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Reviews

Vapor–Liquid Critical Properties of Elements and Compounds. 1. An Introductory Survey

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This review is an introductory survey of the vapor–liquid critical properties of pure substances. It will be followed by a series of reviews on the critical properties of elements and compounds, each dealing with a well-defined group of substances in detail. The historical background of the vapor–liquid critical point is outlined, and this is followed by a discussion of the nature of the critical point and of the experimental methods used to determine critical temperatures, pressures, and volumes. The effect of impurities, including mercury, on the apparent critical properties is examined. Many substances decompose at or near their critical point; methods designed to minimize this problem or procedures to allow for decomposition are presented. Finally, a classification of methods, to be used in subsequent parts of this project, is given, and the accuracy and reproducibility of the results are discussed.

Introduction

Cagniard de la Tour was the first to observe the phenomenon now called the critical point. He sealed a marble in a section of musket barrel filled to about one-third of its volume with alcohol and heated it. As the temperature was raised and the marble was rolled in the barrel, the sound of it rebounding from the wall eventually indicated that there was no liquid present [1822-del]. (The actual words of ref 1822-del describing the apparatus are "j'ai introduit dans une petite marmite à Papin, construite avec un bout de canon de fusil très-épais, une certaine quantité d'alcool à 36 degrés et une bille ou sphère de silex; le liquide occupait à-peu-près le tiers de la capacité intérieure de l'appareil", from which it is apparent that the experiment was on a less heroic scale than is implied by the statement in ref 53-kob/lyn that the apparatus was made from a "cannon barrel".) He continued his experiments with apparatus of a type that is more familiar to us today and observed the disappearance and reappearance of the meniscus in sealed glass tubes. These tubes, as is also well-known to us, burst if they were overfilled, leading de la Tour to the correct conclusion that the liquid is more compressible at the critical temperature than at lower temperatures. He obtained values for the critical temperatures of ether, alcohol, and water and attempted to measure the critical pressure [1822-del-1, 1823-del]. At about the same time, Faraday started his work on the liquefaction of gases [1823-far, 1845-far-3]. It is clear, especially from his correspondence with Whewell [71-wil], that when Faraday had finished this work he understood the significance of the critical point. The word "critical" is used with so many different connotations that the authors of this review of critical properties may perhaps be permitted to regret that Whewell's suggestion of the term "Tourian state" was not adopted in place of the "critical state" that Andrews proposed in his papers on the properties of carbon dioxide [1869-and, 1876-and, 1887-and]. Van der Waals provided a theoretical framework for the understanding of fluid properties in 1873 with the equation that bears his name [1873-van, 70-rig, 74-deb, 74-kle]. The consequent law of corresponding states utilized reduced quantities defined by dividing temperatures, pressures, and volumes by their respective values at the critical point, the critical temperature, the critical pressure, and the critical volume.

Early work was surveyed by Heilborn [1891-hei]. Since then, values of vapor–liquid critical properties have been available in many reference books and the compilations in *International Critical Tables* [28-ict] and *Landolt-Börnstein* [23-lan/bor and later publications], in particular, may be noted. Pickering [24-pic] provided a review on some gases. From 1953, the review by Kobe and Lynn [53-kob/lyn], which included discussion of the critical point, of the experimental methods, and of individual investigations, was for many years the standard source for these properties. That review was supplemented by reviews of similar scope by Kudchadker *et al.* [68-kud/ala] and by Mathews [72-mat]; the first of these dealt with organic compounds and the second with elements and inorganic compounds. Since that time there has been much experimental work in the field, and one of the present authors (D.A.) has collected the experimental results into tables of what he assessed to be the best values [80-amb, 83-amb, 91-lid]. The tables do not include any critical discussion.

