	288.52	25.087	0.240	McMicking and Kay, 1965	99.89 ± 0.07, A	28
3-Ethylhexane	292.27	25.738	0.251	McMicking and Kay, 1965	99.75 ± 0.20, A	28
2,2-Dimethylhexane	276.65	24.961	0.239	McMicking and Kay, 1965	99.89 ± 0.11, A	28
2,3-Dimethylhexane	290.27	25.938	0.244	McMicking and Kay, 1965	99.85 ± 0.10, A	28
2,4-Dimethylhexane	280.30	25.229	0.242	McMicking and Kay, 1965	99.75 ± 0.20, A	28
2,5-Dimethylhexane	276.84	24.542	0.237	McMicking and Kay, 1965	99.97 ± 0.005, A	28
3,3-Dimethylhexane	288.80	26.187	0.258	McMicking and Kay, 1965	99.75 ± 0.20, A	28
3,4-Dimethylhexane	295.63	26.569	0.245	McMicking and Kay, 1965	99.75 ± 0.20, A	28
2-Methyl-3-ethylpentane	293.87	26.651	0.258	McMicking and Kay, 1965	99.78 ± 0.11, A	28
3-Methyl-3-ethylpentane	303.36	27.706	0.251	McMicking and Kay, 1965	99.93 ± 0.04, A	28
2,2,3-Trimethylpentane	290.28	26.937	0.262	McMicking and Kay, 1965	99.68 ± 0.20, A	28
2,3,3-Trimethylpentane	300.34	27.833	0.251	McMicking and Kay, 1965	99.79 ± 0.05, A	28
2,3,4-Trimethylpentane	293.19	26.941	0.248	McMicking and Kay, 1965	99.83 ± 0.06, A	28
				t. *n*-Alkanes, $n > 8$		
n-Nonane	321.41[b]			Ambrose, *et al.*, 1960	99.68, P	17
n-Nonane	320.4	22.83[b]		Kay and Hissong, 1967	P	31
n-Decane	344.4[d]			Ambrose, *et al.*, 1960	99.73, D	17
n-Decane	344.23[d]	20.72[b]		Kay and Hissong, 1960	P	31
n-Decane	348.2			Francis, 1957		88
n-Undecane	365.58[b]			Ambrose, *et al.*, 1960	99.97, A	17
n-Dodecane	385.1[b]			Ambrose, *et al.*, 1960	99.975, A	17
n-Dodecane	391.5			Francis, 1957		88
n-Tetradecane	421 ± 1[b]			Ambrose, 1963	>99, BP	89
n-Hexadecane	444 ± 2[b]			Ambrose, 1963	>99, BP	89
n-Octadecane	483			Ambrose, 1963	>99, BP	89
n-Docosane	>490			Ambrose, 1963		89

u. 2,2,5-Trimethylhexane

Year	t_c, °C	Investigator	Method	Ref
1957	296.7	Francis	1	88
Selected value	294.8			

[a] A, American Petroleum Institute Research hydrocarbon supplied by American Petroleum Institute Research Project 44, Texas A&M University, College Station, Texas. [b] Selected values. [c] The code letters represent the following sources: A, American Petroleum Institute Research hydrocarbon supplied by American Petroleum Institute Research Project 44, Texas A&M University, College Station, Texas; BP, British Petroleum Co.; D, Distillers Co.; P, Phillips Petroleum Co. [d] Average value selected.

mole % purity. Four determination of t_c were carried out with range of observation of 0.04°.

American Petroleum Institute Research Project 44 supplied an API Research hydrocarbon of 99.66 ± 0.18 mole % purity which was used without further purification by McMicking and Kay.[28]

The agreement between the two investigators is excellent for critical temperature, and the value selected is the mean of the two. Critical pressure and critical density values selected are those of McMicking and Kay.

r. 2,2,4-Trimethylpentane[86,87]

Phillips Petroleum Co. supplied a sample of 99.87 ± 0.05 mole % purity to Kay and Warzel,[87] which was used without further purification.

Ambrose, Cox, and Townsend used a National Chemical Laboratory sample of 99.9 mole % purity. Three determinations of t_c were carried out with a range of observation of 0.06°.

McMicking and Kay obtained an API Research hydrocarbon sample of 99.95 ± 0.04 mole % purity through the American Petroleum Institute Research Project 44.

Kobe and Lynn[1] selected average values between Beattie and Edwards[86] and Kay and Warzel[87] for the critical temperature and the critical pressure and selected the latter's value for critical density.

Kay and Warzel's values of t_c, P_c, and d_c fall within the experimental uncertainties of McMicking and Kay. However, Ambrose, Cox, and Townsend's value for t_c is 0.3° lower. This difference may be due to a slightly impure sample used by them. McMicking and Kay's values of t_c, P_c, and d_c are selected.

s. Other isomers of octane

The data reported in Table IIs on isomeric octanes except 2-methylheptane and 2,3,4-trimethylpentane (these two compounds are discussed earlier) are McMicking and Kay's determinations on highly pure American Petroleum Institute Research hydrocarbons. Earlier, Kobe and Lynn reported American Petroleum Institute Research Project 44 tabulated values of t_c, P_c, and d_c for these compounds. These were correlated and not experimental values. McMicking and Kay's values are most precise, and hence their values are selected.

t. *n*-Alkanes, $n > 8$

Table IIt reports experimental values of the critical temperature for *n*-alkanes beyong *n*-octane available in the literature. Most of the data are from Ambrose, Cox, and Townsend[17] and represent the "best" values available. For *n*-nonane, three determinations were carried out with one experimental tube giving a range of observation of 0.08°.

Kay and Hissong[31] used a highly purified sample of *n*-nonane supplied by the Phillips Petroleum Co. The values reported by them were for the air-saturated sample.

Kay and Hissong's value of t_c for the air-saturated sample of *n*-nonane is lower by 1° than that of Ambrose, Cox, and Townsend. The t_c of Ambrose, Cox, and Townsend and the P_c of Kay and Hissong are selected for *n*-nonane.

Francis[88] did not mention the source or purity of *n*-decane used. The melting point and the boiling point of this sample were −29.7 and 174.1°, respectively. These can be compared to the values of −29.661 and 174.123° reported for these properties by American Petroleum Institute Research Project 44.[34] Ambrose, Cox, and Townsend used two experimental tubes for *n*-decane and carried out six determinations with the range of observation of 0.15°. The slight difference in the results obtained with the two tubes could be due to noncritical filling or to impurities in the sample.

Kay and Hissong used *n*-decane of 99.49 mole % purity supplied by the Phillips Petroleum Co. It was percolated through silica gel and subjected to ten freeze–pump–melt–distil cycles under high vacuum and then stored in the solid state. Before the sample was transferred to the experimental tube, it was subjected to six additional degassing cycles. A detailed study was made by Kay and Hissong to determine the effects of the following impurities: air dissolved in liquid hydrocarbons; mercury dissolved in the hydrocarbon sample as a result of using mercury as the confining liquid; and the possible decomposition of hydrocarbon sample with high critical temperatures.

The agreement between the t_c values of Ambrose, Cox, and Townsend[17] and of Kay and Hissong[31] is satisfactory. However, Francis's value of t_c is much higher and was not considered in the final selection. An average of the values of Ambrose, *et al.*, and Kay and Hissong is selected for t_c. Kay and Hissong's value of P_c is selected.

Normal alkanes, undecane and higher, were found by Ambrose and his coworkers to be unstable at and near t_c, and the critical temperature of such substances was determined in the rapid heater. Francis did not mention the source or the purity of the *n*-dodecane sample used by him. The melting point and the normal boiling point of the sample were determined to be −9.9 and 216.1°, respectively. The literature values are −9.587 and 216.278° for these properties.[34]

The critical temperatures of *n*-tetradecane, *n*-hexadecane, *n*-octadecane, and *n*-docosane were also determined by Ambrose in the rapid heater. The rate of decomposition of *n*-octadecane was such that only the initial disappearance was determined, and all of the tubes containing *n*-docosane burst after the first disappearance. Hence the t_c values reported by Ambrose are not very reliable.

For the remaining normal alkanes reported in Table IIt, the experimental t_c's of Ambrose, Cox, and Townsend and of Ambrose[89] are recommended except for *n*-octadecane and *n*-docosane. For these compounds, predicted values based on precise data for lower alkanes

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(86) J. A. Beattie and D. G. Edwards, *J. Am. Chem. Soc.*, **70**, 3382 (1948).

(87) W. B. Kay and F. M. Warzel, *Ind. Eng. Chem.*, **43**, 1150 (1951).

(88) A. W. Francis, *ibid.*, **49**, 1779 (1957).

(89) D. Ambrose, *Trans. Faraday Soc.*, **59**, 1988 (1963).

should be considered more accurate than the experimental results.[34]

u. 2,2,5-Trimethylhexane

Francis[88] measured t_c for this compound but gave no details regarding the source or the purity of the sample. The critical temperature was taken as the highest temperature at which a meniscus could be seen while cooling the tube about 0.5°/min. This is the only experimental value of t_c for this compound available in the literature. Comparison of Francis' values of t_c for 2,4-dimethylpentane, *n*-decane, and *n*-dodecane with the more reliable recent values shows his values to be consistently higher by 2° or more, probably due to impurities in his samples. Therefore an uncertainty of ±2° is assigned to Francis' value of t_c for 2,2,5-trimethylhexane.

For isomeric nonanes and decanes, a reliable correlation procedure was developed by Kudchadker, Holcomb, and Zwolinski.[90] Because of the large uncertainty in Francis' experimental value, the calculated value, 294.8 ± 1.°, is recommended.

2. Cycloalkanes (Cycloparaffins) (Table III)

a. Cyclopropane

Booth and Morris[91] did not mention the source and purity of the sample used in their investigation. They utilized a very accurate type of apparatus described by Booth and Swinehart.[92] Cyclopropane, which exhibited a constant density at constant temperature and pressure, was fractionally distilled to a manifold to which Cailletet tubes were sealed. The manifold and cells were rinsed 20 times with dry air and 15 times with cyclopropane, and the tubes were finally filled to a pressure of slightly less than 1 atm. The temperatures were measured using a platinum resistance thermometer which was calibrated at points in the range 100 to −183° at the carbon dioxide point and the oxygen point. The pressures were measured by the deadweight gauge. The critical temperature was determined by raising the temperature of the sample gradually and maintaining it at the meniscus disappearance temperature for 15–20 min to attain equilibrium. The highest temperature at which there were two phases visible and at which the meniscus did not re-form after disappearing on stirring was taken as the critical temperature. The critical pressure determined at this temperature was the pressure at which the mercury thread in the capillary did not move after standing for a long enough period to assure equilibrium.

As these are the only data available, they are selected as most reliable.

b. Cyclopentane

Ambrose and Grant[18] used a sample of 99.95 mole % purity obtained from the National Chemical Laboratory. The estimated uncertainty in the critical temperature was ±0.02°.

Kay[26] used an API-NBS Research hydrocarbon sample supplied by the American Petroleum Institute Research Project 44. The stated impurity of the sample was 0.02 ± 0.01 mole %. The temperature was measured with a two-junction copper–constantan thermocouple using a Leeds and Northrup Type "K" potentiometer which measures emf to 1 μV. The couple was calibrated using the standard temperatures of the ice point, transition point of sodium sulfate decahydrate, steam point, boiling point of naphthalene, and boiling point of benzophenone with the cold junction in a bath of melting ice. With the aid of the magnetic stirrer, the critical temperature could be located to within 0.01° with the variation in pressure in separate determinations on the same sample amounting to about 0.01 atm.

The difference of 0.2° in critical temperature between these two investigators is beyond the experimental uncertainty of both investigations. The experimental determinations were carried out carefully on very pure samples by both investigators, although Kay's sample was of slightly higher purity. Therefore, an average of these two values for t_c is selected as most probable. The P_c value is calculated at the selected t_c from the vapor pressure equation reported by Kay.[26] Kay's value of the critical density is selected.

c. Methylcyclopentane

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.99 mole % purity. Two experimental tubes were used, and four determinations were carried out with the range of observation of 0.04°.

Kobe and Lynn[1] selected Kay's[26] values for the critical temperature, the critical pressure, and the critical density. There is good agreement for the critical temperature between the two investigators; therefore an average of the two determinations is selected. The critical pressure is calculated at the selected critical temperature using Kay's vapor pressure equation. Kay's critical density value is selected.

d. Cyclohexane[93–95]

Kay and Albert[94] used a Phillips Petroleum Co. sample containing less than 1% impurity. It was frac-

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[90] A. P. Kudchadker, W. D. Holcomb, and B. J. Zwolinski, *J. Chem. Eng. Data*, **13**, 182 (1968).

[91] H. S. Booth and W. C. Morris, *J. Phys. Chem.*, **62**, 875 (1958).

[92] H. S. Booth and C. F. Swinehart, *J. Am. Chem. Soc.*, **57**, 1337 (1935).

[93] S. Young and E. C. Fortey, *J. Chem. Soc.*, **75**, 873 (1893).

[94] W. B. Kay and R. E. Albert, *Ind. Eng. Chem.*, **48**, 422 (1956).

[95] M. Simon, *Bull. Soc. Chim. Belges*, **66**, 375 (1957).

TABLE III

CYCLOALKANES (CYCLOPARAFFINS)

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
a. Cyclopropane						
1958	124.65	54.23		Booth and Morris	1	91
Selected value	124.65	54.23				
b. Cyclopentane						
1947	238.6	44.55	0.27	Kay	1	26
1957	238.4			Ambrose and Grant	1	18
1953	238.6	44.55	0.27	Kobe and Lynn		1
Selected value	238.5	44.49	0.27			
c. Methylcyclopentane						
1947	259.61	37.364	0.264	Kay	1	26
1957	259.55			Ambrose, Cox, and Townsend	1	17
1953	259.61	37.364	0.264	Kobe and Lynn		1
Selected value	259.58	37.35	0.264			
d. Cyclohexane						
1893	280.0	39.96	0.2735	Young and Fortey	1	93
1910	280	39.84	0.2735	Young	1, 19	73
1956	279.80	40.2		Kay and Albert	1	94
1957	281	40.57		Glaser and Rüland		79
1957	280.2		0.2718	Simon	1, 19	95
1957	280.3			Ambrose and Grant	1	18
1953	280	40.0	0.273	Kobe and Lynn		1
Selected value	280.3	40.2	0.273			
e. Methylcyclohexane						
1947	299.13	34.322	0.266	Kay	1	26
1957	299.5		0.2666	Simon	1	95
1960	298.97			Ambrose, Cox, and Townsend	1, 19	17
1953	299.1	34.32	0.285	Kobe and Lynn		1
Selected value	298.97	34.26	0.267			
f(1). *cis*-Decalin (*cis*-Bicyclo[4.4.0]decane)						
1962	429.0			Cheng, McCoubrey, and Phillips	1	96
Selected value	429.0					
f(2). *trans*-Decalin (*trans*-Bicyclo[4.4.0]decane)						
1962	413.8			Cheng, McCoubrey, and Phillips	1	96
Selected value	413.8					

tionally distilled at a reflux ratio of 20:1 under atmospheric pressure. The middle fraction used for the t_c determination had a normal boiling point of 80.748° (lit.[34] bp 80.738°). The difference in the bubble and dew point pressures was 0.015 atm at 253.92°. The temperature of the sample was measured to within 0.003° by means of a copper–constantan thermocouple. The pressure was measured by a dead-weight gauge with a sensitivity of 0.015 atm.

The discussion regarding Glaser and Rüland's[79] values is found under *n*-Hexane (section IV.B.1.i).

Simon determined the critical constants of ten hydrocarbons. The experimental work was actually performed in 1938 on well-purified samples. The precision of t_c measurement was ±0.05°.

A National Chemical Laboratory purified sample of 99.99 mole % purity was used by Ambrose and Grant.[18] The uncertainty in t_c is ±0.02°.

Kobe and Lynn selected Young's values[73] rounded off to three significant figures. Glaser and Rüland's values are higher than the other values and are not considered in the final selection. Kay and Albert[94] did not report final purity of the sample used in their investigations. It appears that Ambrose and Grant used a sample of higher purity than the one used by Kay which might account for the difference between the two t_c values. The agreement between Simon[95] and Ambrose and Grant[18] for t_c is satisfactory. Therefore, Ambrose's value of t_c is selected and P_c is calculated at t_c using Kay's vapor pressure data. An average of Young's and of Simon's values is selected for d_c because both values were obtained by the law of rectilinear diameters.

e. Methylcyclohexane

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.98 mole % purity. Two experimental tubes were used and four determinations of t_c were carried out giving a range of observation of 0.02°.

The details regarding Simon's determinations are discussed under cyclohexane.

Kobe and Lynn[1] selected Kay's values[26] for the critical temperature, the critical pressure, and the critical density. Kay used high-purity samples supplied by the American Petroleum Institute Research Project 44. However, there is a difference of 0.15° between Kay's determination of the critical temperature and that of Ambrose, Cox, and Townsend. This discrepancy is probably due to a slightly impure sample (impurity 0.10 ± 0.08 mole %) used by Kay. Simon's value[95] of t_c is considerably higher; however, his d_c value compares satisfactorily with that of Kay. The critical temperature of Ambrose, Cox, and Townsend is selected, and the critical pressure and critical density values are calculated at this selected critical temperature using appropriate equations given by Kay. Kay had originally reported 0.285 g/cm^3 for critical density which was subsequently corrected to 0.266 g/cm^3. Kobe and Lynn had selected 0.285 g/cm^3 for the critical density.

f. Decalins (bicyclo[4.4.0]decanes)

The decalins, both *cis* and *trans*, used by Cheng, McCoubrey, and Phillips[96] were "pure" samples supplied by the Esso Research Department. Exact purity of the samples was not determined, but the following physical properties give an indication of purity; values in brackets are the literature values.[34]

	Bp, °C (mm)	n_D^{20}
cis-Decalin	195.7–195.8 (769)	1.4810
	[195.774 (760)]	[1.48098]
trans-Decalin	187.2–187.3 (763)	1.4693
	[187.273 (760)]	[1.46932]

Glaser and Rüland reported $t_c = 372°$ and $P_c = 20.5$ atm for decalin but did not specify which isomer was investigated by them. As it is probable that the measurements were carried out on an equilibrium *cis–trans* mixture, these values were not considered in the final selection.

These are the only values of t_c for the two decalins available in literature and they are selected as most reliable.

C. UNSATURATED HYDROCARBONS

1. *Alkenes* (*Monoolefins*) (*Table IV*)

a. *cis*-2-Butene

Ambrose, Cox, and Townsend[17] used a sample of 99.4 mole % purity supplied by the National Physical Laboratory. Two experimental tubes were used, and five determinations of t_c were carried out with the range of observation of 0.03°.

Kobe and Lynn[1] selected critical constants for the *cis–trans* mixture although they had available values for the individual forms, *cis* and *trans*, recommended by Cragoe.[97] There was some discrepancy in reporting Cragoe's values as they appeared to have been switched for the two isomers. In fact, the properties reported by Kobe and Lynn for *cis* under Cragoe should have been for *trans* and *vice versa*.