In 1986, at the suggestion of one the authors (D.A.), a Working Group under the Commission on Thermodynamics (I.2) of the International Union of Pure and Applied Chemistry was established for the preparation of a successor review to those by Kobe and Lynn [53-kob/lyn], by Kudchadker *et al.* [68-kud/ala], and by Matthews [72-mat]. The underlying data, except for some that are very old, and some that have been published in sources that are not easily accessible (for which it has been necessary to rely on *Chemical Abstracts*) have been extracted afresh from the primary literature and are being stored on computer at the Thermodynamics Research Center, Texas A&M University, so that they will be available to facilitate future revisions.

It has been decided to publish the review in sections as they become available, rather than to hold up any finished parts until the whole is complete. This section provides a general discussion of the experimental methods, and

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subsequent sections will give critical assessments of the experimental results for particular groups or compounds beginning with the normal alkanes in part 2. Parts 3 and 4 will deal with the critical properties of aromatic compounds and alkanols, respectively. It is intended that the tables of experimental values shall be comprehensive, *i.e.*, that they will include all values that have been measured even though the early results may now be only of historical interest and may have been included in earlier reviews. Ohse and von Tippelskirch published a review covering elements and some refractory materials with high critical temperatures on behalf of Commission II.3 of the International Union of Pure and Applied Chemistry [77-ohs/tip]. The present review will not deal with refractory materials.

Note must be made of two volumes by Simmrock *et al.* [86-sim/jan]. Use of this compilation except by those already knowledgeable in the subject cannot be recommended because the authors apparently did not understand the difference between observed and estimated values, and as a result they reported critical properties of about 200 more substances than the 400 or so that have been studied experimentally. They then included estimated values in tests of methods of estimation, thus invalidating the results of the tests. The tables of values for individual substances have been generated by computer, and standard deviations are given. These are meaningless since many of the values are repetitions from other compilations and may derive from a relatively few original observations. The original observations themselves have sometimes been downgraded in the selection of the recommended values. The books contain an extensive bibliography.

The present series of reviews is not concerned with critical properties of mixtures. This topic has been treated by several authors in review papers and books, and the interested reader is referred to publications by Hicks and Young [75-hic/you], Sadus [92-sad-3], McGlashan [85-mcg], Schneider [78-sch-1, 91-sch], and Kay [68-kay]. The first two of these publications contain compilations of experimental data. A comprehensive compilation is in preparation by one of the authors of this paper (C.L.Y.) and the DIPPR Project 882, sponsored by the American Institute of Chemical Engineers, is collecting experimental data on the critical properties of selected mixtures [93-gam/mar, 94-gam/mar].

Vapor–Liquid Critical Point

The vapor–liquid critical point is weakly defined in comparison with many other physical points, for example, the triple point. The so-called point is in fact a region, of undefined boundaries, where the stability of the system breaks down and responses to disturbances become very large. Paradoxically, therefore, the critical state extends, albeit only by an amount to be measured in millikelvins, above the critical temperature. There is a large amount of literature on the anomalies that arise; early reviews are those by Clark [38-cla] and by Maass [38-maa]. In the years following, a teasing question was whether the coexistence curve was smooth at the critical point or whether there was a "flat top"; by 1968 when the review by Kudchadker *et al.* [68-kud/ala] was published, this question had effectively been resolved, chiefly by the work of W. G. Schneider and his co-workers [51-ata/sch, 51-mac/sch, 52-wei/sch, 52-wei/sch-1, 52-sch-2, 53-sch/hab, 54-hab/sch-1], and the flat top anomalies that had been noted were shown to be due to the effects of gravity and the time required for equilibrium to be reached when a fluid is in the critical or near-critical state.

Attribution of the flat top to gravity did not solve all of the problems of the critical point. Theory, which originally expected the coexistence curve to be quadratic, has had to accommodate the reality that it is approximately cubic, and it is the present consensus opinion that the behavior in the critical region is nonanalytic. A considerable body of research on critical behavior of simple substances that are stable at their critical points has been aimed at investigating nonanalytic behavior. Its consequences have been surveyed by Egelstaff and Ring [68-ege/rin], by Sengers and Levelt Sengers [68-sen/lev], and by Levelt Sengers [75-lev-1]. A modern example of a nonanalytic equation of state is that given, together with a review of earlier work, by Jin *et al.* for methane [92-jin/tan-1].