The critical temperature of Ambrose, Cox, and Townsend and the critical pressure and critical density of Cragoe are selected.

b. *trans*-2-Butene

Ambrose, Cox, and Townsend[17] used a National Chemical Laboratory sample of 99.98 mole % purity. Three experimental tubes were used, and five determinations of t_c were carried out with the range of observation of 0.04°.

Discussion on Kobe and Lynn's selection is found under *cis*-2-Butene, section a. Cragoe[97] recommended 155.0° for the critical temperature. Ambrose, Cox, and Townsend's value for critical temperature and Cragoe's values for critical pressure and critical density are selected.

c. 1-Pentene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.82 mole % purity. Two experimental tubes were used, and four determinations of t_c were carried out giving the range of observation of 0.06°.

The discussion part of Kobe and Lynn[1] did not mention whose values of the critical constants were selected for this compound. It is believed that they selected Day, Nicholson, and Felsing's value[98] for the critical temperature and Vespignani's value[99] for the critical pressure. All the older values for the critical temperature, as reported by Kobe and Lynn, are higher than that of Ambrose, Cox, and Townsend. The discrepancy could be due to the impure samples used by the previous authors. Ambrose, Cox, and Townsend

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[96] D. C-H. Cheng, J. C. McCoubrey, and D. G. Phillips, *Trans. Faraday Soc.*, **58**, 224 (1962).

[97] C. S. Cragoe, National Bureau of Standards, Letter Circular, LC-736, U. S. Government Printing Office, Washington, D. C., 1943.

[98] H. O. Day, D. E. Nicholson, and W. A. Felsing, *J. Am. Chem. Soc.*, **70**, 1784 (1948).

[99] G. R. Vespignani, *Gazz. Chim. Ital.*, **33**, 73 (1903).

Table IV

Alkenes (Monoolefins)

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
				a. *cis*-2-Butene		
1943	160.0	41.5	0.2398	Cragoe	14, 19	97
1960	162.40			Ambrose, Cox, and Townsend	1	17
1953	157	41	0.238	Kobe and Lynn for *cis–trans* mixture		1
Selected value	162.40	41.5	0.240			
				b. *trans*-2-Butene		
1943	155.0	40.5	0.2359	Cragoe	14, 19	97
1960	155.46			Ambrose, Cox, and Townsend	1	17
1953	157	41	0.238	Kobe and Lynn for *cis–trans* mixture		1
Selected value	155.46	40.5	0.236			
				c. 1-Pentene		
1903	202.4	40.4		Vespignani	1	99
1950	201			Day, Nicholson, and Felsing	5	98
1960	191.59			Ambrose, Cox, and Townsend	1	17
1953	201	40		Kobe and Lynn		1
Selected value	191.59	40				
				d. 1-Hexene		
1893	243.5			Altschul	1	100
1960	230.83			Ambrose, Cox, and Townsend	1	17
1953	243.5			Kobe and Lynn		1
Selected value	230.83					
				e. 1-Heptene		
1960	264.08			Ambrose, Cox, and Townsend	1	17
Selected value	264.08					
				f. 1-Octene		
1893	304.8			Altschul	1	100
1960	293.4			Ambrose, Cox, and Townsend	1	17
Selected value	293.4					

comment that the apparent critical temperatures of certain olefins increase with aging. Therefore it is possible that the earlier observers could have made their observations on a sample of 1-pentene which had begun to polymerize. These effects were minimized considerably by Ambrose and his coworkers by use of an API Research hydrocarbon.

Ambrose, Cox, and Townsend's value for the critical temperature and Vespignani's value for the critical pressure, rounded off to two significant figures, are selected.

d. 1-Hexene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.87 mole % purity. Two experimental tubes were used, and five determinations of t_c were carried out giving the range of observation of 0.01°.

The only previous value of the critical temperature available is that of Altschul[100] determined in 1893. No details are given by Altschul as to the preparation and purity of the sample used. The value of Ambrose, Cox, and Townsend is selected for the critical temperature. No experimental determinations are available for P_c and d_c.

e. 1-Heptene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.84 mole % purity. As this substance is unstable at or near the critical temperature, the critical temperature was determined in the rapid heater. Four experimental tubes were used, and 16 determinations of t_c were carried out. The rate of change of apparent t_c was +0.5°/hr. The uncertainty in t_c was ±0.05°.

Because no other values for t_c are available, the value of Ambrose, Cox, and Townsend is selected as most reliable.

f. 1-Octene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.77 mole % purity. The critical temperature of this unstable substance was determined in the rapid heater. Three experimental tubes were used, and 12 deter-

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(100) M. Altschul, *Z. Physik. Chem.*, **11**, 577 (1893).

TABLE V

CYCLOALKENES (CYCLOOLEFINS)

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
			a. Cyclopentene			
1957	232.9			Ambrose and Grant	1	18
Selected value	232.9					
			b. Cyclohexene			
1960	287.27			Ambrose, Cox, and Townsend	1	17
1962	287.25			Cheng, McCoubrey, and Phillips	1	96
Selected value	287.26					

minations of t_c were carried out. The rate of change of apparent t_c was +3.0°/hr.

Altschul determined the critical temperature of this compound but did not give the details as to the preparation and purity of the sample used. The value of Ambrose, Cox, and Townsend for the critical temperature is selected.

2. *Cycloalkenes* (*Cycloolefins*) (*Table V*)

a. Cyclopentene

Ambrose and Grant[18] used a sample of 99.87 mole % purity supplied by the National Chemical Laboratory as chemical standards. Decomposition of cyclopentene occurred near the critical temperature as shown by a rise in t_c of 0.5° after 72 hr in the oven. The uncertainty in t_c was ±0.05°.

This is the only value available in the literature for this compound, and this value is selected.

b. Cyclohexene

Ambrose, Cox, and Townsend used a 99.9 mole % sample of cyclohexene purified by the National Chemical Laboratory. As this compound is unstable at its critical temperature, the measurements were carried out in the rapid heater. Two experimental tubes were used, and three determinations of t_c were carried out. The rate of change of apparent t_c was found to be +0.03°/hr, and the estimated uncertainty in extrapolation to zero time was ±0.02°.

Cheng, McCoubrey, and Phillips[96] purified a commercial sample by treating it with ferrous ammonium sulfate to destroy the peroxide and fractionated it in nitrogen atmosphere. The normal boiling point of the sample was 83.0°. The literature value is 82.979°.[34]

As agreement between these two investigations is excellent, an average value of t_c is selected.

3. *Alkynes* (*Acetylenes*) (*Table VI*)[101–107]

a. Ethyne (acetylene)

The sample used by Ambrose[51] was from a commercial acetylene batch. It was purified by removing the acetone in which it was dissolved with activated charcoal, dried with alumina gel, and fractionally distilled in a Podbielniak low-temperature column. A middle cut was removed, and a final sublimation *in vacuo* was carried out to remove traces of air. The purity was determined by the differential comparison of vapor pressures of two samples, one of which was nearly all in the gas phase and the other nearly all in the liquid phase. The two pressures agreed within 0.1 mm at 980 mm which indicated a high-purity sample. At the conclusion of the experiments, the sample was analyzed by gas–liquid chromatography which showed no presence of vinyl- or methylacetylenes. The exact purity of the sample used was not specified, but it is believed to have been of high purity. The temperature was measured by means of a platinum resistance thermometer, sensitive to 0.001°. Three tubes were used for measurements, and the reappearance of the meniscus, which was the more sharply defined phenomenon, occurred between 0.002 and 0.009° below the temperature of the disappearance of the meniscus. The value reported is the mean of 18 readings.

Ambrose and Townsend[104] used the same sample used earlier by Ambrose.[51] The experimental tube was heated in a vapor jacket containing *n*-pentane. With this arrangement, it was possible to insert a platinum resistance thermometer beside the tube. A value of the critical temperature determined simultaneously with the pressure agreed exactly with the one reported by Ambrose.

Kobe and Lynn[1] selected an average of the value of Cardoso and Baume[103] and of McIntosh[10] for both the critical temperature and the critical pressure. Because of a wide scattering of the experimental values, they

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(101) D. McIntosh, *J. Phys. Chem.*, **11**, 306 (1907).

(102) E. Mathias, *J. Chem. Soc.*, **96**, 552 (1909).

(103) E. Cardoso and G. Baume, *J. Chim. Phys.*, **10**, 509 (1912).

(104) D. Ambrose and R. Townsend, *Trans. Faraday Soc.*, **60**, 1025 (1964).

(105) O. Maass and C. H. Wright, *J. Am. Chem. Soc.*, **43**, 1098 (1921).

(106) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(107) S. P. Vohra, T. L. Kang, K. A. Kobe, and J. J. McKetta, *J. Chem. Eng. Data*, **7**, 150 (1962).

TABLE VI
ALKYNES (ACETYLENES)

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
			a. Ethyne (Acetylene)			
1907	36.5	61.6	0.314	McIntosh	1, 19	101
1909	37.05		0.2306	Mathias	?, 19	102
1912	35.4	61.65		Cardoso and Baume	3	103
1956	35.18			Ambrose	1	51
1964	35.18	60.586		Ambrose and Townsend	1.19	104
1953	36	61.6	0.231	Kobe and Lynn		1
Selected value	35.18	60.59	0.231			
			b. Propyne (Methylacetylene)			
1921	127.9			Maass and Wright	1	105
1947	128	52.8		Stull	14	106
1962	129.23	55.54	0.2449	Vohra, Kang, Kobe, and McKetta	5, 19	107
1953	128	52.8		Kobe and Lynn		1
Selected value	129.23	55.54	0.245			

only reported critical temperature rounded off to 1°. They selected the d_c of Mathias.[102]

It is likely that the previous values which are all higher than the one reported by Ambrose were measured on relatively impure samples. The critical temperature of Ambrose and the critical pressure of Ambrose and Townsend are selected. No newer determinations on critical density are available, therefore the d_c value recommended by Kobe and Lynn is selected.

b. Propyne (methylacetylene)

Vohra, Kang, Kobe, and McKetta[107] used propyne supplied by the Air Reduction Chemical Co. with the specified purity of 98.65 mole %. The initial purification by superfractionation yielded a product of 99.9+ mole % purity. It was further purified by freezing with liquid nitrogen and evacuating the permanent gases. The sample was then melted, and the first 10% was evacuated. This procedure was repeated until the mass spectrograph and the freezing point analysis showed almost 100% pure (at least greater than 99.99+ mole %) sample. Critical constants of propyne were obtained from a large-scale, pressure–volume plot of isotherms in the critical region. These isotherms were spaced 0.02° apart near the critical temperature, so that the horizontal point of inflection could be determined. The uncertainties in the measurements were t_c ±0.02° and P_c ±0.02 atm.

Kobe and Lynn recommended Maass and Wright's value[105] for the critical temperature and Stull's value[106] for the critical pressure.

Vohra, Kang, Kobe, and McKetta's value[107] for t_c is considerably higher than the older values. This variation cannot be accounted for by the different methods used by the three investigators. Vohra and his coworkers used a sample of high purity, and hence their values of the critical constants are selected as most reliable.

D. AROMATIC HYDROCARBONS

1. *Alkylbenzenes (Table VII)*

a. Benzene[108–110]

Kreglewski[84] used Research Grade benzene and purified it by rectification in the presence of metallic sodium.

Ambrose and Grant[18] used a National Chemical Laboratory sample of 99.99 mole % purity. Temperatures were measured by means of nichrome–constantan thermocouples used with a precision potentiometer. The potentiometer was checked by calibration against the boiling point of mercury. The temperature calculated from the pressure agreed with that obtained from a Pt resistance thermometer to within 0.01°. The thermocouples were positioned approximately at the same height as the meniscus in each tube.

The details regarding Simon's determinations[95] are found under cyclohexane (section IV.B.2.d). Connolly and Kandalic[85] used American Petroleum Institute Standard samples of 99.98 mole % purity. Traces of air were removed by distillation *in vacuo*.

Ambrose, Cox, and Townsend[17] used a 99.99 mole % benzene sample purified at the National Chemical Laboratory. In the apparatus used, temperatures were measured by means of a Pt resistance thermometer and Mueller bridge. The resistance thermometer was mounted with its platinum element uppermost and with the specimen tube resting on the outer sheath. The temperature gradients within the sample chamber were found to be less than 0.02°.

Partington, Rowlinson, and Weston[75] also used a sample provided by the National Chemical Laboratory.

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(108) E. J. Gornowski, E. H. Amick, and A. N. Hixson, *Ind. Eng. Chem.*, **39**, 1348 (1947).

(109) P. Bender, G. T. Furukawa, and J. R. Hyndman, *ibid.*, **44**, 387 (1952).

(110) G. Oldenburg, *Erdoel Kohle*, **8**, 445 (1955).

The exact purity of the sample was not given, although they mentioned that the purities of all of the compounds investigated by them were between 99.8 and 99.99 mole %.

Ambrose and Townsend[19] determined P_c of benzene in order to check the accuracy of their experimental set-up. Although no reference was made to the source and the purity of the sample, it is believed to be one of 99.99 mole % purity used earlier by Ambrose and other coworkers.

Ambrose, Broderick, and Townsend[16] used a 99.99 mole % purity sample and determined P_c at the observed t_c. The sample tube was transferred into the main body of the equipment, in absence of air, by modifying the technique used previously (Ambrose and Townsend[19]). The P_c value reported was the average of the results obtained for the two tubes from this investigation and the results of Ambrose and Townsend.

Kobe and Lynn[1] selected t_c good only to 1° due to the wide scattering in the experimental data existing at that time. For the critical temperature and the critical pressure, they selected an average of the data reported by Gornowski, Amick, and Hixson[108] and by Bender, Furukawa, and Hyndman.[109] The critical density value was taken as the average of the data of Gornowski, *et al.*,[108] and of Young.[72]

The agreement between the t_c values of Kreglewski,[84] Ambrose and Grant,[18] and Connolly and Kandalic[85] is very good. However, they are lower than the value of Ambrose, Cox, and Townsend.[17] Bender, Furukawa, and Hyndman's values[109] for t_c and P_c are in exact agreement with the newer values of Ambrose and coworkers, and for this reason 288.94° and 48.34 atm are selected for t_c and P_c.

Simon's value of d_c agrees well with that of Young. The d_c values obtained by the law of rectilinear diameters were corrected to the selected critical temperature by using the respective saturated liquid and vapor densities. An average of these corrected values is selected for d_c.

b. Toluene[111–114]

Ambrose and Grant[18] used a National Chemical Laboratory toluene sample of 99.98 mole % purity. The details of the measurements are found under benzene.

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.97 mole % purity. Two experimental tubes were used, and four determinations were carried out giving the range of observation of 0.02°. Just before the reappearance of the meniscus, the vapor became dark gray and opaque. The experiment was repeated using a sample of different origin, and virtually the same value for the critical temperature was obtained. The agreement was excellent between the results of this investigation and the one carried out earlier by Ambrose and Grant.

Partington, Rowlinson, and Weston[75] used a National Chemical Laboratory sample. Their value of t_c is a little higher than that reported by Ambrose and Grant but agrees satisfactorily with the measurements of Fischer and Reichel.[114]

Ambrose, Broderick, and Townsend's sample[16] for determining the P_c of toluene was the one used earlier in the same laboratory for measuring the critical temperature. Three tubes were used in the P_c determination.

Kobe and Lynn[1] selected the t_c value of Fischer and Reichel which is over 2° higher than the more recent values.

Simon's value[95] of t_c is considerably higher than that of Ambrose and coworkers. Ambrose, Cox, and Townsend's value of t_c and Ambrose, Broderick, and Townsend's value of P_c are selected as most reliable. The difference between the d_c values of Mathias[111] and Simon[95] is beyond the experimental uncertainty in d_c of the latter. Using the equation for the rectilinear diameter line given by Simon, d_c was calculated at the selected t_c, and the resulting value is selected.

c. Ethylbenzene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.972 mole % purity. Two experimental tubes were used, and four determinations of t_c were carried out giving the range of observation of 0.04°. Just before the reappearance of the meniscus, the vapor became black and opaque.

Ambrose obtained a sample of 99.81 mole % purity from the Phillips Petroleum Co. for determinations of t_c and P_c.

Kobe and Lynn[1] selected the critical temperature and the critical pressure values determined by Altschul.[100] The agreement between Ambrose's and Ambrose, Cox, and Townsend's t_c values is within the experimental error of both investigations.

The agreement between Simon's value[95] (see section IV.B.2.d) and those of Ambrose and coworkers is satisfactory. The t_c value selected is the average of the values reported by Ambrose and coworkers. Ambrose's value for P_c is recommended as most reliable. The selected d_c was calculated at 343.94° using the equation for the rectilinear diameter line given by Simon.

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(111) E. Mathias, *Compt. Rend.*, **115**, 34 (1892).

(112) N. W. Krase and J. B. Goodman, *Ind. Eng. Chem.*, **22**, 13 (1930).

(113) J. Harand, *Monatsh. Chem.*, **65**, 153 (1935).

(114) R. Fischer and T. Reichel, *Mikrochem. Acta*, **31**, 102 (1943).

d. *o*-Xylene

Ambrose and Grant[18] used a sample of 99.95 mole % purity supplied by the National Chemical Laboratory. The uncertainty in t_c was $\pm 0.05°$.

Ambrose, Broderick, and Townsend[16] used the same batch of sample as had Ambrose and Grant earlier and determined the critical pressure in the modified apparatus.

Glaser and Rüland[79] did not mention the source or the purity of the three xylenes used in their investigation. As they report the same value of t_c for the three xylenes, this value of t_c is uncertain. P_c values of all these xylenes are lower than Ambrose's values and as a result were not considered in the final selection.

Francis[88] did not give any details of his measurements of t_c for the three xylenes.

Kobe and Lynn[1] selected an average of the values reported by Altschul[100] and by Fischer and Reichel[114] for the critical temperature and Altschul's value for the critical pressure.

Ambrose and Grant's value[18] for the critical temperature and Ambrose, Broderick, and Townsend's value[16] for the critical pressure are selected. The d_c selected is calculated at the selected t_c using the equation for the rectilinear diameter line given by Simon[95] (see section IV.B.2.d).

e. *m*-Xylene

Ambrose and Grant[18] used a 99.97 mole % purity sample supplied by the National Chemical Laboratory. The uncertainty in t_c was $\pm 0.05°$. The same sample was used recently by Ambrose, Broderick, and Townsend[16] who reported a more precise value of t_c. This value differed considerably from their previous one. The low value obtained earlier is incompatible with the vapor pressure results, and therefore, 343.82° is the more reliable value for t_c.

Kobe and Lynn[1] selected Altschul's values[100] for the critical temperature and the critical pressure. American Petroleum Institute Research Project 44 recommended a value for the critical density, but, because it was not experimental, Kobe and Lynn[1] did not select any value for this property.

The agreement for t_c between Simon[95] (see section IV.B.2.d) and Ambrose, Broderick, and Townsend is satisfactory. The data of Ambrose for t_c and P_c are selected as most reliable. The d_c selected was calculated at 343.82° using the equation for the rectilinear diameter line given by Simon.

f. *p*-Xylene

Ambrose and Grant[18] used a 99.98 mole % purity sample supplied by the National Chemical Laboratory. The uncertainty in t_c was $\pm 0.05°$. Ambrose, Broderick, and Townsend[16] used the same sample to determine P_c of *p*-xylene.