Table 1. Critical Indices

property	index	comment
C_V	$-\alpha^+$	along the critical isochore $T > T_c$
	$-\alpha_1^-$	through isobaric states of homogenous fluid
	$-\alpha_2^-$	along the critical isochore $T < T_c$
$V_g - V_c$, $V_c - V_1$	β	through isobaric states
$-(\partial p/\partial V)_T$	γ^+	along the critical isochore $T > T_c$
	γ^-	through isobaric states of homogeneous fluid
$\lvert p - p_c\rvert$ as a function of $\lvert V - V_c\rvert$		along the critical isotherm
$(\partial^2 p/\partial T^2)_\sigma$	$-\theta$	curvature of the vapor pressure line

The shape of the coexistence curve in the critical region cannot be represented precisely by any analytic equation of state. Systematic studies of the deviations from analytic behavior were first undertaken by Guggenheim [45-gug], who showed that the experimental liquid–vapor coexistence curve near the critical region was cubic. The differences in density ($\varrho - \varrho_c$) for both the liquid and vapor branch were approximately proportional to $(T_c - T)^{1/3}$, where ϱ is the density, T is the Kelvin temperature, and subscript c indicates the value at the critical point. The nonanalytic nature of the critical region is conveniently discussed by introducing critical point exponents or indices. If $V = 1/\varrho$, consider the rate of change of various properties $Y(T,V)$ as functions of $\Delta\varrho = (\varrho - \varrho_c)/\varrho_c$ and $\Delta T = (T - T_c)/T_c$ on logarithmic plots. A critical index is defined by equations of the type

$$\chi^\pm = \lim_{(T \to T_c)^\pm} [\ln Y(T,V)/\ln|\Delta T|] \qquad (1)$$

where the plus sign indicates approach to the critical point from above T_c and the minus sign indicates approach from below T_c. Five basic indices are distinguished: α, β, γ, δ, and θ. Following Rowlinson [69-row] the indices are defined in Table 1.

The indices χ^+ and χ^- can be different, and χ^- can sometimes be divided further into χ_1^- and χ_2^- as the approach to the critical point is made along a path in the one-phase or in the two-phase region [69-row, 70-lev, 75-lev-1, 84-kre]. Other critical indices for pure substances are discussed by Stephenson [71-ste-1]. Critical indices for mixtures have been discussed by Scott [78-sco]. Determination of the indices requires careful experimental work, and there is a need to take into account all of the factors that might distort the equilibrium curves in the critical region. Measurements of suitable accuracy are difficult to make near the critical point, and the nearer the critical point is approached, the more difficult the measurements become.

There are a number of reviews of this topic. Table 2 gives Kreglewski's [84-kre] values of the first four indices. The classical values are those obtained by Taylor expansion for any equation of state around the critical point with the criticality conditions applied. The real values are different from those obtained by Taylor expansion (*i.e.*, the critical

Table 2. First Four Critical Indices Given by Kreglewski [84-kre]

index	classical	real fluid	index	classical	real fluid
α^+, α^-	0	0.07 ± 0.05	γ^+, γ^-	1	1.22 ± 0.04
β	0.5	0.35 ± 0.01	δ	3	4.4 ± 0.2

region is nonanalytic). It can be shown that

$$\alpha^- + \beta(\delta + 1) \geq 2 \tag{2}$$

and

$$\alpha^- + 2\beta - \gamma^- \geq 2 \tag{3}$$

Furthermore, it can be argued by introducing the scaling hypothesis [63-rus, 65-gri, 65-wid] that the inequalities are equalities. One important consequence is that empirical extrapolations up to the critical point are not confirmed. In particular, if the densities of liquid and vapor are indicated by subscript l and g, respectively, the "law" of rectilinear diameters

$$(\varrho_l + \varrho_g)/2 = \varrho_c + a[(T - T_c)/T_c] \tag{4}$$

as discovered by Cailletet and Mathias in 1887 (see discussion on critical volume) needs to be replaced by the result from the scaling equations

$$(\varrho_l + \varrho_g)/2 = \varrho_c + a'[(T - T_c)/T_c]^{1-\alpha} \tag{5}$$

The rectilinear diameter, then, exhibits a slight curvature in the immediate vicinity of the critical point, and the value of ϱ_c obtained from the scaling equation is less than that obtained from the linear extrapolation. The resulting error is small.