Kobe and Lynn[1] selected the critical temperature determined by Fischer and Reichel[114] and the critical pressure from Altschul.[100]

Ambrose and Grant's value for t_c and Ambrose, Broderick, and Townsend's value for P_c are selected as most reliable. Using the equation for the rectilinear diameter line given by Simon[95] (see section IV.B.2.d), the d_c was calculated at the selected t_c and is recommended.

g. *n*-Propylbenzene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.80 mole % purity. Two experimental tubes were used, and four determinations were carried out giving the range of observation of 0.02°. As in the case of ethylbenzene, the vapor became black just before the reappearance of the meniscus.

Ambrose, Broderick, and Townsend's recent determinations[16] were made on the same sample used earlier by Ambrose, Cox, and Townsend, but the difference in t_c is slightly beyond the experimental uncertainty.

Kobe and Lynn selected Altschul's values[100] of t_c and P_c as these were the only values available at that time.

For t_c, an average of the two values from the National Chemical Laboratory is selected. Ambrose, Broderick, and Townsend's value of P_c is selected as most reliable. The selected d_c was calculated using the equation for the rectilinear diameter line given by Simon[95] (see section IV.B.2.d).

h. Isopropylbenzene

Ambrose and Grant[18] used a sample of 99.80 mole % purity supplied by the National Chemical Laboratory. The uncertainty in t_c was $\pm 0.05°$.

Ambrose, Broderick, and Townsend[16] reported new determinations of P_c on the same sample used earlier by Ambrose and Grant.[18]

Ambrose and Grant's value for the critical temperature and Ambrose, Broderick, and Townsend's value for the critical pressure are selected as most reliable.

i. *n*-Butylbenzene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.91 mole % purity. This substance is unstable at the critical temperature; therefore, the determinations were carried out in the rapid heater. Three experimental tubes were used, and 25 determinations were carried out. The rate of change of apparent t_c was $-1.3°/\text{hr}$.

Ambrose, Broderick, and Townsend[16] used the same sample and determined t_c and P_c. This newer value of t_c was 0.4° lower than the earlier one. As this substance is unstable at its critical temperature, extrapolation in

TABLE VII

ALKYLBENZENES

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
a. Benzene						
1910	288.5	47.9	0.3045 (0.3040)	Young	2, 19	72
1947	289.5	48.7	0.297	Gornowski, Amick, and Hixson	1, 19	108
1952	288.94	48.34	0.308	Bender, Furukawa, and Hyndman	5	109
1955	289	48		Oldenburg	1	110
1955	288.80			Kreglewski	1	84
1957	288.8			Ambrose and Grant	1	18
1957	288.5		0.3044	Simon	1, 19	95
1960	288.94			Ambrose, Cox, and Townsend	1	17
1960	288.7			Partington, Rowlinson, and Weston	1	75
1962	288.84	48.28		Connolly and Kandalic	1	85
1963		48.36		Ambrose and Townsend	1	19
1967		48.34		Ambrose, Broderick, and Townsend	1	16
1953	289	48.6	0.300	Kobe and Lynn		1
Selected value	288.94	48.34	0.302			
b. Toluene (Methylbenzene)						
1892			0.287	Mathias	19	111
1893	320.6	41.6		Altschul	1	100
1930		41.6		Krase and Goodman	16	112
1935	320.8			Harand	1	113
1943	320.8			Fischer and Reichel	4	114
1957	319.9		0.2913	Simon	1, 19	95
1957	318.6			Ambrose and Grant	1	18
1960	318.8			Partington, Rowlinson, and Weston	1	75
1960	318.57			Ambrose, Cox, and Townsend	1	17
1967		40.55		Ambrose, Broderick, and Townsend	1	16
1953	320.8	41.6	0.29	Kobe and Lynn		1
Selected value	318.57	40.55	0.292			
c. Ethylbenzene						
1893	346.4	38.1		Altschul	1	100
1957	344.0		0.2835	Simon	1, 19	95
1960	343.97			Ambrose, Cox, and Townsend	1	17
1967	343.92	35.62		Ambrose, Broderick, and Townsend	1	16
1953	346.4	38		Kobe and Lynn		1
Selected value	343.94	35.62	0.284			
d. *o*-Xylene (1,2-Dimethylbenzene)						
1893	358.3	36.9		Altschul	1	100
1943	358.5			Fischer and Reichel	4	114
1957	358			Francis	1	88
1957	357.1			Ambrose and Grant	1	18
1957	344.3	31.5		Glaser and Rüland	7	79
1957	357.9		0.2877	Simon	1, 19	95
1967		36.84		Ambrose, Broderick, and Townsend	1	16
1953	358.4	36.9		Kobe and Lynn		1
Selected value	357.1	36.84	0.288			
e. *m*-Xylene (1,3-Dimethylbenzene)						
1893	345.6	35.8		Altschul	1	100
1957	343.3			Ambrose and Grant	1	18
1957	344.3	33.0		Glaser and Rüland	7	79
1957	347			Francis	1	88
1957	343.6		0.2822	Simon	1, 19	95
1967	343.82	34.95		Ambrose, Broderick, and Townsend	1	16
1953	346	36		Kobe and Lynn		1
Selected value	343.82	34.95	0.282			
f. *p*-Xylene (1,4-Dimethylbenzene)						
1893	344.4	35.0		Altschul	1	100
1943	345.0			Fischer and Reichel	1	114
1957	343.0			Ambrose and Grant	1	18
1957	344.3	33.0		Glaser and Rüland	7	79

TABLE VII (*Continued*)

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
1957	346			Francis	1	88
1957	342.75		0.2807	Simon	1, 19	95
1967		34.65		Ambrose, Broderick, and Townsend	1	16
1953	345	35		Kobe and Lynn		1
Selected value	343.0	34.65	0.280			
				g. *n*-Propylbenzene		
1893	365.6	32.3		Altschul	1	100
1957	366.0		0.2727	Simon	1, 19	95
1960	365.21			Ambrose, Cox, and Townsend	1	17
1967	365.09	31.58		Ambrose, Broderick, and Townsend	1	16
1953	365.6	32		Kobe and Lynn		1
Selected value	365.15	31.58	0.273			
				h. Isopropylbenzene (Cumene)		
1893	362.7	32.2		Altschul	1	100
1957	357.9			Ambrose and Grant	1	18
1967		31.67		Ambrose, Broderick, and Townsend	1	16
1953	362.7	32		Kobe and Lynn		1
Selected value	357.9	31.67				
				i. *n*-Butylbenzene		
1957	387.8		0.2697	Simon	1, 19	95
1960	387.3			Ambrose, Cox, and Townsend	1	17
1967	386.9	28.49		Ambrose, Broderick, and Townsend	1	16
Selected value	387.3	28.49	0.270			
				j. 1,4-Diethylbenzene		
1960	384.72			Ambrose, Cox, and Townsend	1	17
1967	384.74	27.66		Ambrose, Broderick, and Townsend	1	16
Selected value	384.73	27.66				
				k. 1,2,3-Trimethylbenzene		
1960	391.35			Ambrose, Cox, and Townsend	1	17
1967	391.24	34.09		Ambrose, Broderick, and Townsend	1	16
1953	395	31	0.28	Kobe and Lynn		1
Selected value	391.30	34.09				
				l. 1,2,4-Trimethylbenzene		
1893	381.2	33.2		Altschul	1	100
1960	375.87			Ambrose, Cox, and Townsend	1	17
1967	375.94	31.90		Ambrose, Broderick, and Townsend	1	16
1953	381.2	33		Kobe and Lynn		1
Selected value	375.90	31.90				
				m. 1,3,5-Trimethylbenzene (Mesitylene)		
1893	367.7	33.2		Altschul	1	100
1960	364.14			Ambrose, Cox, and Townsend	1	17
1967	364.12	30.86		Ambrose, Broderick, and Townsend	1	16
1953	368	33		Kobe and Lynn		1
Selected value	364.13	30.86				

the critical pressure experiments of Ambrose, Broderick, and Townsend is considered more uncertain than that in the earlier measurement of t_c made by him and his coworkers.

The value of Ambrose, Cox, and Townsend for t_c and the value of Ambrose, Broderick, and Townsend for P_c are selected as most reliable. The d_c selected was calculated at 387.3° using the equation for the rectilinear diameter line given by Simon[95] (see section IV.B.2.d).

j. 1,4-Diethylbenzene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.88 mole % purity. Two experimental tubes were used, and four determinations of t_c were carried out with the range of observation of 0.06°. They reported t_c for isobutylbenzene, but it was later discovered that the sample used was in fact 1,4-diethylbenzene and not isobutylbenzene.[16]

Ambrose, Broderick, and Townsend[16] used a sample of 99.98 mole % purity obtained from the American Petroleum Institute Research Project 6. The two determinations from the same laboratory are almost identical. An average of the two values for t_c and Ambrose, Broderick, and Townsend's value of P_c are selected. No previous experimental determinations are available for this compound.

k. 1,2,3-Trimethylbenzene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.990 mole % purity. Two experimental tubes were used, and four determinations of t_c were carried out with the range of observation of 0.02°. Ambrose, Broderick, and Townsend[16] used the same sample, and obtained a new value of t_c which was almost within the experimental uncertainty of their previous value.

Kobe and Lynn[1] reported American Petroleum Institute Research Project 44 values for all critical constants which are the correlated values. No previous experimental values are available for this compound.

As there are two values of t_c from the same laboratory differing by 0.11°, a mean of the two values for t_c and Ambrose, Broderick, and Townsend's value of P_c are selected as most reliable.

l. 1,2,4-Trimethylbenzene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.987 mole % purity. Two experimental tubes were used, and five determinations of t_c were carried out with the range of observation of 0.02°. Ambrose, Broderick, and Townsend[16] carried out his determinations on the same sample and obtained t_c which agreed satisfactorily with the earlier one.

Kobe and Lynn[1] selected Altschul's values,[100] which were the only previous experimental values of the critical temperature and the critical pressure available.

The recent values of t_c are considerably lower than Altschul's value. This difference could be due to impurities in the sample used by Altschul. An average of the values for t_c from the National Chemical Laboratory and Ambrose, Broderick, and Townsend's value of P_c are selected.

m. 1,3,5-Trimethylbenzene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.96 mole % purity. Two experimental tubes were used, and four determinations were carried out with the range of observation of 0.01°. Just before the reappearance of the meniscus, the vapor became black (becoming gray as the meniscus formed). Ambrose, Broderick, and Townsend[16] used the same sample for his determinations, and the agreement of this t_c value with the earlier value was excellent.

Kobe and Lynn[1] selected Altschul's values[100] for the critical temperature and the critical pressure. No experimental critical density value was available.

An average of the two values of Ambrose and his coworkers for t_c and Ambrose, Broderick, and Townsend's value for P_c are selected.

2. Biphenyls and Terphenyls (Table VIII)[115–118]

a. Biphenyl

Cork[117] used a sample supplied by the Federal Phosphorus Co., without further purification. The P_c value was determined at the t_c from the log P *vs.* $1/T$ plot.

The starting material used by Mandel and Ewbank[118] was an Eastman Kodak White Label sample. The material was sublimed under vacuum to give 99.9 mole % purity. Another sample, recrystallized from methanol and then sublimed, showed 100 mole % purity. Both of these samples were used for measurements, and the same experimental results were obtained in each case. The temperatures were measured with four chromel–alumel thermocouples and a Leeds and Northrup potentiometer. The temperature gradients were controlled to within 1–2°. The P_c was obtained at the T_c from the log P *vs.* $1/T$ plot using the experimental vapor pressure data of Silvey.[119] The experimental uncertainty in P_c was ±0.15 atm.

The large variation in the critical constants of biphenyl may be attributed to impurities in the samples used by various investigators. Mandel and Ewbank[118] purified their sample with care, and hence their critical constants are selected as the most probable values.

b. *o*-, *m*-, and *p*-Terphenyls

Experimental values of t_c, P_c, and d_c for the three terphenyls, *o*-, *m*-, and *p*-, were determined by Mandel and Ewbank.[118] These are the only data available in the literature and are reported in Table VIIIb.

The terphenyls were Eastman Kodak White Label materials. The *o*- and *p*-terphenyls, initially of 99.0 +% purity, were sublimed under vacuum to give a final purity of 99.9 mole %. The *m*-terphenyl contained 4.75% of the *para* isomer as indicated by the gas chro-

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(115) T. Carnelley, *J. Chem. Soc.*, **37**, 701 (1880).

(116) P. A. Guye and E. Mallet, *Compt. Rend.*, **133**, 1287 (1901).

(117) J. M. Cork, *Rev. Sci. Instr.*, **1**, 563 (1930).

(118) H. Mandel and N. Ewbank, Atomics International, NAA-S-R-5129, 1960.

(119) F. C. Silvey, "Vapor Pressure of Polyphenyl Coolant and Components," NAA-S-R-5128, submitted for publication.

TABLE VIII

BIPHENYLS AND TERPHENYLS

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
			a. Biphenyl (Diphenyl)			
1880	374.5			Carnelley	1	115
1901	495.6	31.8		Guye and Mallet	1	116
1930	528	41.32	0.343	Cork	1, 16, 19	117
1957	496	30.8		Glaser and Rüland	7	79
1960	515.6	37.5	0.307	Mandel and Ewbank	1, 16, 19	118
Selected value	516	38	0.307			
			b. Terphenyls (*o*-, *m*-, and *p*-)—Selected Values			
1960 (*o*-)	617.8	38.5	0.306	Mandel and Ewbank	16, 19	118
1960 (*m*-)	651.7	34.6	0.300	Mandel and Ewbank	16, 19	118
1960 (*p*-)	652.8	32.8	0.302	Mandel and Ewbank	16, 19	118

matographic analysis. It was used as such because of the difficulty in separating the two isomers.

The temperature profiles were measured with four chromel–alumel thermocouples and a Leeds and Northrup potentiometer. The temperature gradients were controlled to within 1–2°.

These compounds have very high critical temperatures, and so specially designed equipment was used for the determinations. The experimental method was the one used earlier by Cork and described in detail in the main article. At such high temperatures, these substances undergo pyrolytic decomposition, and the visual observation of the critical temperature is not possible. They determined t_c and d_c by plotting the orthobaric liquid, vapor, and mean densities and drawing the best line or curve through the plotted points up to the point where pyrolitic decomposition was observed. The mean density line was then extended as a straight line, and the liquid and vapor density curves extended in compliance with the law of rectilinear diameters up to the point where they intersected the mean density line and where the tangent to the apex of the resulting curve is zero. The use of this method resulted in the best approximation of t_c and d_c and did not yield the absolute values.

The critical pressure was obtained by plotting the experimental vapor pressure data for each substance on a log P *vs.* $1/T$ chart and extrapolating the resulting almost straight line to the critical temperature.

Some uncertainty exists in the values of these critical constants due to extrapolations from the experimental points to the critical point. The shape of the coexistence curve of the terphenyls was assumed to be parabolic. As the height of the experimental tubes was about 33 mm, the shape of the actual coexistence curve may very well be slightly flat at the top because of the gravitational effects. It is therefore likely that the "true" critical temperature is somewhat lower than that reported by Mandel and Ewbank.[118] As a result the d_c and P_c values are affected accordingly.

The error in t_c, P_c, and d_c for *o*-terphenyl is ±2% and that for *m*- and *p*-terphenyls is ±3%.

3. *Alkylnaphthalenes (Table IX)*[120,121]

a. Naphthalene

Ambrose, Cox, and Townsend[17] used a sample of 99.99 mole % purity obtained from the National Chemical Laboratory. One experimental tube was used, and three determinations of t_c were carried out with the range of observation of 0.10°. They quoted a previously determined experimental value of Zhuravlev[120] which is higher by 1.3°. (No details on Zhuravlev's value are available.)

Cheng, McCoubrey, and Phillips[96] obtained a "molecular weight determination" sample from Hopkin and Williams Ltd. The sample was purified by chromatography on alumina with benzene as eluent. It was recrystallized from benzene which was then removed by vacuum sublimation. The melting point of the sample was 80.3°. The literature value is 80.290°.[34]

Ambrose, Broderick, and Townsend[16] also used 99.99 mole % pure naphthalene supplied by the National Chemical Laboratory. The uncertainties in t_c and P_c were ±0.1° and ±0.05 atm, respectively.

Although the agreement between both investigations of Ambrose and his coworkers and Cheng, McCoubrey, and Phillips is fairly satisfactory for t_c, the values of Ambrose, Broderick, and Townsend are selected for the critical temperature and the critical pressure.

b. 1-Methylnaphthalene

Ambrose, Cox, and Townsend[17] used an American Petroleum Institute Research hydrocarbon of 99.98 mole % purity. One experimental tube was inserted in the oven which had been preheated to 495°. After 10 min, darkening was apparent in the sample, but after an additional hour the meniscus was still present at the oven temperature of 498°. When the tube was removed, the sample had been transformed to a black tar, indicating that the decomposition of the compound proceeded too fast for the critical temperature to be measured in their apparatus.

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(120) D. I. Zhuravlev, *Zh. Fiz. Khim.*, **9**, 875 (1937).

(121) E. Z. Schröder, *Z. Physik. Chem.*, **49B**, 271 (1941).

TABLE IX

ALKYLNAPHTHALENES

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
			a. Naphthalene			
1937	476.5			Zhuravlev	?	120
1941	479.5	41.61	0.314	Schröder		121
1960	475.2			Ambrose, Cox, and Townsend	1	17
1962	474.8			Cheng, McCoubrey, and Phillips	1	96
1967	475.20	39.98		Ambrose, Broderick, and Townsend	1	16
Selected value	475.20	39.98	0.31			
			b. 1-Methylnaphthalene			
1960	495			Ambrose, Cox, and Townsend	1	17
1963	499			Ambrose	1	89
Selected value	499					
			c. 2-Methylnaphthalene			
1963	488			Ambrose	1	89
Selected value	488					

Ambrose[89] used a sample of 99.93 mole % purity purified by the American Petroleum Institute Research Project 6. The determinations were made in the rapid heater. The estimated uncertainty in the measurement was ±1°, and the rate of change of apparent critical temperature was +0.7°/min.

The more recent value of Ambrose for the critical temperature is selected as most reliable.

c. 2-Methylnaphthalene

Ambrose[89] used a sample, supplied by the National Chemical Laboratory, of 99.80 mole % purity as determined from the freezing point measurements. One experimental tube was used, and the value of t_c was obtained in the rapid heater. The estimated uncertainty of measurement was ±1°, and the rate of change of apparent critical temperature was +0.3°/min.

As this is the only value of critical temperature available in literature, it is selected.

E. COMPOUNDS OF CARBON, HYDROGEN, AND OXYGEN

1. *Alcohols (Table X)*[122–130]

a. Methanol

Kay and Donham[27] used a high-purity commercial sample of methanol as the starting material. Purification was carried out by distillation at a reflux ratio of 19:1 or higher in the presence of metallic sodium, and the middle fraction was taken for subsequent determinations. The physical properties of the sample determined compared satisfactorily with other reliable published values, indicating high purity of the sample.

Efremov[122] measured the critical constants of C_1–C_{10} normal alcohols. Chemically Pure (CP) grade alcohols were further purified by distillation, and the liquids were degassed before transferring them into the sample tubes. The temperature was measured with a mercury-in-glass thermometer to within 0.1°. The t_c was determined to within 1°. The density at the critical point was calculated from the density–temperature plot based on the law of rectilinear diameters.

Kobe and Lynn[1] recommended Young's values[72] for t_c, P_c, and d_c as most reliable. Kay and Donham's value of t_c is slightly lower than that of Young, while P_c differs considerably from Young's value. Both investigations were carried out with utmost care on samples that appear to have been of high purity, although final purity was not reported. However, Kay and Donham's sample was likely to be more pure. Efremov's value of t_c is not as precise as other values. Therefore the values of Kay and Donham are recommended for t_c and P_c. Excellent agreement exists between the d_c values of all the investigations, and 0.272 g/cm³ is selected.

b. Ethanol

Details regarding the determination of the t_c and d_c by Efremov[122] are the same as discussed for methanol. These newer values for ethanol are in very good agreement with the older values of Young.[72] Young's values for the critical constants are selected.

c. 1-Propanol

Ambrose and Townsend[19] used the alcohol prepared at the National Chemical Laboratory by purification of

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(122) Y. V. Efremov, *Russ. J. Phys. Chem.*, **40**, 667 (1966).

(123) A. Kreglewski and B. J. Zwolinski, *J. Phys. Chem.*, **65**, 1050 (1961).

(124) W. Herz and E. Neukirch, *Z. Physik. Chem.*, **104**, 433 (1923).

(125) R. Singh and L. W. Shemilt, *J. Chem. Phys.*, **23**, 1370 (1955).

(126) J. C. Brown, *J. Chem. Soc.*, **89**, 311 (1906).

(127) A. Nadejdine, *Rept. Physik*, **23**, 639 (1887).

(128) A. Kreglewski, *Bull. Acad. Polon. Sci., Classe III*, **2**, 191 (1954).

(129) B. Pawlewski, *Chem. Ber.*, **16**, 2633 (1883).

(130) L. H. Krone and R. C. Johnson, *A.I.Ch.E. J.*, **2**, 552 (1956).

commercially available samples. The purity of the sample determined by means of gas–liquid chromatography and melting- or freezing-point measurements was 99.94 mole %. It was dried over calcium hydride for several days before it was transferred under vacuum into the experimental tubes. There was visible reaction with the calcium hydride, which showed that the treatment was necessary for obtaining consistent results. Temperatures were measured with a small thermometer made in the laboratory and designed to fit in the space available in the oven. It was frequently calibrated against a Pt resistance thermometer.

The piston and cylinder assemblies for the pressure measurement were calibrated at the National Physical Laboratory.

Kobe and Lynn[1] selected the average of t_c values reported by Young[72] and by Fischer and Reichel.[114] The P_c and d_c values of Young were selected as most probable.

There is very good agreement between Young's value of t_c and that of Ambrose and Townsend,[19] but P_c values differ by almost 1 atm. Because Ambrose and Townsend used a sample of higher purity than the one used by Young, their values of t_c, P_c, and d_c are selected.

d. 1-Butanol

Kay and Donham[27] used a high-purity commercial sample as starting material. Further purification involved distillation in the presence of magnesium turnings as dessicating agents since the butanol forms an azeotrope with water. Physical properties of the sample used for the determination agreed satisfactorily with the reliable literature values. The temperatures were measured to within 0.02° with a copper–constantan thermocouple and a sensitive potentiometer.

Singh and Shemilt[125] used a CP grade sample distilled at high reflux successively from calcium oxide, fresh magnesium, and activated alumina. Middle cuts were collected, and the final product gave a refractive index, n_D^{25} 1.3973, and bp 117.5° (760 mm). The literature values are n_D^{25} 1.3973 and normal bp 117.73°.[35] The temperatures were measured by copper–constantan thermocouples calibrated against a NBS platinum resistance thermometer.

Ambrose and Townsend[19] purified a commercial sample in the same manner described earlier for 1-propanol. The purity of the sample used for the measurements was 99.94 mole %.

Kobe and Lynn[1] did not have very precise data available for selection in 1953. At present, these are excellent determinations of two independent investigating groups, namely Kay and Donham[27] and Ambrose and Townsend,[19] who agree very satisfactorily for all the three critical properties. Values reported by Singh and Shemilt[125] differ considerably from those of the other two. This is especially difficult to understand as the sample they used appears to be of high purity. An average value of Kay and Donham and Ambrose and Townsend is selected for t_c. Ambrose and Townsend's values for P_c and d_c are recommended because of their higher precision over Kay's values.

e. Some normal alcohols (Table Xe and h)

The data reported for 1-pentanol, 1-hexanol, 1-nonanol, and 1-decanol are determined by Efremov[122] on CP grade alcohols which were purified further before use. Final purity of the samples was not reported. The critical temperature was determined to within 1°.

From the analysis of t_c data on these compounds, it is observed that a constant increment of 25° exists for the $-CH_2$ increment in the homologous series beyond 1-heptanol. If this were true, then one would obtain an infinite value of t_c for an infinitely long 1-alcohol. It is empirically shown, however, that $T_{c,\infty}$ reaches a constant value, namely 961°K.[123] Efremov also determined surface tensions of these alcohols from 0° to the near-critical temperature. Efremov's data were plotted and the critical temperatures of these alcohols determined from the surface tension–temperature plot. Values of t_c determined in this way were consistently lower than the observed t_c values for 1-nonanol and 1-decanol, affording reason to believe that the observed values for these two alcohols may be in error. Hence the t_c values obtained from the surface tension plots for 1-nonanol and 1-decanol are recommended. The d_c values selected for these two compounds were calculated at the selected t_c using the experimental saturated liquid and vapor densities given by Efremov.

f. 1-Heptanol

Brown[126] carried out two experiments, and a total of eight observations of t_c were made. The value of t_c reported was the mean of the maximum value of 366.5° and the minimum value of 363.25°.

Efremov[122] used a CP grade sample and measured t_c to within 1°.

The agreement between the two investigators is poor. It is very difficult in such cases to recommend the "best" value as no details regarding sample purity, etc., are available. The surface tension–temperature plot of Efremov predicts a value close to 360°, and on this basis his reported value of 360° for t_c is selected. The critical density of Efremov is selected.

g. 1-Octanol

Brown[126] made eight observations for t_c obtaining a maximum value of 387.25° and a minimum value of 383.5°. The mean of these two values was reported as t_c. No details of the sample purity were given. Fischer and Reichel[114] used "pure" material but gave no additional details. Efremov[122] used CP grade alcohol and obtained t_c good to within 1°.

TABLE X
ALCOHOLS

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
a. Methanol (Methyl Alcohol)						
1910	240.0	78.47	0.2722	Young	2, 19	72
1955	239.43	79.9	0.272	Kay and Donham	5, 19	27
1966	240		0.272	Efremov	1, 19	122
1953	240.0	78.5	0.272	Kobe and Lynn		1
Selected value	239.43	79.9	0.272			
b. Ethanol (Ethyl Alcohol)						
1910	243.1	63.0	0.2755	Young	2, 19	72
1966	243		0.275	Efremov	1, 19	122
1953	243	63.0	0.276	Kobe and Lynn		1
Selected value	243.1	63.0	0.276			
c. 1-Propanol (*n*-Propyl Alcohol)						
1910	263.7	50.16	0.2734	Young	2, 19	72
1943	264.1			Fischer and Reichel	4	114
1963	263.56	51.02	0.2754	Ambrose and Townsend	1, 19	19
1966	264		0.273	Efremov	1, 19	122
1953	264	50.2	0.273	Kobe and Lynn		1
Selected value	263.56	51.02	0.275			
d. 1-Butanol (*n*-Butyl Alcohol)						
1923	287.0	48.4		Herz and Neukirch	1	124
1943	288.0			Fischer and Reichel	4	114
1955	289.74	43.6	0.267	Kay and Donham	5, 19	27
1955	286.95	48.60	0.2700	Singh and Shemilt	1, 19	125
1963	289.83	43.55	0.2699	Ambrose and Townsend	1, 19	19
1966	288		0.271	Efremov	1, 19	122
1953	288	49		Kobe and Lynn		1
Selected value	289.78	43.55	0.270			
e(1). 1-Pentanol						
1966	313		0.270	Efremov	1, 19	122
Selected value	313		0.270			
e(2). 1-Hexanol						
1966	337		0.268	Efremov	1, 19	122
Selected value	337		0.268			
f. 1-Heptanol						
1906	365.3			Brown	1	126
1966	360		0.267	Efremov	1, 19	122
Selected value	360		0.267			
g. 1-Octanol						
1906	385.46			Brown	1	126
1943	384.6			Fischer and Reichel	1	114
1966	385		0.266	Efremov	1, 19	122
Selected value	385		0.266			
h(1). 1-Nonanol						
1966	410		0.265	Efremov	1, 19	122
Selected value	404		0.264			
h(2). 1-Decanol						
1966	435		0.264	Efremov	1, 19	122
Selected value	427		0.264			
i. 2-Propanol (Isopropyl Alcohol)						
1883	253.0	53.1		Nadejdine	1	127
1904			0.274	Mathias	19	39

TABLE X (*Continued*)

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
1943	235.6			Fischer and Reichel	4	114
1955	235.30			Kreglewski	1	84, 128
1963	235.09	47.02	0.2727	Ambrose and Townsend	1, 19	19
1953	235.6	53	0.274	Kobe and Lynn		1
Selected value	235.16	47.02	0.273			
j. 2-Butanol (*sec*-Butyl Alcohol)						
1906	265.19			Brown	1	126
1963	262.80	41.39	0.2755	Ambrose and Townsend	1, 19	19
1953	265			Kobe and Lynn		1
Selected value	262.80	41.39	0.276			
k. 2-Octanol						
1906	364.12			Brown	1	126
Selected value	364					
l. 2-Methyl-1-propanol (Isobutyl Alcohol)						
1906	277.63			Brown	1	126
1955	276.65			Kreglewski	1	84, 128
1955	274.59	42.4	0.269	Kay and Donham	1, 19	27
1963	274.56	42.39	0.2722	Ambrose and Townsend	1, 19	19
Selected value	274.58	42.39	0.272			
m. 2-Methyl-2-propanol (*t*-Butyl Alcohol)						
1883	234.9			Pawlewski	1	129
1956	235.72	41.8	0.26	Krone and Johnson	1, 16, 19	130
1963	233.0	39.20	0.2700	Ambrose and Townsend	1, 19	19
Selected value	233.0	39.20	0.270			
n. 3-Methyl-1-butanol						
1883	306.6			Pawlewski	1	129
1906	309.77			Brown	1	126
1943	307.2			Fischer and Reichel	1	114
1955	306.25			Kreglewski	1	84, 128
Selected value	306.25					
o. 2-Methyl-2-butanol						
1906	271.77			Brown	1	126
Selected value	272					

The agreement between the three investigators for t_c is reasonably satisfactory; therefore a mean value of 385° is recommended. The critical density of Efremov is selected as most reliable.

h. 1-Nonanol and 1-decanol

These compounds are discussed in section E.1.e above.

i. 2-Propanol

Kreglewski[128] purified his material by submitting it to careful rectification. The slight amount of moisture present was removed by treating the sample with metallic sodium. The boiling range of the sample was 0.01°. The sample had bp 82.3° (750 mm) as compared to the literature value of 82.33° (760 mm).[35]

Ambrose and Townsend[19] used a sample of 99.96 mole % purity. The purification of the commercial sample was carried out in the same way as for 1-propanol.

Kobe and Lynn[1] selected the t_c of Fischer and Reichel,[114] the P_c of Nadejdine,[127] and the d_c of Mathias.[39]

An average of the values reported by Ambrose and Townsend and of Kreglewski is selected for t_c. The P_c and d_c of Ambrose and Townsend are selected.

j. 2-Butanol

Ambrose and Townsend[19] started with a sample of 99.95 mole % purity which was further purified in the same manner described for 1-propanol. Kobe and Lynn[1] report Brown's value[126] of t_c which is about 2° higher than the recent value of Ambrose and Townsend.

The values of Ambrose and Townsend for t_c, P_c, and d_c are selected as the "best" available so far.

k. 2-Octanol

The purity of the sample used by Brown[126] was not given. For 2-octanol, the difference between the two observations was about 0.8° and the value of t_c reported was the mean of the two extreme values. This is the only value available in the literature for this compound and is selected.

l. 2-Methyl-1-propanol

Kreglewski[84,128] purified his sample in the manner described for 2-propanol. The boiling point of the sample was 107.85° (755 mm).

Kay and Donham[27] purified their sample in the same way as described for 1-butanol. The exact purity of the sample used for the measurement of t_c was not stated. However, from the physical properties of this sample, it appears to be of high purity.

Ambrose and Townsend[19] used a sample of 99.93 mole % purity, purified as mentioned earlier.

Kobe and Lynn[1] did not report critical data for this compound, though Brown's value[126] for t_c was available at that time. Kay and Donham's values of t_c and P_c are in excellent agreement with Ambrose and Townsend's values. Kreglewski's value is too high; this fact cannot be accounted for on the basis of purity. Therefore an average of the values of Kay and Donham and of Ambrose and Townsend for t_c and Ambrose's values of P_c and d_c are selected as most reliable.

m. 2-Methyl-2-propanol

Krone and Johnson[130] distilled a starting material of 99% purity, and the center cut was withdrawn and dried over anhydrous calcium sulfate. The dried material was fractionally crystallized. The freezing point of the final sample indicated a purity of 99.8 mole % or better, while the refractive index measurements indicated a purity of 100 mole %. Temperatures were measured by means of copper–constantan thermocouples and a precision potentiometer calibrated against a NBS thermometer. Pressure measurements were carried out with a calibrated Heise pressure gauge.

Ambrose and Townsend[19] used a sample of 99.96 mole % purity. The purification of the material was carried out as described earlier. The uncertainty in t_c was ±0.2°.

Kobe and Lynn[1] did not report critical data for this compound. Pawlewski[129] reported a t_c in 1883 which lies between the two more recent investigations. Though Krone and Johnson used a high-purity sample, their value of t_c is much higher than that of Ambrose and Townsend. Confidence in the work of Ambrose and his coworkers was the deciding factor in the selection of their values for t_c, P_c, and d_c.

n. 3-Methyl-1-butanol

No details on Pawlewski's value[129] are available in the original article. Brown[126] used a sample with a normal boiling point of 130.0° with no additional comments regarding the purity of the sample. Two experiments were made with concordant results, and the mean of the two values was reported for t_c. Fischer and Reichel[114] stated that their sample was very pure but did not give any details regarding its purification.

Kreglewski[84,128] purified his sample in the manner described for 2-propanol and reported a boiling point for the sample of 131.85° (755 mm).

Since Kreglewski's value for t_c was carefully determined on a well-purified sample, it was selected as the best value.

o. 2-Methyl-2-butanol

Brown[126] did not mention the source and purity of the sample used in his investigation. Two experiments were carried out and concordant results were obtained.

Brown's value for t_c is the only one available in the literature and it was selected.

2. Ketones (Table XI)[131–133]

a. Acetone

Swietoslawski and Kreglewski[132] used a reagent grade acetone as the starting material. Initially it was treated with potassium iodide to remove impurities other than ketones and then dehydrated by redistilling over P_2O_5. The P_2O_5 treatment was repeated until the sample contained less than 0.0002% of water. The anhydrous acetone was kept in sealed tubes. The temperatures were measured with a calibrated mercury-in-glass thermometer.

Kobe, Crawford, and Stephenson[83] used commercially available acetone as the starting material. The sample was allowed to stand over Drierite for 24 hr to remove water present. It was then distilled through a packed column operated at a total reflux for at least 2 hr before the distillation was started. The middle fraction was distilled until a constant-boiling product was obtained. No observable change was noted in vapor pressure with changes in the liquid–vapor ratio indicating the sample of satisfactory purity. The sample had the following physical properties: n_D^{25} 1.35602, bp 56.4° (744.0 mm). These may be compared with the respective literature values of n_D^{25} 1.35596 and bp 56.29° (760 mm).[35]

The critical temperature was taken as the highest point of deviation from the smooth vapor pressure curve when either of the one-phase regions was entered. In this method it is difficult to locate the break point exactly and the error of measurement of t_c was ±0.3°. The temperatures, however, were measured to a precision of ±0.03°. The error in the measurement of the

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(131) M. Rosenbaum, M. S. Thesis, University of Texas, Austin, Texas, 1951.

(132) W. Swietoslawski and A. Kreglewski, *Bull. Acad. Polon. Sci., Classe III*, **2**, 187 (1954) (in English).

(133) W. B. Kay, *J. Phys. Chem.*, **68**, 827 (1964).

TABLE XI
ALKANONES (KETONES)

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
			a. 2-Propanone (Acetone)			
1951	235.5	46.6	0.273	Rosenbaum	8	131
1954	234.95			Swietoslawski and Kreglewski	1	132
1955	236.3	47.2	0.278	Kobe, Crawford, and Stephenson	8	83
1964	234.5	46.4		Kay	1	133
1953	235.5	46.6	0.273	Kobe and Lynn		1
Selected value	235.0	46.4	0.278			
			b. 2-Butanone (Methyl Ethyl Ketone)			
1951	260.5	39.46	0.252	Rosenbaum	8	131
1955	262.5	41.0	0.270	Kobe, Crawford, and Stephenson	8	83
1953	260	39.5	0.25	Kobe and Lynn		1
Selected value	262.5	41.0	0.270			
			c. 3-Methyl-2-butanone (Methyl Isopropyl Ketone)			
1955	280.2	38.0	0.278	Kobe, Crawford, and Stephenson	8	83
Selected value	280	38.0	0.278			

d. Some C_5 and C_6 Ketones—Selected Values

Compound	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators, year	Method	Ref
2-Pentanone (methyl *n*-propyl ketone)	290.8	38.4	0.286	Kobe, Crawford, and Stephenson, 1955	8	83
3-Pentanone (diethyl ketone)	287.8	36.9	0.256	Kobe, Crawford, and Stephenson, 1955	8	83
4-Methyl-2-pentanone (methyl isobutyl ketone)	298.3[a]	32.3		Kobe, Crawford, and Stephenson, 1955	8	83

[a] Selected value rounded off to three significant figures.

critical pressure amounted to about ±0.1 atm. The critical volumes were reported as accurate to only 0.5% owing to difficulties in locating sharp breaks in the vapor pressure–specific volume curve near the critical point.

Kay[133] used reagent grade acetone as the starting material. It was dried with dehydrated calcium sulfate and the decanted acetone was distilled in a 1.5-in. silvered and vacuum-jacketed fractionating column using a reflux ratio of 20:1.