These theoretical considerations are not significant for the generality of substances, and the practical need is for knowledge of the critical properties of as many substances as possible so that corresponding state correlations may be devised and applied for the estimation of properties away from the critical point. The number of substances that are stable at their critical temperatures is limited, and ways have to be found for determining the critical properties of compounds that are unstable at their critical temperatures. The values for such substances are less certain than those for stable substances.

The aims of different investigators differ in accord with the distinction made in the preceding paragraphs between what is interesting scientifically and what is needed practically. Those concerned with the former carry out the most refined studies, almost always on substances that have critical temperatures close to ambient (such as ethylene or carbon dioxide), whereas those concerned with the latter have neither the time, nor do the more difficult experimental requirements at higher temperatures permit them, to emulate their colleagues in the thoroughness and precision of their work.

The critical point of a pure substance is defined mathematically as the point at which

$$p > 0, (\partial p/\partial V)_T = 0, (\partial^2 p/\partial V^2)_T = 0 \tag{6}$$

where p is the pressure. The criticality conditions for a binary mixture may be written as

$$(\partial^2 G/\partial x_2^{\,2})_{T,p} = 0 \qquad (\partial^3 G/\partial x_2^{\,3})_{T,p} = 0 \qquad (\partial^4 G/\partial x_2^{\,4})_{T,p} > 0 \tag{7}$$

where G is the Gibbs function and x_2 is the mole fraction of component 2. These criticality conditions are often expressed in terms of A, the Helmholtz function [75-hic/you]. The criticality conditions for multicomponent systems were given by Gibbs [06-gib] and have been discussed more recently by Sadus and Young [87-sad/you].

Disappearing Meniscus—Critical Temperature and Pressure

Apart from de la Tour's initial experiment, all early studies of the critical point were made by visual observation of the disappearance of the meniscus in glass tubes. If an appropriate amount of the substance (*i.e.*, that corresponding approximately to the critical density) is sealed in the tube, critical temperatures only can be observed. However, if the tube is open, pressure may be transmitted by use of an immiscible fluid (generally mercury) to a measuring device and the critical pressure may also be observed, while if the tube is of calibrated volume the measurements that lead to the critical volume may also be made. Because of the infinite compressibility of the fluid at the critical point, the critical volume cannot usually be determined, except with considerable uncertainty, by direct measurement at the critical point (see next section). The unsealed tube was used by Andrews [1869-and, 1876-and, 1887-and]. It was subsequently developed by Hannay and Hogarth [1880-han/hog], by Ramsay and Young [1887-ram/you-1], who also first described use of a vapor jacket for control of the temperature [1885-ram/you-1], by S. Young [10-you-1], by Cailletet [1869-cai], and by Kay [36-kay, 47-kay]. Today the name of S. Young or Kay frequently identifies this type of apparatus, but that of Cailletet has also been used [12-car-1, 35-boo/swi, 48-die/sch, 10-car/bau]. In these last references distinction is made between the glass experimental tube and the metal part into which it is fitted: in ref 12-car-1 the "Cailletet tube" is the metal part, whereas in refs 35-boo/swi and 48-die/sch it is the glass tube. Cardoso and Baume [10-car/bau] described their apparatus as incorporating a Ramsay and Young compressor connected with two Cailletet blocks, one being a nitrogen manometer and the other containing the gas under study. The apparatuses used by de la Tour, by Andrews, and by S. Young are illustrated in the review by Kobe and Lynn [53-kob/lyn].