Kobe and Lynn[1] recommended Rosenbaum's values[131] of t_c, P_c, and d_c. No experimental details are available regarding Rosenbaum's values. The t_c of Kobe, Crawford, and Stephenson is considerably higher than Swietoslawski and Kreglewski's value,[132] while Kay's is lower by 0.4°. As it is very difficult to remove water from acetone, it is likely that the sample used by Kobe and his coworkers contained traces of water. Swietoslawski and Kreglewski purified their sample with great care. For this reason, their value of t_c, rounded off to four significant figures, is selected. The P_c value of Kay and the d_c of Kobe, Crawford, and Stephenson are selected as most reliable.

b. 2-Butanone

Kobe, Crawford, and Stephenson[83] purified their sample in the manner described for acetone. The following properties determined by them were compared with the literature values in order to obtain an indication of purity: $n^{25}\text{D}$ 1.37629, bp 87.7° (743.5 mm) (lit.[35] $n^{25}\text{D}$ 1.3764, bp 79.64° (760 mm)). There appears to be a typographical error in the original article in reporting the boiling point at 743.5 mm.

Kobe and Lynn[1] selected Rosenbaum's values[131] as most reliable. The newer values of Kobe, Crawford, and Stephenson are much higher than Rosenbaum's values. If any water was present in Rosenbaum's sample, his critical constants should be higher than those of Kobe and his coworkers.

The values of Kobe, Crawford, and Stephenson are selected as most reliable.

c. 3-Methyl-2-butanone

Kobe, Crawford, and Stephenson[83] purified the commercial product as described for the purification of acetone. The physical properties of the sample were compared with the literature values as follows: $n^{25}\text{D}$ 1.38599, bp 93.6° (748.7 mm) (lit.[35] $n^{25}\text{D}$ 1.3857, bp 94.4° (760 mm)). This compound gave an increase in vapor pressure with time at the same specific volume as well as larger volumes. It decomposed at higher temperatures but slowly enough to determine the critical constants. The critical constants for this compound were not as reliable as those for acetone and others, because only one isometric was determined and so only one point of deviation was established.

TABLE XII
ETHANOIC ACID (ACETIC ACID)

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
1891	321.65	57.10		Young	2	134
1910	321.60	57.11	0.3506	Young	2, 19	72
1954	321.30			Swietoslawski and Kreglewski	1	135
1953	321.6	57.1	0.351	Kobe and Lynn		1
Selected value	321.30	57.1	0.351			

These are the only values available at this time and are recommended as most reliable.

d. Some C_5 and C_6 ketones

The critical constants of the ketones listed in Table XId were determined by Kobe, Crawford, and Stephenson.[83] No other experimental critical constants were found for these compounds. These compounds were purified in the manner described earlier for acetone. As the refractive indices at 25° and the boiling points close to the atmospheric pressure compared satisfactorily with the literature values, the compounds were assumed to be of high purity except methyl isobutyl ketone. This compound gave an increase in the vapor pressure with time at the same specific volume as well as at larger volumes, indicating decomposition at higher temperatures. Therefore, the critical volume of methyl isobutyl ketone could not be determined. These values of the critical constants are recommended as most reliable.

3. *Ethanoic Acid (Acetic Acid) (Table XII)*[134,135]

Swietoslawski and Kreglewski[135] fractionally distilled high-grade acetic acid to which a small amount of acetic anhydride was added. The main fraction, boiling from 118.1 to 118.3° (755 mm), was purified further by recrystallizing many times. The melting point of the sample was found to be 16.60 ± 0.03° (lit[35] 16.66°). The temperature was determined to within ±0.05°. In all, nine tubes were used and the meniscus in four tubes disappeared in the upper part, while in the remaining five tubes it disappeared in the lower part. Both sets of tubes gave an identical value for t_c of 321.30°.

Kobe and Lynn[1] selected Young's values[72] because of the high purity of the sample and extreme care taken in both of his determinations. The newer value of Swietoslawski and Kreglewski differs by only 0.3° from the 1910 value of Young.[72] As Swietoslawski and Kreglewski purified their sample with extreme care, their value of t_c is selected, and Young's values of P_c and d_c are selected.

4. *Esters of Mono- and Dicarboxylic Acids (Table XIII)*[136-140]

a. Methyl dodecanoate (methyl laurate)

Ambrose[89] used methyl laurate of 99.77 mole % purity. The t_c reported was the average of determinations on three tubes. The determinations were carried out in the rapid heater and the estimated uncertainty of extrapolation to zero time was ±2°. The rate at which the apparent t_c changed with time was −1°/min. Since no other literature values are available, Ambrose's value is selected.

b. Alkanoates (esters)

The critical constants reported in Table XIIIb for esters are old, and the uncertainty in t_c is estimated to be ±1.0 or more. Kobe and Lynn[1] did not report these data in their review article. These values should be considered only approximate.

c. Dimethyl oxalate

Eastman Kodak Co. supplied a Research Grade sample to Stern and Kay.[140] It was further purified by fractional crystallization from ethyl alcohol several times and degassed under high vacuum, and a portion was distilled into the experimental tubes. Dimethyl oxalate decomposed to a dark-colored liquid and a relatively insoluble gas above 200°. The critical temperature was determined by rapidly heating the sample to the temperature at which the meniscus disappeared. This procedure minimized the effect of the decomposition products on t_c but introduced a large uncertainty of ±7° in the t_c value. It was not possible to determine the critical pressure experimentally, but the vapor pressure from 163.3 to 260° was determined. The experimental data were fitted to an equation of the type, $\log P = A - (B/T)$, and P_c was calculated at t_c using this vapor pressure equation. This procedure involves a large extrapolation with a resulting uncertainty of ±4 atm in P_c.

Regnault[138] and Weger[139] reported P_c and t_c values, respectively, which are quoted in the "International

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(134) S. Young, *J. Chem. Soc.*, **59**, 903 (1891).

(135) W. Swietoslawski and A. Kreglewski, *Bull. Acad. Polon. Sci., Classe III*, **2**, 77 (1954)(in English).

(136) B. Pawlewski, *Chem. Ber.*, **15**, 2460 (1882).

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(139) F. Weger, *Ann. Chem.*, **221**, 61 (1883).

(140) S. A. Stern and W. B. Kay, *J. Phys. Chem.*, **61**, 374 (1957)

Critical Tables."[141] No details on sample purity or the procedure were available.

The difference between Stern and Kay's value[140] and the older ones is too large. Though Stern and Kay values are inaccurate to some extent owing to experimental difficulties, we believe they are nearer to the "true" values. Stern and Kay also applied Lydersen's empirical method and calculated $t_c = 366°$ and $P_c = 39.4$ atm.

From the above considerations, the values of Stern and Kay are recommended at the present time owing to lack of more precise values.

5. *Ethers* (*Table XIV*)[142–149]

a. Ethyl ether

Kobe, Ravicz, and Vohra[144] determined the critical constants of a number of compounds. The purification procedure and the temperature and pressure measurements for all these compounds were the same and are described in detail below.

The compound was first treated with Drierite to remove water, and those compounds containing peroxides were treated with ferrous sulfate. The sample was distilled, and 80% heat cuts were run through packed columns three times at a reflux ratio of 80:1. A double-junction chromel–alumel thermopile, capable of measuring temperature differences of the order 1/80°, was used to measure the temperatures. Temperatures were corrected by a calibration curve obtained by determining the vapor pressure curve of deaerated, triple-distilled water. Pressure measurements were corrected with a dead-weight gauge tester calibration. Corrections due to hydrostatic head, vapor pressure of Hg, and change of barometric pressure were also applied. The specific volume was corrected for thermal expansion of the steel bomb and the mercury it contained.

The boiling range for ethyl ether was 0.02°. The refractive index at 25° was 1.34955, and the boiling point at 753 mm was 34.2°. The literature values are $n^{25}\text{D}$ 1.34954 and bp 34.55° (760 mm).[35] The uncertainties in the measured quantities were t_c ±0.4°, P_c ±0.3 atm, and d_c ±0.010 g/cm^3.

Kay and Donham[27] used ethyl ether of analytical reagent grade without further purification. Air and other noncondensable gases were removed from the liquid samples by a series of operations which involved freezing with liquid nitrogen and pumping off the residual gas over the solid, followed by melting and distillation at low pressure. The normal boiling point and the density at 0° were determined, and both compared satisfactorily with the literature values.[35,36] The temperature was measured to within 0.02° with a copper–constantan thermocouple. The pressure was measured with a dead-weight piston gauge.

Zawisza[145] purified ethyl ether (commercial CP grade) by shaking first with $FeSO_4$ solution in dilute sulfuric acid then with water, drying with ($MgSO_4$), and carefully rectifying in the presence of metallic sodium. The purified sample was kept over sodium in darkness. Its purity was tested by determining the critical constant ($t_c = 193.6°$) and by finding the vapor pressure to be constant within ±0.05 atm between the bubble and the dew points. The uncertainty in the critical volume was 0.2%.

Kobe and Lynn[1] selected an average of the values reported by Young[72] and by Schroer.[142] The agreement between the t_c values of Kay and Donham and of Zawisza is good while that of Kobe, Ravicz, and Vohra is considerably lower. From comparison of the physical properties of their sample with the selected literature values, the sample used by Kobe, Ravicz, and Vohra appears to be of high purity. The lower value may be attributed to the different technique used for their t_c determination. Zawisza purified his sample by an elaborate procedure, and his values for t_c and P_c are selected as most reliable. Zawisza obtained 280.3 cm^3/mole for V_c corresponding to $d_c = 0.2619$ g/cm^3. An error of 0.2% in V_c as stated by Zawisza yields a value of $d_c = 0.2639$ g/cm^3 which is close to the other available d_c values. Kay and Donham's value of d_c is selected because it was calculated from the law of rectilinear diameters.

b. Ethylene oxide

Walters and Smith[148] obtained ethylene oxide with a maximum impurity of 0.5% by weight from Union Carbide Corp. The temperature was measured with two copper–constantan thermocouples calibrated at the sodium sulfate, steam, naphthalene, benzophenone, and lead points. Pressure was measured on a dead-weight gauge. They measured the volumetric behavior of ethylene oxide up to the critical point. However, they recommended the t_c and P_c of Hess and Tilton.[147] The V_c was determined by Walters and Smith with an uncertainty of 3% in V_c.

Kobe and Lynn[1] selected the t_c and P_c of Hess and Tilton and d_c of Post.[146]

The values of t_c and P_c selected are of Hess and Tilton rounded off to three significant figures. The value of

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(141) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1931, p 248.

(142) E. Schroer, *Z. Physik. Chem.*, **140,** 240 (1929).

(143) E. Schroer, *ibid.*, **140,** 379 (1929).

(144) K. A. Kobe, A. E. Ravicz, and S. P. Vohra, *J. Chem. Eng. Data*, **1,** 50 (1956)

(145) A. C. Zawisza, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **15,** 291 (1967).

(146) R. G. Post, Chemical Engineering Report No. 362, University of Texas, Austin, Texas, 1950.

(147) L. G. Hess and V. V. Tilton, *Ind. Eng. Chem.*, **42,** 1251 (1950).

(148) C. J. Walters and J. M. Smith, *Chem. Eng. Progr.*, **48,** 337 (1952).

(149) K. Hojendahl, *Kgl. Danske Videnskab. Selskab., Mat.-Fys. Medd.*, **24** (2), 1 (1946).

TABLE XIII

ESTERS OF MONO- AND DICARBOXYLIC ACIDS

a. Methyl Dodecanoate (Methyl Laurate)

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
1963	439			Ambrose	1	89
Selected value	439					

b. Alkanoates (Esters)

Compound	t_c, °C	P_c, atm	d_c, g/cm³	Investigator	Method	Ref
Isobutyl methanoate (isobutyl formate)	278.2[a]			Nadejdine	1	127
n-Pentyl methanoate (amyl formate)	302.6[a]			Nadejdine	1	127
Isopentyl methanoate (isoamyl formate)	304.6[a]			Pawlewski	1	136
n-Butyl ethanoate (*n*-butyl acetate)	305.9[a]			Pawlewski	1	136
Isobutyl ethanoate (isobutyl acetate)	295.8			Pawlewski	1	136
	288.3[a]			Nadejdine	1	127
Isopentyl ethanoate (isoamyl acetate)	326.2[a]			Brown	1	126
Methyl propanoate (methyl propionate)	257.4[b]	39.52[b]	0.312[b]	Young	2, 19	72
	262.7			Pawlewski	1	136
Ethyl propanoate (ethyl propionate)	272.9[b]	33.18[b]	0.296[b]	Young	2, 19	72
	280.6			Pawlewski	1	136
n-Propyl propanoate (*n*-propyl propionate)	304.8[a]			Pawlewski	1	136
Isobutyl propanoate (isobutyl propionate)	318.7[a]			Pawlewski	1	136
Isopentyl propanoate (isoamyl propionate)	338.2[a]			Brown	1	126
Ethyl butanoate (ethyl butyrate)	304.3			Pawlewski	1	136
	292.8[a]			Nadejdine	1	127
n-Propyl butanoate (*n*-propyl butyrate)	326.6[a]			Pawlewski	1	136
n-Propyl-2-methylpropanoate (*n*-propyl isobutyrate)	316.0[a]			Pawlewski	1	136
Isobutyl butanoate (isobutyl butyrate)	338.2[a]			Brown	1	126
Isobutyl 2-methylpropanoate (isobutyl isobutyrate)	328.7[a]			Brown	1	126
Isopentyl butanoate (isoamyl butyrate)	345.6[a]			Brown	1	126
Methyl pentanoate (methyl valerate)	293.7[a]			Nadejdine	1	127
Ethyl pentanoate (ethyl valerate)	297.0[a]			De Heen	?	137
Ethyl 3-methylbutanoate (ethyl isovalerate)	314.8[a]			Brown	1	126
n-Propyl 3-methylbutanoate (*n*-propyl isovalerate)	335.9[a]			Brown	1	126
Isobutyl 3-methylbutanoate (isobutyl isovalerate)	348.2[a]			Brown	1	126
Ethyl octanoate	385.6[a]			Brown	1	126
Ethyl nonanoate	400.8[a]			Brown	1	126

c. Dimethyl Oxalate

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigator	Method	Ref
1862		9.48		Regnault	?	138
1883	260			Weger	?	139
1957	355	39.3		Stern and Kay	1, 17	140
Selected value	355	39.3				

[a] Selected values rounded off to three significant figures. [b] Selected values.

d_c of Walters and Smith is selected and an uncertainty of ±0.009 g/cm³ is assigned.

c. Furan

Kobe, Ravicz, and Vohra[144] purified this sample in the manner described earlier for ethyl ether. A boiling range of 0.02° was observed for this sample. The following properties were determined: bp 30.7° (754 mm) and n^{25}D 1.41871. Decomposition of the compound was observed near the critical temperature; however, it was slow enough to enable measurements of the critical constants to be made. The estimated uncertainties were t_c ±1.7°, P_c ±1 atm, and d_c 0.01 g/cm³.

Cheng, McCoubrey, and Phillips[96] used a redistilled sample supplied by the Imperial Chemical Industries, Ltd. It was further treated with 5% potassium hydroxide, dried over anhydrous sodium sulfate, and distilled under vacuum over sodium. The boiling point of the sample was 31.33° (765 mm). The reproducibility of measurements and the agreement between the disappearance and the reappearance temperature was better than 0.1°.

The critical temperature of furan, determined by two independent investigators, differs by 3°. This difference does not seem to be due to the presence of impurities in the sample used by each. The method

TABLE XIV
ETHERS

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
a. Ethyl Ether (Diethyl Ether)						
1910	193.8	35.61	0.2625	Young	2, 19	72
1929	193.4	34.98	0.265	Schroer	1, 19	142
1929	194.6	35.6	0.265	Schroer	5	143
1943	192.3			Fischer and Reichel	4	114
1955	193.41	36.04	0.265	Kay and Donham	1, 19	27
1956	192.7	35.6	0.270	Kobe, Ravicz, and Vohra	8	144
1967	193.55	35.90	0.2619	Zawisza	1	145
1953	194	35.6	0.264	Kobe and Lynn		1
Selected value	193.55	35.90	0.265			
b. Ethylene Oxide						
1950			0.32	Post	19	146
1950	195.8	70.97		Hess and Tilton	?	147
1952			0.314	Walters and Smith	5	148
Selected value	196	71.0	0.314			
c. Furan						
1956	214	52.5	0.312	Kobe, Ravicz, and Vohra	8	144
1962	217.0			Cheng, McCoubrey, and Phillips	1	96
Selected value	217.0	54.3	0.312			
d. Tetrahydrofuran						
1956	268	51.2	0.322	Kobe, Ravicz, and Vohra	8	144
1962	267.0			Cheng, McCoubrey, and Phillips	1	96
Selected value	267.0	51.2	0.322			
e. Dioxane						
1946	312	50.7	0.36	Hojendahl	1, 16, 19	149
1956	314	51.4	0.370	Kobe, Ravicz, and Vohra	8	144
1957	315	54		Glaser and Rüland	7	79
1953	312	50.7	0.36	Kobe and Lynn		1
Selected value	314	51.4	0.370			

f. Miscellaneous Ethers—Selected Values

Compound	t_c, °C	P_c, atm	d_c, g/cm³	Method	Ref
Isopropyl ether	226.9 ± 0.2	28.4 ± 0.2	0.265 ± 0.010	8	144
Vinyl ethyl ether	202 ± 2	40.2 ± 0.7		8	144
1,2-Dimethoxyethane	263 ± 0.5	38.2 ± 0.3	0.333 ± 0.010	8	144
Propylene oxide	209.1 ± 0.4	48.6 ± 0.3	0.312 ± 0.010	8	144
2-Methylfuran	254 ± 2	46.6 ± 1	0.333 ± 0.020	8	144
2-Methyltetrahydrofuran	264 ± 1	37.1 ± 0.8	0.322 ± 0.020	8	144

used by Kobe, Ravicz, and Vohra is not as precise as the visual method of observation. Moreover, due to decomposition near the critical temperature, they might not have measured the "true" critical temperature. As Cheng, McCoubrey, and Phillips did not observe any decomposition of their sample, their t_c value is believed to be more reliable and was selected. The critical pressure was then calculated at the selected critical temperature using Kobe, Ravicz, and Vohra's vapor pressure data and their critical density value was also selected.

d. Tetrahydrofuran

The purification of the sample used by Kobe, Ravicz, and Vohra[144] was similar to the procedure described earlier for ethyl ether. The boiling range of the sample was found to be 0.02°. The boiling point at 748 mm was measured as 65.5°, and the refractive index at 25° was 1.40496. This compound was stable at the critical temperature. The estimated uncertainties were t_c ±1.1°, P_c ±0.7 atm, and d_c ±0.010 g/cm³.

Cheng, McCoubrey, and Phillips[96] obtained a redistilled sample from the Imperial Chemical Industries, Ltd. It was allowed to stand for 48 hr over freshly fused sodium hydroxide and for 24 hr over clean sodium wire. It was fractionally distilled under dry nitrogen and finally redistilled over lithium aluminum hydride *in vacuo*. The boiling range of this sample was 66.2–66.4° at 766 mm.