Altschul described a method for determination of critical pressure in which the tube containing the sample confined over mercury was heated in such a way that its upper end was above the critical temperature while the lower end was below it [1893-alt]. The pressure was increased and the meniscus moved up the tube until it disappeared at the critical pressure. Control of the heating could be relatively coarse and critical pressure only was determined (the critical temperature was determined in the usual way with a sealed glass tube). A more refined apparatus using this method was that described by Eck for the determination of the critical pressure of water [39-eck]. Ambrose and Townsend [63-amb/tow], in whose apparatus mercury was kept at ambient temperature with the sample passing through a temperature gradient, described their method as a refinement of Altschul's. A more correct connection would perhaps have been with S. Young's work on carbon tetrachloride in which he kept the mercury out of the heated zone because it reacted with the carbon tetrachloride [1891-you-1].

The modern apparatus does not differ in principle from the early apparatus. The meniscus is normally observed directly by eye, sometimes with the assistance of a lens or telescope. Photographic observation has been used primarily for demonstration purposes [51-swi/gru, 51-swi/gut, 51-swi/mar, 54-pal, 56-wen, 89-kab/tan]. Originally, temperatures were measured by means of mercury thermometers and pressures by measuring the compression of air or nitrogen confined in a secondary tube communicating with the experimental tube. Today, improved measurement of temperature is provided by thermocouples or platinum resistance thermometers and the control equipment now available, while the improved measurement of pressure is provided by use of elastic gauges, such as Bourdon or diaphragm gauges, or pressure balances (dead-weight testers). Heating by means of a vapor jacket becomes less satisfactory as the temperature is raised, and some workers

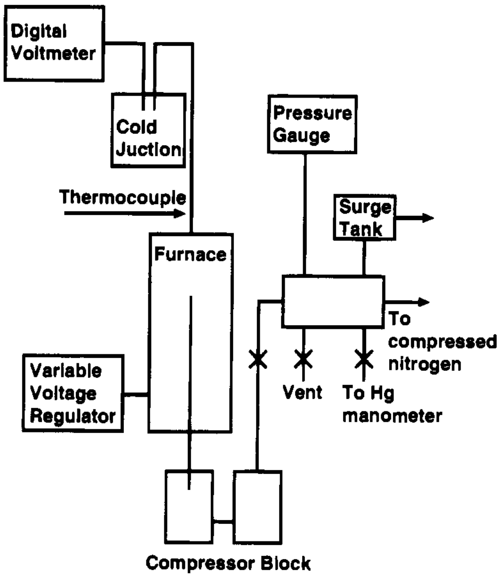

Figure 1. Block diagram of apparatus of Pak and Kay [80-kay/pak].

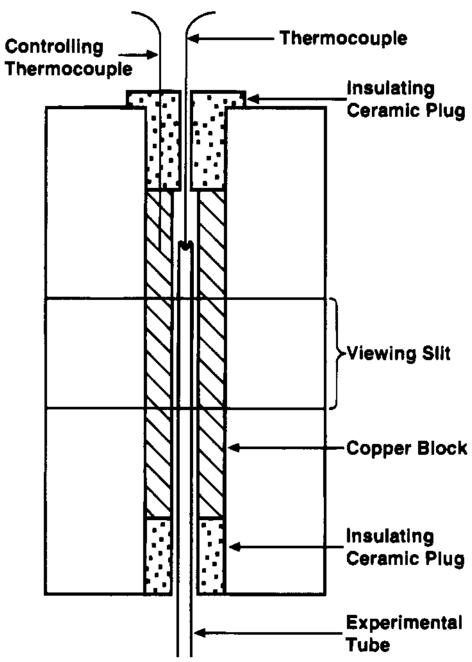

Figure 2. Critical point furnace of Pak and Kay [80-kay/pak].

have preferred to put the tube in a heated metal block provided with suitable lighting and viewing windows. In addition to that described by Kay [36-kay, 47-kay], some examples of modern apparatuses are those described by Connolly and Kandalic [62-con/kan], Ambrose and Townsend [63-amb/tow], Ambrose *et al.* [67-amb/bro], Young [72-you-1], Hugill and McGlashan [78-hug/mcg-1], Anselme and Teja [88-ans/tej], and Quadri *et al.* [91-qua/khi, 91-qua/kud]. Kay and Pak [80-kay/pak] described an apparatus for use with gallium as the confining fluid.