The difference in t_c obtained by the above investigators is 1°, within the experimental uncertainty of the value of Kobe and his coworkers. Cheng, McCoubrey, and Phillips measured their value precisely on a well-purified sample, so their value of t_c is selected. The critical pressure is calculated at the selected t_c using Kobe, Ravicz, and Vohra's vapor pressure data. As this calculated value of 51.0 atm falls within the uncertainty quoted by them for P_c, their values for P_c and d_c are selected.

e. Dioxane

Kobe, Ravicz, and Vohra[144] purified this sample in the same manner as described earlier for ethyl ether. The refractive index at 25° was 1.41923 and the boiling point at 745 mm was 100.5°. The literature values are $n^{25}{}_D$ 1.4202 and bp 101.5° (760 mm).[36] The sample decomposition near the critical temperature was small enough to enable determination of t_c with a precision of ±1°. Uncertainties of measurements were t_c ±1°, P_c ±0.8 atm, and d_c ±0.010 g/cm^3.

Glaser and Rüland's value[79] of t_c agrees satisfactorily with that of Kobe, Ravicz, and Vohra, but the P_c value is much higher. As no details regarding sample purity, etc., were available from Glaser and Rüland's article, Kobe, Ravicz, and Vohra's values are selected.

f. Miscellaneous ethers

The critical constants of the ethers listed in Table XIVf were determined by Kobe, Ravicz, and Vohra.[144] The purification procedure was the same as described earlier for ethyl ether. Kobe and his coworkers determined refractive indices at 20, 25, and 30° and the boiling point ranges in the neighborhood of 1 atm. The boiling ranges were 0.05° or less for all these compounds. The critical density of vinyl ethyl ether could not be determined because of the decomposition of the sample.

These reported values of Kobe, Ravicz, and Vohra are the only ones available in literature.

6. *Phenols* (*Table XV*)

a. Phenol

Ambrose[89] used a 99.93 mole % pure sample purified by the National Chemical Laboratory. Determinations were made on three tubes and the experimental uncertainty in measurement of t_c was ±0.1°. The rate of change of apparent critical temperature was +0.01°/min. In general, the rate of decomposition for phenols was low enough for the change in their critical temperature to be followed, allowing extrapolation to the beginning of the experiment.

Kobe and Lynn[1] selected the critical temperature and the critical pressure values of Herz and Neukirch.[124]

TABLE XV

PHENOLS

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
			a. Phenol			
1923	419.2	60.5		Herz and Neukirch	1	124
1963	421.1			Ambrose	1	89
1953	419.2	60.5		Kobe and Lynn		1
Selected value	421.1	60.5				
			b. *o*-Cresol (2-Methylphenol)			
1899	422.3			Radice	1	1, 150
1923		49.4		Herz and Neukirch	15	124
1957	422	48		Glaser and Rüland	7	79
1963	424.4			Ambrose	1	89
1953	422	49.4		Kobe and Lynn		1
Selected value	424.4	49.4				
			c. *m*-Cresol (3-Methylphenol)			
1902	432.0	45.0	0.346	Guye and Mallet	1	151
1957	432	45		Glaser and Rüland	7	79
1963	432.6			Ambrose	1	89
1953	432	45.0	0.35	Kobe and Lynn		1
Selected value	432.6	45.0	0.35			
			d. *p*-Cresol (4-Methylphenol)			
1899	426.0			Radice	1	1, 150
1923		50.8		Herz and Neukirch	1	124
1957	699	45		Glaser and Rüland	7	79
1963	431.4			Ambrose	1	89
1953	426	50.8		Kobe and Lynn		1
Selected Value	431.4	50.8				

e. Ethylphenols and Xylenols (Ambrose, 1963[89])—Selected Values

Compound	Obsd t_c, °C	Range of observation	Rate of change, deg/min	Purity, mole %
o-Ethylphenol	429.8	0.2	+0.01	99.94
m-Ethylphenol	443.3	0.1	+0.01	99.94
p-Ethylphenol	443.3	0.5	+0.02	99.97
2,3-Xylenol	449.7	0.25	+0.02	99.92
2,4-Xylenol	434.4	0.2	+0.03	99.97
2,5-Xylenol	449.9	0.3	+0.02	99.96
2,6-Xylenol	427.8	0.1	+0.01	99.89
3,4-Xylenol	456.7	0.5	+0.05	99.95
3,5-Xylenol	442.4	0.5	+0.02	99.96

The recent value of Ambrose for t_c appears to be more reliable and is selected, while for P_c the value of Herz and Neukirch is recommended.

b. *o*-Cresol

Ambrose[89] used a sample of 99.96 mole % purity supplied by the National Chemical Laboratory. Determinations of t_c were made with at least three experimental tubes giving an uncertainty of ±0.15°. The rate of change of apparent critical temperature was ±0.01°/min.

Glaser and Rüland's[79] values of t_c and P_c are lower than the more recent values of Ambrose. No details regarding their sample purity are available for all three cresols.

Kobe and Lynn[1] selected Radice's value[150] for the critical temperature and Herz and Neukirch's value[124] for the critical pressure.

Ambrose's value of t_c and Herz and Neukirch's value for P_c are recommended.

c. *m*-Cresol

Ambrose[89] used a sample of 99.91 mole % purity obtained from the National Chemical Laboratory. At least three experimental tubes were used for the determination of t_c giving an uncertainty of ±0.3°. The rate of change of apparent critical temperature was 0.02°/min.

Glaser and Rüland's values[79] for t_c and P_c agree satisfactorily with the values of other investigators.

The only values available for the critical constants prior to 1950 were those of Guye and Mallet[151] which were selected by Kobe and Lynn.[1]

The t_c value reported by Ambrose is selected. For P_c and d_c, the values of Guye and Mallet and of Glaser and Rüland are recommended as the most probable values.

d. *p*-Cresol

Ambrose[29] used a 99.96 mole % purity sample purified by the National Chemical Laboratory. At least three experimental tubes were used for the determination of t_c, giving an uncertainty of ±0.2°. The rate of change of apparent critical temperature was ±0.01°/min.

There appears to be an error in Glaser and Rüland's value[79] for t_c, which is disregarded.

Kobe and Lynn[1] selected Radice's value[150] of the critical temperature and Herz and Neukirch's value[124] of the critical pressure. The difference between Radice's value and that of Ambrose for critical temperature is rather large.

Ambrose's value for the critical temperature is selected, and for P_c the value reported by Herz and Neukirch is recommended.

e. Ethylphenols and xylenols

Ambrose[89] measured the critical temperature of the ethylphenols and the xylenols. Table XVe shows the purities of the compounds, the critical temperatures observed, the estimated uncertainty in the observed values, and the rate of change of apparent critical temperature with time in the last column. All these determinations were made on at least three experimental tubes except for 3,5-xylenol, where only two tubes were used.

No previous experimental values of the critical temperatures for these compounds were available in the literature. Therefore, Ambrose's values are recommended.

7. *Miscellaneous Compounds of Carbon, Hydrogen, and Oxygen* (*Table XVI*)

Pawlewski[129] obtained samples of dimethoxymethane (methylal) and 1,1-diethoxyethane (acetal) from Kahlbaum. The purities were checked by measuring the

TABLE XVI

MISCELLANEOUS COMPOUNDS OF CARBON, HYDROGEN, AND OXYGEN

Year	t_c, °C	P_c, atm	Investigators	Method	Ref
		a. Dimethoxymethane (Methylal)			
1883	223.6		Pawlewski	1	129
Selected value	224				
		b. 1,1-Diethoxyethane (Acetal)			
1883	254.4		Pawlewski	1	129
Selected value	254				
		c. Cyclohexanol			
1957	352	37	Glaser and Rüland	7	79
Selected value	352	37			
		d. Cyclohexanone			
1957	356	38	Glaser and Rüland	7	79
Selected value	356	38			
		e. Benzaldehyde			
1957	352	21.5	Glaser and Rüland	7	79
Selected value	352	21.5			
		f. Methoxybenzene (Anisole)			
1957	368.5	41.25	Glaser and Rüland	7	79
Selected value	368	41.2			
		g. Ethoxybenzene (Phenetole)			
1902	374	33.8	Guye and Mallet	1	151
Selected value	374	33.8			
		h. 2,4,6-Trimethyl-*s*-trioxane (Paraldehyde)			
1903	290		Hollmann	1	152
Selected value	290				

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(150) G. Radice, Doctoral Thesis, Genève, 1899; Landolt-Börnstein Tabellen, Vol. 1, Springer-Verlag, Berlin, 1923, p 256.

(151) P. A. Guye, and E. Mallet, *Compt. Rend.*, **134**, 168 (1902).

boiling points but the method of purification was not indicated.

These critical temperatures measured by Pawlewski are old values and should be considered only approximate.

Glaser and Rüland[79] determined critical constants for a number of technically important organic compounds: cyclohexanol, cyclohexanone, benzaldehyde, and methoxybenzene (anisole). No details as to purity or source of these compounds are given in the original article which dealt with the experimental determination of vapor pressure data in the high-temperature–high-pressure region. Critical constants for only 4 of the 22 compounds appearing in the original article are given in Table XVI. However, a number of the remaining compounds are discussed together with the work of other investigators elsewhere in this review. As agreement between Glaser and Rüland's values and those of other investigators is not satisfactory, the values reported in Table XVIc–f should be considered approximate.

No details regarding the measurements of Guye and Mallet[151] for ethoxybenzene (phenetole) are available.

Hollman[152] purified 2,4,6-trimethyl-*s*-trioxane (paraldehyde), commercial product, by repeated distillation. A fraction boiling between 123 and 124° was collected and distilled with sodium to remove water and acetaldehyde present in trace quantities. The freezing point of the sample used for the t_c measurement was 12.55°.

This is the only value of t_c available and is selected.

F. COMPOUNDS OF CARBON AND FLUORINE

1. *Perfluoroalkanes* (*Table XVII*)

a. Perfluoromethane (tetrafluoromethane)

No information was given regarding the preparation and purification of the sample or the determination of the t_c and P_c values by Fiske.[153]

No details regarding the Du Pont values[154] were available. Thermodynamic data were published in their Technical Bulletin T-14[154e] based on the experimental data taken at the University of Michigan.

Cheng and McCoubrey[155] reported the t_c value received from the Minnesota Mining and Manufacturing Co. No experimental details were given regarding this value.

The agreement between the t_c values of Fiske[153] and of Du Pont[154e] is satisfactory. The t_c reported by Cheng and McCoubrey is not considered in the final selection because it is much lower than the other t_c values. Averages of the values of Fiske and of Du Pont are selected for t_c, P_c, and d_c.

b. Perfluoroethane

Swarts[156] prepared hexafluoroethane by the electrolysis of trifluoroacetic acid. It was purified by fractional distillation and by crystallization. These crystallizations were followed by evacuation to remove completely the carbon tetrafluoride formed during electrolysis. The fluorine content of the sample was found to be 82.49% as compared with the true values of 82.59%. The freezing point and the normal boiling point of the sample were determined to be −106.3 and −79 to −78.6°, respectively. The literature values are normal freezing point −100.7° and normal boiling point −78.2°.[35] From the comparison of the freezing points, the sample used by Swarts[156] does not seem to be of high purity. The uncertainty in t_c was ±0.05°.

These are the only values of t_c and d_c available and are selected.

c. Perfluoro-*n*-propane

The sample used by Brown[157] was prepared in a jet reactor by burning *n*-propane in fluorine. The product was then distilled in a column having approximately 50 plates. The fore and the end cuts were discarded. The final product was analyzed by infrared spectroscopy and gas chromatography. These analyses showed a total of 0.06 mole % impurity consisting most probably of C_3F_7H isomers in the C_3F_8 sample. The sample was purged of noncondensable gases by freezing it in liquid nitrogen, pumping off the residual gas, closing off the cylinder, and allowing it to reach room temperature. This process was repeated until no pressure was observed on a manometer upon cooling the sample in liquid nitrogen. The purity of the sample used for the measurements was believed to be better than 99.9 mole %.

The temperatures were measured with a chromel–constantan thermocouple in conjunction with a Wenner potentiometer. The thermocouple was calibrated by comparison with a Leeds and Northrup Pt resistance thermometer which had been compared to a certified NBS thermometer. Pressures were measured with a 1000-psi Heise gauge having 1-lb subdivisions.

The critical volume and the critical pressure values were calculated from the isochore data taken near the critical density utilizing the observed t_c. The measured

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(152) R. Hollman, *Z. Physik. Chem.*, **43**, 129 (1903).

(153) D. L. Fiske, *Am. Soc. Heating Refrig. Aircond. Engrs. J.*, **57**, 336 (1949).

(154) E. I. Du Pont de Nemours and Co., Wilmington, Del.: (a) Freon-113, Technical Bulletin T-113A, 1938; (b) Freon-21, Technical Bulletin T-21, 1939; (c) Freon-115, Technical Bulletin T-115, 1958; (d) Freon-13, Technical Bulletin T-13, 1959; (e) Freon-14, Technical Bulletin T-14, 1961; (f) Freon-13 B1, Technical Bulletin T-13B1, 1963; (g) Freon-22, Technical Bulletin T-22, 1964; (h) Freon-11, Technical Bulletin T-11, 1965; (i) Freon, Technical Bulletin B-2, 1966; (j) Freon-12, Technical Bulletin T-12, 1966.

(155) D. C-H. Cheng and J. C. McCoubrey, *J. Chem. Soc.*, 4993 (1963).

(156) F. Swarts, *Bull. Soc. Chim. Belges*, **42**, 114 (1933).

(157) J. A. Brown, *J. Chem. Eng. Data*, **8**, 106 (1963).

liquid densities and the calculated vapor densities from the equation of state were used to derive a rectilinear diameter equation. The d_c value, calculated by the rectilinear diameter equation, differed by one unit in the third figure from that calculated from the isochore data. The experimental uncertainty in t_c was ±0.2°.

These are the only values available in the literature and therefore are selected.

d. Perfluoro-*n*-butane[158–160]

Brown and Mears[159] prepared perfluoro-*n*-butane by fractionating a commercial sample on a 24-bubble-plate Oldershaw column and taking a center cut. Comparison of liquid and vapor infrared spectra and information from the vapor chromatograph indicated the presence of low-boiling impurities. Those were removed from the sample by distillation in a vacuum-jacketed column of 50 theoretical plates packed with Helipak. Distillation was continued until no variation was observed in the infrared spectrum of the vapor. Further purification was carried out in the manner described earlier for perfluoro-*n*-propane. Gas chromatograph studies of the final sample showed less than 0.1 mole % impurity. From the studies of boiling point of the sample, it was believed to be of a purity better than 99.8 mole %. The temperature and pressure measurements were made in the manner discussed earlier for perfluoro-*n*-propane. The uncertainty in t_c was ±0.1°. The liquid densities were measured in a high-pressure steel pycnometer. The volume of the saturated vapor was obtained by solving the equation of state implicitly for vapor density at the vapor pressure corresponding to the desired temperature. The $P-V-T$ runs made near the critical density were used to calculate the critical pressure and the critical volume.

Zawisza[160] used perfluorobutane supplied by K and L Laboratories, New York, N. Y. It was deaerated and used without further purification. The difference between the dew- and the bubble-point pressures was about 0.03 atm.

Kobe and Lynn[1] selected Fowler and coworkers' values of t_c, P_c, and d_c because these were the only data available at that time.

The agreement between the recent values of Brown and Mears[159] and those of Fowler, *et al.*,[158] is very good. However, Zawisza's values[160] of t_c and P_c are lower. Brown and Mears carried out careful purification of the sample and for this reason their t_c and P_c values are selected as most reliable. The d_c value of 0.600 g/cm^3 was calculated by Brown and Mears from the isochore data. They also determined d_c using the rectilinear diameter equation derived by them from the experimental liquid densities and the calculated vapor densities. This procedure yielded a d_c of 0.629 g/cm^3, which is in good agreement with Fowler and his coworkers and is in fair agreement with Zawisza's value. Hence, the d_c of 0.629 g/cm^3 determined by Brown and Mears from the rectilinear diameter law is selected.

e. Perfluoro-*n*-pentane

Ermakov and Skripov[161] obtained the liquid sample from Urals Polytechnic Institute. It was purified by fractionation and was analyzed by infrared and nuclear magnetic resonance spectroscopy and by gas–liquid chromatography. The analysis showed that the compound contained hardly any hydrogen but was appreciably contaminated with isomers. The temperature was measured to a precision of ±0.1° with a copper–constantan thermocouple. The emf was determined with a low-resistance potentiometer using an M-25 galvanometer as the null instrument. The pressure in the chamber was measured with a piston manometer, the maximum error being ±0.01 atm. The pressure readings were corrected for the hydrostatic head. The t_c was determined to within 0.2° from the appearance and the disappearance of the liquid meniscus.

These are the only values of t_c and P_c available in literature. Because of the impurities present in the sample, these values should be considered only approximate.

f. Perfluoro-*n*-hexane

Dunlap, Murphy, and Bedford[162] obtained a sample of perfluoro-*n*-hexane through the Minnesota Mining and Manufacturing Co. The crude fluorocarbon was distilled in a fractionating column having 90 theoretical plates. A fraction having a boiling range from 56.9 to 57.6° was passed through a 200 cm × 1 cm adsorption column packed with silica gel. The sample was then passed through a cast iron pipe packed with cobalt trifluoride at 330°. No appreciable change in the gas and liquid densities was achieved with these two purifying processes. Fractional crystallization was carried out by cooling the liquid to −120° to initiate crystallization. After 21 crystallizations, the sample obtained had a molecular weight of 337.9 ± 0.3 g/mole. One further crystallization was carried out to yield the sample of 99.98 mole % purity determined from a freezing point curve. The density of the purified sample saturated with air at 25° was 1.66970 g/cm^3. Temperatures were measured with copper–constantan thermocouples calibrated against a standard thermometer between 0 and 50° and the vapor pressure of hexane above 50°. The calibrations were made at the

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(158) R. D. Fowler, J. M. Hamilton, J. S. Kasper, C. E. Weber, W. B. Burford, and H. C. Anderson, *Ind. Eng. Chem.*, **39,** 375 (1947).

(159) J. A. Brown and W. H. Mears, *J. Phys. Chem.*, **62,** 960 (1958).

(160) A. C. Zawisza, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **15,** 307 (1967).

(161) G. V. Ermakov and V. P. Skripov, *Russ. J. Phys. Chem.*, **41,** 39 (1967).

(162) R. D. Dunlap, C. J. Murphy, and R. G. Bedford, *J. Am. Chem. Soc.*, **80,** 83 (1958).