A block diagram of Pak and Kay's apparatus [80-kay/pak] for determining critical temperatures and pressures of both pure compounds and mixtures is shown as Figure 1 and a simplified diagram of their furnace as Figure 2. This type of apparatus is commonly used for the measurement of critical temperatures and pressures. Several designs of vessel for containing the sample have been described. The simple J-tube of Young [72-you-1], illustrated in Figure 3, is easy to manufacture and clean, and the sample can be thoroughly degassed, but filling the tube requires some manual dexterity. Other vessels have been described by Ambrose and Townsend [63-amb/tow] and by Quadri *et al.* [91-qua/kud]. In their design, a balance needs to be achieved between ease of cleaning, filling, degassing, and use in the furnace.

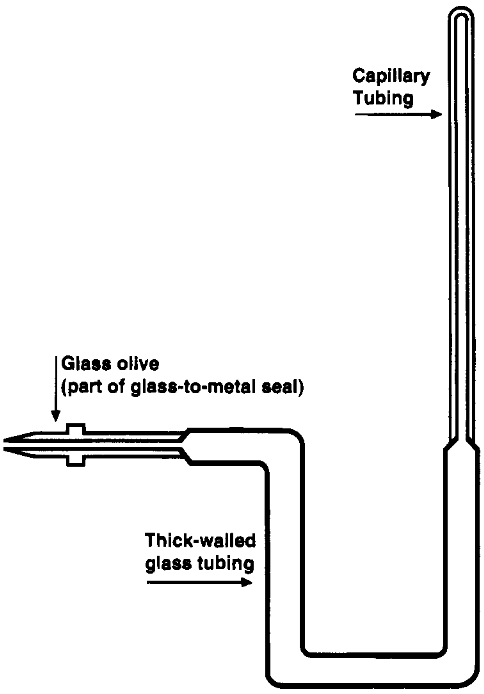

Figure 3. Critical point J-tube of Young [72-you-1].

The thick-walled tubing required for critical point experiments has commonly been of 2−3 mm internal diameter. Kay has published results of bursting tests on such tubing [52-kay]. When the tube is sealed for temperature-only measurement, lengths of 5−15 cm are usual. It is simpler to fill the longer tubes with the correct amount of liquid, but uniform temperatures are more easily established in the shorter ones. Kennedy [29-ken] found that the critical point of carbon dioxide was more sharply defined in tubes of only 0.05 mm diameter than in those of 2 mm, and this was confirmed by Ambrose, who used tubes of 0.1 mm diameter and 10 mm length for carbon dioxide and acetylene [56-amb]. It was difficult to obtain the correct filling fraction with these tubes, and Moldover [74-mol] suggested that the maintenance of purity would be more difficult with such a small sample. Small tubes were also used by Harand [35-har] and by Fischer and Reichel [43-fis/rei] for determining critical temperatures with the aid of melting-point heating blocks. The practice of using very small tubes has not been widely adopted.

What is seen in an experiment to observe the disappearance of the meniscus depends on how closely the experimental conditions are controlled and, for the reappearance, on how far the temperature has been raised above the critical value. The beautiful phenomena that may be observed have been described on numerous occasions, for example refs 38-cla, 12-car-1, and 57-amb/gra; the most detailed technical analysis is that given by Moldover [74-mol]. It is more difficult to be precise in determining the temperature of disappearance than in determining that of reappearance because the latter is accompanied by intense disturbance of the contents of the tube and the formation of droplets of liquid and bubbles of vapor, whereas the former proceeds imperceptibly and its exact moment of disappearance is a matter of judgment. Even when the temperature has been raised to a level at which no meniscus can be seen, there is usually a perceptible discontinuity in the refractive index at the wall of the tube. However, under favorable conditions the difference between the temperatures of disappearance and reappearance can be less than 0.1 K, and Moldover claimed to identify the temperature of disappearance to within ±0.001 K in carbon dioxide and ethylene [74-mol]. If the pressure is balanced at the same time, it is possible to maintain indefinitely a state of disappearance and reappearance with the slightest possible variation in pressure and no measurable variation in temperature.