TABLE XVII

PERFLUOROALKANES

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
a. Perfluoromethane (Tetrafluoromethane)						
1949	−45.5	36.91	0.635	Fiske	?	153
1961	−45.7	36.96	0.626	E. I. du Pont de Nemours		154e
1963	−47.3			Cheng and McCoubrey	?	155
Selected value	−45.6	36.9	0.630			
b. Perfluoromethane (Hexafluoroethane)						
1933	19.7		0.617	Swarts	1, 19	156
Selected value	19.7		0.617			
c. Perfluoro-*n*-propane						
1963	71.9	26.45	0.628	Brown	1, 17, 19	157
Selected value	71.9	26.45	0.628			
d. Perfluoro-*n*-butane						
1947	113.3	23.	0.63	Fowler, Hamilton, Kasper, Weber, Burford, and Anderson	1, 16, 19	158
1958	113.2	22.93	0.600 0.629	Brown and Mears	1	159
1967	112.69	22.60	0.640	Zawisza	1	160
1953	113.3	23.	0.63	Kobe and Lynn		1
Selected value	113.2	22.93	0.629			
e. Perfluoro-*n*-pentane						
1967	148.7	20.1		Ermakov and Skripov	1	161
Selected value	149.	20.1				
f. Perfluoro-*n*-hexane						
1958	174.5			Dunlap, Murphy, and Bedford	1	162
1963	176.4			Cheng and McCoubrey	1	155
1967	178.5	18.8		Ermakov and Skripov	1	161
Selected value	174.5	18.8				
g. Perfluoro-*n*-heptane						
1947	202.5	19.(?)		Fowler, Hamilton, Kasper, Weber, Burford, and Anderson	1, 16	158
1951	201.7	16.0	0.584	Oliver, Blumkin, and Cunningham	1, 19	163
1952	201.5	15.95		Milton and Oliver	5	164
1967	204.6	17.3		Ermakov and Skripov	1	161
1953	201.6	16.0	0.584	Kobe and Lynn		
Selected value	201.6	16.0	0.584			

h. Perfluoro-*n*-alkanes, C_8, C_9, and C_{10}

Compound	t_c, ° C^a	P_c, atm^a	Investigators, year	Method	Ref
Perfluoro-*n*-octane	229.1	16.4	Ermakov and Skripov, 1967	1	161
Perfluoro-*n*-nonane	250.8	15.4	Ermakov and Skripov, 1967	1	161
Perfluoro-*n*-decane	269.2	14.3	Ermakov and Skripov, 1967	1	161

[a] Selected values rounded off to three significant figures.

Dry Ice point and at the mercury and sodium sulfate hydrate points. The precision in temperature measurement was ±0.01°.

The sample used by Cheng and McCoubrey[155] was supplied by the Imperial Chemical Industries, Ltd. The normal boiling point of the sample was found to be 56.6°. Nuclear magnetic resonance analysis indicated 5–10% impurities, consisting of other fluorocarbons of comparable chain length, which might affect the measured critical temperature by a degree or two. The sample was used without further purification.

The purification of the sample used by Ermakov and Skripov[161] was done in the manner described earlier for perfluoro-*n*-pentane. The sample was not very pure, containing a number of isomers. The uncertainty in t_c was ±0.2°.

The higher values of t_c of Cheng and McCoubrey and of Ermakov and Skripov may be due to the impurities in their samples which may have contained higher molecular weight fluorocarbons resulting in critical temperature greater than the "true" value. The sample used by Dunlap, Murphy, and Bedford[162] was of high purity, and on this basis their value for the critical temperature is selected. The critical pressure of Ermakov and Skripov[161] is recommended as the most probable value.

g. Perfluoro-*n*-heptane[163,164]

The sample used by Ermakov and Skripov[161] was purified in the manner described for perfluoro-*n*-pentane. The sample contained an appreciable quantity of isomers.

Kobe and Lynn[1] selected an average of the data of Oliver, Blumkin, and Cunningham[163] because of the higher purity of their sample. Ermakov and Skripov's values are considerably higher probably because of impurities in their sample.

The present selection is the same as that of Kobe and Lynn.[1]

h. Perfluoro-*n*-alkanes, C_8, C_9, and C_{10}

The critical constants of the perfluoro-*n*-alkanes reported in Table XVIIh were measured by Ermakov and Skripov.[161] The method and the purification procedure were the same as discussed for perfluoro-*n*-pentane. These are the only data available in the literature for these compounds.

On comparison of the critical constants of Ermakov and Skripov for the lower perfluoroalkanes with the other reliable values, it is found that Ermakov and Skripov's values are, on the average, higher by 3° in t_c. This difference may be due to the presence of a considerable amount of isomers in these samples. Therefore, these values of the critical constants should be considered only approximate.

2. Perfluorocycloalkanes (Table XVIII)

a. Perfluorocyclobutane[165,166]

The sample used by Douslin, Moore, and Waddington[24] was supplied by E. I. du Pont de Nemours & Co. The infrared analysis did not detect any impurities, but a vapor phase chromatographic analysis showed the presence of 0.2–0.3 mole % of a less volatile impurity. This impurity was removed by fractional distillation, and a center cut of at least 99.9 mole % purity was used for the experimental work. The temperature was measured to within 0.001° with a platinum resistance thermometer calibrated by the National Bureau of Standards. The critical constants were determined from the phase boundary curve. All pressure data inside the two-phase region, as well as in the single-phase gaseous and liquid regions, were corrected for the weight of the sample.

Martin[166] used perfluorocyclobutane which contained no impurities detectable by infrared analysis. The moisture content was about 0.0005% by weight, and the air content of the vapor phase was 0.11% by volume. The temperature was measured with a platinum resistance thermometer which was calibrated by the National Bureau of Standards.

In general, Bambach's values[165] for the critical constants are higher than those reported by Douslin, Moore, and Waddington, while Martin's values fall between those of Bambach[165] and Douslin and his coworkers[24] though closer to the latter's. The work of Douslin, *et al.*, was done with extreme care, and therefore their values are selected as most reliable. The critical pressure is rounded off to four significant figures and the critical density to three significant figures.

b. Perfluorocyclohexane

Rowlinson and Thacker[167] obtained a crude sample from the Atomic Energy Authority (U. K.) which was prepared by the fluorination of benzene. The material was purified first by sublimation *in vacuo* to remove nonvolatile impurities and then fractionally distilled at a pressure of 2 atm absolute. It was further purified by repeated fractional crystallization. From the infrared spectrum, it was estimated that the final sample used for the determinations contained at least 96% (molar) C_6F_{12} with the principal impurity being $C_6F_{11}H$. This impurity was analyzed further by vapor-phase chromatography which showed the presence of about 3 parts per 1000 (molar) of an impurity probably $C_6F_{11}H$ or an open-chain fluorocarbon.

As these are the only data available in the literature, they are selected as most reliable at present.

c. Perfluoromethylcyclohexane

The material used by Rowlinson and Thacker[167] was supplied by the Imperial Chemical Industries, Ltd. and was purified by fractional distillation. The fraction was then dried and analyzed by vapor phase chromatography. This analysis showed three impurities which were not identified by the authors nor did they specify the purity of the final sample used for determinations. The critical temperature was reproducible to 0.1°. The critical pressure determination was approximate.

Kobe and Lynn[1] selected Fowler and coworkers'[158] values which were the only ones available at that time.

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(163) G. D. Oliver, S. Blumkin, and C. W. Cunningham, *J. Am. Chem. Soc.*, **73**, 5722 (1951).

(164) H. T. Milton and G. D. Oliver, *ibid.*, **74**, 3951 (1952).

(165) G. Bambach, *Kaeltetechnik*, **11**, 334 (1956).

(166) J. J. Martin, *J. Chem. Eng. Data*, **7**, 68 (1962).

(167) J. S. Rowlinson and R. Thacker, *Trans. Faraday Soc.*, **53**, 1 (1957).

TABLE XVIII

PERFLUOROCYCLOALKANES

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
				a. Perfluorocyclobutane		
1956	115.39	27.68	0.631	Bambach		165
1959	115.22	27.412	0.6159	Douslin, Moore, and Waddington	5, 19	24
1962	115.32	27.46	0.620	Martin	1, 17, 19	166
Selected value	115.22	27.41	0.616			
				b. Perfluorocyclohexane		
1957	184.0	24		Rowlinson and Thacker	1	167
Selected value	184.0	24				
				c. Perfluoromethylcyclohexane		
1947	213.4	23		Fowler, Hamilton, Kasper, Weber, Burford, and Anderson	1, 16	158
1957	213.6	23		Rowlinson and Thacker	1	167
1953	213.4	24 (?)		Kobe and Lynn		1
Selected value	213.6	23				

There is remarkably good agreement in the critical temperature of these two investigations. Fowler, *et al.*, determined the critical temperature within 0.2°. The values of Rowlinson and Thacker for the critical temperature and the critical pressure are selected because they are within the experimental uncertainty of Fowler, *et al.*

3. Perfluoro Unsaturated and Aromatic Compounds (Table XIX)

a. Perfluoroethene (tetrafluoroethylene)

No experimental details for this compound are available. Renfrew and Lewis[168] reported that the critical constants were obtained from the Du Pont Co.

b. Perfluoro-1-hexene, -1-heptene, -cyclohexene, and -naphthalene

Cheng and McCoubrey[155] determined the critical temperature for a number of fluorocarbons. As these are the only experimental determinations available so far in the literature, the results for these compounds and their boiling points to indicate approximate purity are given in Table XIXb. In general, nmr studies revealed that these materials have 5–10% impurities, presumably other fluorocarbons of comparable chain length. For perfluorocyclohexene, a boiling point of 53.0° at 768 mm was obtained. It was estimated that these impurities would cause an error of less than 1–2° in the critical temperature.

c. Perfluorobenzene (hexafluorobenzene)

Cheng and McCoubrey[155] obtained the material of stated purity of 99 mole % from the Imperial Smelting Corp. The normal boiling point of the sample was found to be 80.6°, and the sample was used without further purification. Temperatures were measured with mercury-in-glass thermometers, checked against National Physical Laboratory calibrated thermometers, or with a calibrated thermocouple which had been thoroughly tested in measurements of the critical temperatures of standard hydrocarbons within 0.1–0.2°.

Patrick and Prosser[169] prepared their material by the pyrolytic defluorination over heated iron of a mixture of octafluorocyclohexa-1,3- and -1,4-dienes and then purification by preparative gas chromatography. Gas chromatography analysis showed only a peak corresponding to that of hexafluorobenzene. The probable impurities were the isomeric fluorinated dienes used as starting materials and pentafluorobenzene. Neither mass spectrometry nor the infrared spectrum revealed any impurities, which indicated them to be less than 0.1%, if present. The effect of variation of the amounts of liquid in the sample tube was investigated. The temperatures were reproducible to 0.2° on heating and cooling the sample through the critical state.

Counsell, Green, Hales, and Martin[170] obtained a sample of hexafluorobenzene from the National Smelting Co. It was purified by 12 fractional freezings and by rejecting 1% of the charge after each freezing. Gas-chromatographic examination of the purified specimen revealed traces of two impurities which were probably partially fluorinated benzenes. A calorimetric study of the melting behavior of the specimen indicated a purity of 99.97 ± 0.01 mole %. These critical constants were measured by Ambrose with the uncertainty of ±0.03° in t_c and ±0.05 atm in P_c.

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[168] M. M. Renfrew and E. E. Lewis, *Ind. Eng. Chem.*, **38**, 870 (1946).

[169] C. R. Patrick and G. S. Prosser, *Trans. Faraday Soc.*, **60**, 700 (1964).

[170] J. F. Counsell, J. H. S. Green, J. L. Hales, and J. F. Martin, *ibid.*, **61**, 212 (1965).

TABLE XXV

ALIPHATICS

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
a. Chlorotrifluoromethane (Freon 13)						
1941	28.8	39.4	0.581	Riedel	1, 16, 19	182
1952	28.86	38.2	0.578	Albright and Martin	1, 16, 19	183
1966	29.15	38.60	0.579	Michel, Wassenaar, Wolkers, Prins, and Klundert	5	184
1953	28.8	39	0.58	Kobe and Lynn		1
Selected value	28.9	38.7	0.579			
b. Dichlorodifluoromethane (Freon 12)						
1931	111.5	39.56	0.555	Gilkey, Gerardi, and Bixler	1, 19	185
1938	111.5	39.6	0.555	Benning and Machwood	1, 16, 19	186
1966	111.80	40.71	0.565	Michels, Wassenaar, Wolkers, Prins, and Klundert	5	184
1953	111.5	39.6	0.555	Kobe and Lynn		1
Selected value	111.80	40.71	0.558			
c. Trichlorofluoromethane						
1940	198.0	43.2	0.554	Benning and McHarness	1, 16, 19	187
1965	198.0	43.51	0.554	E. I. du Pont de Nemours		154h
1953	198.0	43.2	0.554	Kobe and Lynn		1
Selected value	198.0	43.5	0.554			
d. Chloropentafluoroethane						
1958	80.0	30.8	0.595	E. I. du Pont de Nemours		154c
1966	80.0	31.16	0.6131	Mears, Rosenthal, and Sinka	1, 18, 19	188
Selected value	80.0	31.16	0.613			
e. 1,1-Dichloro-1,2,2,2-tetrafluoroethane						
1955	145.5	32.6	0.582	Mears, Stahl, Orfeo, Shair, Kells, Thompson, and McCann	1, 16, 19	173
Selected value	145.5	32.6	0.582			
f. 1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)						
1944	145.7	32.3	0.582	Benning and McHarness	1, 16, 19	189
1960	145.7	32.2	0.582	Martin	1, 16, 19	190
1953	145.7	32.3		Kobe and Lynn		1
Selected value	145.7	32.2	0.582			
g. 1,2,2-Trichloro-1,1,2-trifluoroethane (Freon 113)						
1933	187.6			Hovorka and Geiger		191
1939	214.1	33.7	0.576	Benning and McHarness	1, 16, 19	187
1953	214.1	33.7	0.576	Kobe and Lynn		1
Selected value	214.1	33.7	0.576			
h. 1,1,2,2-Tetrachloro-1,2-difluoroethane						
1933	278.0			Hovorka and Geiger	1,?	191
Selected value	278.					
i. Bromotrifluoromethane						
1951	66.6	38.4		Waterman	?	192
1956	67.5	40.0	0.77	Plank		193
1963	67.0	39.12	0.745	E. I. du Pont de Nemours		154f
Selected value	67.0	39.2	0.76			

critical constants are available, the data of Benning and McHarness are selected.

h. 1,1,2,2-Tetrachloro-1,2-difluoroethane

Hovorka and Geiger[191] used the crude material synthesized in their laboratory and refluxed it over barium oxide to remove any water present. It was then fractionally distilled in a special high-fractionating column until a boiling point constant to 0.05° was obtained. Crystallization of this liquid did not affect the boiling point, indicating that the sample used was of satisfactory purity.

TABLE XXVI
AROMATICS

Year	t_c, °C	P_c, atm	Investigators	Method	Ref
			a. Chloropentafluorobenzene		
1966	297.8	31.8	Evans and Tiley	1, 17	171
Selected value	297.8	31.8			
			b. Bromopentafluorobenzene		
1966	397	44.6	Evans and Tiley	1, 17	171
Selected value	397	44.6			

Hovorka and Geiger mentioned that t_c was measured by the usual procedure but did not specify the method. It is assumed here that it was observed visually. This is the only value of t_c available for this compound and is selected.

i. Bromotrifluoromethane

Waterman[192] prepared $CBrF_3$ by heating a mixture of CBr_4, anhydrous SbF_3, and dry bromine to 180–220° under a pressure of 4–5 atm. The gas from the condenser was scrubbed with NaOH, dried, condensed with Dry Ice, and fractionated. The freezing and the boiling points of the sample were $-166°$ and $-58.67°$, respectively.

Plank[193] reported the values of the critical constants, but no source or purity of the sample was given.

No details regarding the values reported by E. I. du Pont de Nemours were found in their Technical Bulletin.[154f]

There is a large variation in the available experimental values for t_c, P_c, and d_c. The critical constants reported by Du Pont are selected as the most probable values.

2. *Aromatics (Table XXVI)*

a. Chloropentafluorobenzene

Evans and Tiley[171] measured the critical temperature of chloropentafluorobenzene of 99.8 mole % purity supplied by the Imperial Smelting Corp. This sample although it discolored near the t_c, gave constant values for t_c. The determination of P_c involved an extrapolation of 24°, and hence this value is only approximate.

b. Bromopentafluorobenzene

Evans and Tiley[171] also attempted to determine the t_c and P_c values on a sample of bromopentafluorobenzene of 99.6 mole % purity, but without much success. Instead they calculated the t_c assuming the same value of T_b/T_c as for the chloropentafluorobenzene. The P_c was calculated from the vapor pressure equation extrapolating through 70°.

The values cited for chloro- and bromopentafluorobenzene are approximate only.

J. COMPOUNDS OF CARBON, CHLORINE, FLUORINE, AND HYDROGEN

1. *Aliphatics (Table XXVII)*

a. Chlorodifluoromethane (Freon 22)

Benning and McHarness[187] purified their sample by repeated fractionation and checked the purity by means of the melting point and the change in the vapor pressure during distillation.

The critical constants reported in Table XXVIIa for chlorodifluoromethane were taken from the Technical Bulletin of E. I. du Pont de Nemours,[154g] where no details regarding the determination of these values are available. In this bulletin citations are given to unpublished new measurements of the vapor pressure and $P-V-T$ relationships for $CClF_2H$ from the University of Michigan and from the University of Amsterdam, respectively. Du Pont probably used Benning and McHarness's values of the critical constants and adjusted the P_c on the basis of some unpublished data. The critical constants of Du Pont are selected.

b. Dichloromonofluoromethane (Freon 21)

Benning and McHarness[187] purified the material in the manner described for chlorodifluoromethane. These values of the critical constants are selected.

c. 1-Chloro-1,1-difluoroethane (Freon 142)[173,193a]

For the discussion of the preparation, purification, and determination of the critical constants for this compound, the reader is referred to Mears, Stahl, Orfeo, Shair, Kells, Thompson, and McCann's work[173] in section IV.G.1.b(1),(2).

d. 2-Chloro-1,1-difluoroethylene

The details regarding the determinations of Mears, *et al.*,[173] are found in text section IV.G.1.b(1),(2). These are the only values available and are selected.

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(192) H. Waterman, U. S. Patent 2,531,752 (1951).

(193) R. Plank, Ed., "Handbuch des Kältetechnik," Vol. IV, Springer-Verlag, Berlin, 1956.

(193a) L. I. Cherneeva, *Teploenerg.*, **5**, 38 (1958); *Chem. Abstr.*, **52**, 193116 (1958).

TABLE XXVII

ALIPHATICS

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
a. Chlorodifluoromethane (Freon 22)						
1939	96.0	48.7	0.525	Benning and McHarness	1, 16, 19	187
1964	96.01	49.123	0.525	E. I. du Pont de Nemours	?	154g
Selected value	96.0	49.12	0.525			
b. Dichloromonofluoromethane (Freon 21)						
1939	178.5	51.0	0.522	Benning and McHarness	1, 16, 19	187
Selected value	178.5	51.0	0.522			
c. 1-Chloro-1,1-difluoroethane (Freon 142)						
1955	137.1	40.7	0.435	Mears, Stahl, Orfeo, Shair, Kells, Thompson, and McCann	1, 16, 19	173
1958	136.45	42.75	0.426	Cherneeva		193a
Selected value	137.1	40.7	0.435			
d. 2-Chloro-1,1-difluoroethylene						
1955	127.4	44.0	0.499	Mears, Stahl, Orfeo, Shair, Kells, Thompson, and McCann	1, 16, 19	173
Selected value	127.4	44.0	0.499			

K. COMPOUNDS OF CARBON, SULFUR, AND HYDROGEN (TABLE XXVIII)

1. *Thiaalkanes and Dithiaalkanes*

a. 2-Thiabutane (methyl ethyl sulfide)

No information is available concerning the preparation and purity of the sample used by Vespignani.[99]

Even though the determinations are not recent, these values for the t_c and the P_c are selected and rounded off to whole numbers.

b. 3-Thiapentane (ethyl sulfide)[194,195]

Kobe and Lynn[1] reported Berthoud and Brun's value[195] for d_c of 0.279 g/cm^3 instead of the actual value of 0.2842 g/cm^3.

Berthoud and Brun's value of t_c is about 0.8° lower and the P_c is lower by 8 atm than the other available values. Because of this variation in t_c and P_c values, Berthoud and Brun's critical constants rounded off to three significant figures are selected.

c. 4-Thiaheptane (*n*-propyl sulfide), 2,8-dimethyl-5-thianonane (isopentyl sulfide) and 3,4-dithiahexane (ethyl disulfide) (Table XXVIIIc–e)

No information is available regarding the preparation and the purity of these samples used by Ferretto.[194]

As these are the only values available for the t_c of these compounds, they are selected and rounded off to three significant figures.

2. *Methanethiol (Methyl Mercaptan)*

Berthoud and Brun[195] prepared methanethiol by the action of sodium methyl sulfate on sodium sulfhydrate in aqueous solution. The solution was treated first with sodium hydroxide to remove hydrogen sulfides and then with lead acetate to remove the remaining traces. The mercaptan was liberated by addition of acid chlorohydrate, condensed, washed in water, and dried with calcined caustic potash. The product was fractionally distilled, and the fraction boiling at 6.1–6.2° (727 mm) was used for the measurements. The reported t_c was the average of four observations.

These are the only values of the critical constants available and are selected.

3. *Thiophene*

Kobe, Ravicz, and Vohra[144] purified thiophene in the same manner described earlier for diethyl ether. The boiling range of the sample was 0.01°. The measured boiling point was 83.2° (744 mm) with $n^{25}\text{D}$ 1.52038. (The literature values are bp 84.16° (760 mm) and $n^{25}\text{D}$ 1.52572.[34]) The sample decomposed near t_c but did not appear to affect the t_c measurements. The estimated uncertainties were t_c ±1°, P_c ±0.8 atm, and d_c ±0.010 g/cm^3.

Cheng, McCoubrey, and Phillips[96] used chemical reagent thiophene supplied by the Hopkin and Williams Co. It was fractionally distilled, and the colorless distillate with a boiling point range of 84.5–84.6 ± 0.1° (772 mm) was collected. This sample was further distilled and the fraction having the following properties was used: bp 84.4–84.5° (769 mm) and $n^{26.5}\text{D}$ 1.5309. The experimental uncertainty in t_c was ±0.1°.

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(194) L. Ferretto, *Gazz. Chim. Ital.*, **30**, 296 (1900).

(195) A. Berthoud and A. Brum, *J. Chim. Phys.*, **21**, 143 (1924).

TABLE XXVIII

COMPOUNDS OF CARBON, SULFUR, AND HYDROGEN

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
				1(a) 2-Thiabutane (Methyl Ethyl Sulfide)		
1903	259.66	41.9		Vespignani	1	99
Selected value	260	42				
				(b) 3-Thiapentane (Ethyl Sulfide)		
1900	284.67			Ferretto	1	194
1903	284.60	47.1		Vespignani	1	99
1924	283.8	39.1	0.2842	Berthoud and Brum	1, 19	195
1953	284	39.1	0.279	Kobe and Lynn		1
Selected value	284	39.1	0.284			
				(c) 4-Thiaheptane (*n*-Propyl Sulfide)		
1900	380.4			Ferretto	1	194
Selected value	380					
				(d) 2,8-Dimethyl-5-thianonane (Isopentyl Sulfide)		
1900	391.25			Ferretto	1	194
Selected value	391					
				(e) 3,4-Dithiahexane (Ethyl Disulfide)		
1900	368.9			Ferretto	1	194
Selected value	369					
				2. Methanethiol (Methyl Mercaptan)		
1924	196.8	71.4	0.3315	Berthoud and Brum	1, 19	195
Selected value	196.8	71.4	0.332			
				3. Thiophene		
1888	317.3	47.7		Pawlewski	1	196
1956	307	56.2	0.385	Kobe, Ravicz, and Vohra	8	144
1962	306.2			Cheng, McCoubrey, and Phillips	1	96
1953	317	48		Kobe and Lynn		1
Selected value	306.2	56.2	0.385			
				4. Tetrahydrothiophene		
1962	358.8			Cheng, McCoubrey, and Phillips	1	96
Selected value	358.8					

The earlier values of t_c differ considerably from those of Cheng, McCoubrey, and Phillips[96] and of Kobe, Ravicz, and Vohra.[144] Pawlewski's work,[196] in general, is fairly accurate, but his value of t_c is about 10° higher while P_c is 8 atm lower than the most recent values. It is likely that the sample used by Pawlewski was impure.

Cheng, McCoubrey, and Phillips' results agree within the experimental limits of Kobe, Ravicz, and Vohra for t_c. It is believed from the comparison of the physical properties that the sample used by Cheng, *et al.*, is of higher purity than that used by Kobe, *et al.* On this basis, the t_c value of the former investigators and the P_c and d_c values of the latter are selected as most reliable.

4. Tetrahydrothiophene

Cheng, McCoubrey, and Phillips[96] obtained a "pure" sample from Robinson Bros., Ltd. It was dried over anhydrous sodium sulfate and distilled under dry nitrogen. The final purity of the sample was not determined, but the following properties were reported: bp 121.0 ± 0.1° (762 mm); $n^{17.0}\mathrm{D}$ 1.5059 (lit.[34] bp 121.117° (760 mm); $n^{20}\mathrm{D}$ 1.50480).

This is the only value of t_c available in the literature and is selected.

L. COMPOUNDS OF CARBON, NITROGEN, AND HYDROGEN

1. Aliphatic Amines (Table XXIX)

a. *n*-Butylamine

The data reported in Table XXIX for this compound and several others, as noted later, are old and should be considered only approximate.

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(196) B. Pawlewski, *Chem. Ber.*, 21, 2141 (1888).

TABLE XXIX
ALIPHATIC AMINES

Year	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Method	Ref
			a. *n*-Butylamine			
1957	251	41		Glaser and Rüland	7	79
Selected value	251	41				
			b. Diethylamine			
1917	223.2	36.58		Berthoud	1	180
1923	223.8		0.243	Herz and Neukirch	1, 19	124
1953	223	36.6		Kobe and Lynn		1
Selected value	223.5	36.6	0.243			
			c. Di-*n*-propylamine			
1917	277.0	31		Berthoud	1	180
Selected value	277	31				
			d. Triethylamine			
1883	267.1			Pawlewski	1	129
1886	259	30		Vincent and Chappius	1	197
1923	262.2		0.257	Herz and Neukirch	1, 19	124
Selected value	262	30	0.26			

These data were not reported by Kobe and Lynn.[1]

b. Diethylamine

Herz and Neukirch[124] used material supplied by Kahlbaum. It was treated with anhydrous sodium sulfate and fractionally distilled. The fraction used for measurements had bp 55.4–55.6°.

A mean of the values of Berthoud[180] and of Herz and Neukirch is selected for t_c. Berthoud's value for P_c and Herz and Neukirch's value for d_c are selected as the most probable values.

c. Di-*n*-propylamine

See remarks in section IV.L.1.a.

d. Triethylamine

Herz and Neukirch[124] obtained their sample from Kahlbaum.

Kobe and Lynn[1] reported the t_c and P_c of Vincent and Chappius[197] only. The t_c and d_c of Herz and Neukirch, with one less significant figure, and the P_c of Vincent and Chappius are selected as the most probable values.

2. Aromatic Amines (Table XXX)

See remarks in section IV.L.1.a as they are applicable to all compounds listed in Table XXX.

3. Heterocycles (Table XXXI)

a. Pyrrole

A specially purified sample of 99.99 mole % purity supplied by the U. S. Bureau of Mines, Laramie, Wyo., was used by Cheng, McCoubrey, and Phillps.[96] The sample had oxidized slightly and had formed a ketone which was removed over calcium hydride to give a colorless liquid. The determinations were carefully carried out on a very pure sample, and this value of t_c is recommended as the most reliable value.

b. Pyrrolidine

Kobe, Ravicz, and Vohra[144] purified their material in the manner described earlier for ethyl ether. The sample had bp 85.8° (748 mm) and n^{25}D 1.44025 (lit.[34] bp 86.5° (760 mm) and n^{25}D 1.044020). The sample decomposed near the critical temperature, but slowly enough that the t_c could be determined with a precision of ±0.2°. The P_c was measured to within ±1 atm, and the d_c to ±0.010 g/cm^3.

TABLE XXX
AROMATIC AMINES

Compound	t_c, °C	P_c, atm	d_c, g/cm^3	Investigators	Ref
Aniline (phenylamine)	425.6^a	52.4^a	0.340^c	Guye and Mallet	151
o-Toluidine (2-methylaniline)	421^a	37^b		Glaser and Rüland	79
m-Toluidine (3-methylaniline)	436^a	41^b		Glaser and Rüland	79
p-Toluidine (4-methylaniline)	394^a	23.5^a		Glaser and Rüland	79
N-Methylaniline	428.6^a			Radice	1, 150
	428.4^a	51.3^a		Herz and Neukirch	124
N,N-Dimethylaniline	414.4^a	35.8^a		Guye and Mallet	151
N,N-Dimethyl-*o*-toluidine	394.8^a	30.8^a		Guye and Mallet	151

^{a} Selected values rounded off to three significant figures. ^{b} Selected values. ^{c} Selected values rounded off to two significant figures.

Cheng, McCoubrey, and Phillips[96] used a 99.85 mole % purity sample supplied by the U. S. Bureau of Mines at Laramie. It was further purified by distillation *in vacuo*. The precision of t_c was ±0.1°.

These two investigations differ by about 1.5° in t_c. This difference may be due to slight decomposition witnessed by Kobe, Ravicz, and Vohra during their measurements. As Cheng, McCoubrey, and Phillips' value of t_c is of higher precision than that of Kobe, Ravicz, and Vohra, it is selected for t_c. Using this selected t_c, P_c is obtained from the extrapolation of vapor pressure measurements of Kobe and his co-

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(197) C. Vincent, and J. Chappius, *J. Phys. Radium*, **5**, 58 (1886).

TABLE XXXI (*Continued*)

Year	t_c, °C	P_c, atm	d_c, g/cm³	Investigators	Method	Ref
				n. Quinoline		
1963	509			Ambrose	1	89
Selected value	509					
				o. Isoquinoline		
1963	530			Ambrose	1	89
Selected value	530					

workers. The d_c of Kobe, *et al.*, is selected as the most reliable.

c. Pyridine

Swietoslawski and Kreglewski[135] purified pyridine by fractional distillation. The boiling temperature of the sample was found to be 115.05 ± 0.03° (755 mm) (lit.[34] 115.2 ± 0.1° (760 mm)). The capillary tubes were carefully filled and sealed to ensure no presence of air in the sample. Since pyridine sample was observed to become yellowish after heating over a long period of time, the thermostat was heated in advance to the desired temperature, and the temperature of the disappearance of the meniscus was observed just 15–30 min after the insertion of the experimental tubes. The critical temperatures were determined to within ±0.05°. Of the 22 tubes used, the disappearance of the meniscus in three tubes occurred in the upper part while in the remaining 19 tubes the meniscus disappeared in the lower part. In both cases the critical temperatures were identical.

Ambrose and Grant[18] used a sample of 99.91 mole % purity obtained from the National Chemical Laboratory. Pyridine samples discolored quite rapidly at the critical temperature, but the discoloration was not accompanied by a change in t_c. The temperature was measured to within ±0.05°.

Kobe, Ravicz, and Vohra[144] purified a commercial compound by treating it first with Drierite to remove any water present. It was then fractionally distilled in three packed columns using reflux ratios of 60:1 to 80:1. The boiling point of the sample used was 114.5° (748 mm) with $n^{25}\text{D}$ 1.50696 (lit.[34] 1.50745). Decomposition of the sample occurred near the critical temperature but was slow enough to determine it with a precision of ±0.2°. The critical pressure was measured within ±1 atm and the critical density within 0.010 g/cm³.

Kobe and Lynn[1] selected Radice's value[150] of t_c and Herz and Neukirch's value[124] of P_c. No details of sample purity or of the methods of measurement used are available for the values of Radice and Herz and Neukirch. The agreement in t_c values of Ambrose and Grant and of Kobe, *et al.*, is very good. Swietoslawski and Kreglewski's value,[135] however, is lower by 1.8°. Both Ambrose and Grant and Swietoslawski and Kreglewski determined t_c with great care on relatively pure samples, and the difference in t_c obtained is rather surprising. It is difficult in such cases to recommend the "best" value. As we have two determinations, *i.e.*, Ambrose, *et al.*, and Kobe, *et al.*, showing satisfactory agreement, the t_c value of Ambrose and Grant is selected as the most probable. The critical pressure and the critical density values of Kobe, Ravicz, and Vohra[144] are selected.

d. α-Picoline (2-methylpyridine)

A sample of 99.85 mole % purity, obtained from the National Chemical Laboratory, was used by Ambrose and Grant.[18] This compound was the least stable of the series of compounds for which t_c was determined, and so no value could be obtained for it. The value reported by them is an estimated one obtained from the use of Guldberg's ratio of absolute boiling point to absolute t_c.

It seems unlikely that an experimental value of t_c for this compound would be available in the near future, and so the estimated value is reported.

e. β-Picoline (3-methylpyridine)

Ambrose and Grant[18] used a sample of purity greater than 99.71 mole %, purified by the National Chemical Laboratory. Two tubes were used for the experimental determinations and identical values of t_c were obtained for both. The estimated uncertainty in t_c is ±0.1°. This is the only value of t_c available in literature and is thus selected.

f. γ-Picoline (4-methylpyridine)

Ambrose and Grant[18] used a sample of 99.97 mole % purity, prepared by the National Chemical Laboratory. The value reported was obtained by extrapolation back to zero time as the apparent critical temperature rose at the rate of 0.3°/hr. The estimated uncertainty of extrapolation was ±0.2°. Two tubes were used in this study. The first enabled an approximate value to be found; then the oven was preset before the more exact determination of t_c was made on the second tube. This latter value of t_c is selected as the most reliable.

g. 2,3-Lutidine (2,3-dimethylpyridine)

Ambrose, Cox, and Townsend[17] used a National Chemical Laboratory sample of 99.91 mole % purity.

As the substance was unstable at the critical temperature, the determinations were carried out in the rapid heater. Two experimental tubes were used as before and five determinations of t_c were made. The rate of change of the apparent t_c observed was +0.07°/hr. The uncertainty in t_c was ±0.05°.

This is the only value of t_c available in literature, and it is recommended.

h. 2,4-Lutidine (2,4-dimethylpyridine)

A National Chemical Laboratory purified sample of 99.80 mole % purity was used by Ambrose and Grant.[18] The apparent t_c rose at the rate of 1°/hr, so the reported t_c was obtained by extrapolation back to zero time. As the precision of observation of critical phenomena for this compound was not as good as for others, the accuracy of t_c was ±1.0°. Since no other values are available for the t_c of this compound, Ambrose and Grant's value is chosen as the most reliable.

i. 2,5-Lutidine (2,5-dimethylpyridine)

Ambrose, Cox, and Townsend[17] used a 99.85 mole % pure sample supplied by the National Chemical Laboratory. Two experimental tubes were again used, and four determinations were carried out with a range of 0.06° in the observations.

As no previous experimental values are available for this compound, Ambrose, Cox, and Townsend's value of the critical temperature is selected.

j. 2,6-Lutidine (2,6-dimethylpyridine)

Ambrose and Grant[18] used a sample of 99.85 mole % purity, prepared by the National Chemical Laboratory. This compound was quite stable at and near the t_c and little discoloration occurred near t_c. The uncertainty in t_c was ±0.02°. This is the only value of t_c available in literature and is selected.

k. 3,4-Lutidine (3,4-dimethylpyridine)

The National Chemical Laboratory supplied a sample of 99.885 mole % purity to Ambrose, Cox, and Townsend.[17] As the apparent critical temperature was found to be a function of time, the determinations were carried out in the rapid heater. The estimated uncertainty in t_c was ±0.03°. Two experimental tubes were used, and nine determinations of t_c were made. The observed rate of change of apparent t_c was +0.3°/hr. Owing to uncertainties in locating the meniscus, the value of the reported critical temperature was weighted more on the temperature of reappearance of the meniscus than on that of the disappearance of the meniscus.

No older values are available for this compound, and the value of Ambrose, Cox, and Townsend is selected.

l. 3,5-Lutidine (3,5-dimethylpyridine)

A sample of 99.91 mole % purity, supplied by the National Chemical Laboratory, was used by Ambrose, Cox, and Townsend.[17] Two experimental tubes were used, and four determinations of t_c were carried out giving a range of observations of 0.04°.

As no other experimental values are available, Ambrose, Cox, and Townsend's value of t_c is chosen.

m. Piperidine

Cheng, McCoubrey, and Phillips[96] used "purified" piperidine supplied by Hopkin and Williams, Ltd. It was allowed to stand for 3 days over freshly fused barium oxide, and then fractionally distilled using a packed vacuum-jacketed column. A fraction boiling over the range of 105.4–105.6° (754 mm) was used for the determination of t_c.

Ambrose[89] used a National Chemical Laboratory sample of 99.90 mole % purity. This compound was stable at its critical temperature, and the apparent critical temperature rose only 0.5° after a tube had remained in the oven for 24 hr at a temperature near the critical point. The uncertainty in t_c was ±0.01°.

On the basis of purity of sample and precision of measurement, Ambrose's value for t_c was selected.

n. Quinoline

Ambrose[89] used a sample of 99.69 mole % purity obtained from the National Chemical Laboratory. This compound was unstable at its critical temperature so that the determinations of t_c were carried out in the rapid heater. Three tubes were used, and the rate of change of apparent t_c was +1°/min. Since this is the only value of t_c available, it is selected.

o. Isoquinoline

A National Chemical Laboratory prepared sample of 99.95 mole % purity was used by Ambrose.[89] Three experimental tubes were used, and the apparent t_c rate of change was found to be −2°/min. This compound was unstable at its t_c, and so the determinations were carried out in the rapid heater. This is the only available value of t_c and is selected.

M. MISCELLANEOUS COMPOUNDS (TABLE XXXII)

1. *Perchloryl Fluoride*

Jarry[198] used perchloryl fluoride prepared by Engelbrecht and Atzwanger and purified by fractional distillations. The mass spectrometric analysis showed a purity of 99.9+ mole %. The samples were sealed in 2-mm i.d. capillary tubing and introduced into a constant-temperature bath. The temperatures were measured by a mercury-in-glass thermometer calibrated by the NBS. The precision of measurement was ±0.10°.

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(198) R. L. Jarry, *J. Phys. Chem.*, 61, 498 (1957).