The disappearing meniscus has also been observed in metal cells provided with transparent windows, generally of sapphire. Apparatuses of this type were described by Palmer [54-pal], by Wentorf [56-wen], by Straub [67-str-3], by Okazaki *et al.* [83-oka/hig], and by Tanikawa *et al.* [90-tan/kab]. These apparatuses were for use near ambient temperatures. Brunner *et al.* [84-bru/mai] described an apparatus useable at temperatures up to 625 K, and Buback and Franck [72-bub/fra] described an apparatus suitable for use with ammonium halides at temperatures up to 1200 K. A cylindrical cell with flat windows offers the advantage for associated volumetric measurements that the internal volume may be calculated from the dimensions of the cell, and it is also more suitable than the simpler glass tube cell for use with optical methods. Palmer [54-pal] used a Schlieren system and Wentorf [56-wen] a photographic method for gases whose critical temperatures are near ambient.

Whatever form of cell is used, experiments on the disappearing meniscus may be divided into those in which the contents of the cell are stirred and those in which they are not. The earliest observations were made without stirring. Cardoso [12-car-1], followed by Kay [36-kay, 47-kay], set the example of stirring the material by moving a steel ball up and down the tube with a magnet. Okazaki *et al.* used a metal cell with optical windows and stirred by rocking the assembly [83-oka/hig], whereas Atack and Schneider [51-ata/sch] claimed that more vigorous stirring is desirable. It seems to be generally agreed that stirring is necessary for good results when mixtures are studied, but there is no clear evidence that the results obtained for single components in a stirred cell are more accurate than those obtained without stirring. In nearly all of the work by Kay and co-workers the sample has been stirred, but when Kay and Pak [80-kay/pak] used gallium as confining fluid, they found it impossible to stir and commented, "While it is unnecessary to stir the sample when determining the critical point of a pure compound, stirring greatly enhances the light scattering, making it easier to identify the critical point." Moldover in his careful and precise work on carbon dioxide and ethylene observed the meniscus disappearance and reappearance in unstirred tubes [74-mol].

Critical Volume

The isotherm on the pressure−volume−temperature diagram at the critical temperature has a horizontal point of inflection; the position of this point of inflection is not a directly measurable quantity, and the critical volume (or density) has to be obtained by indirect means.

Gouy [1892-gou] showed that at the critical temperature the effect of gravity could lead to a density gradient of several percent in tubes of the length normally used for observation of the critical point. At temperatures just below critical, only the vapor and liquid in the immediate vicinity of the surface separating the two phases are actually at their true "*orthobaric densities*", a term introduced by Ramsay and Young to signify densities at the equilibrium pressure of the fluid [1887-ram/you-1]. This behavior facilitates observation of the critical point because it is not necessary for the mean density of filling of the tube to be exactly the critical value; if the filling is slightly above the critical density, the meniscus will disappear toward the upper end of the tube and *vice versa*.

Working with ethylene, carbon dioxide, nitrous oxide, and sulfur dioxide, Cailletet and Mathias [1886-cai/mat, 1887-cai/mat] showed that the mean densities of saturated vapor and liquid phases, when plotted against temperature, fell on a different straight line for each substance, and they called the line the rectilinear diameter. If this line is extrapolated to the critical temperature, the value obtained is the critical density. That is to say, the rectilinear diameter provided a practical definition of the critical density, which had not previously been measurable. More accurate measurements have shown that the rectilinear diameter often has a slight curvature, but this cannot be detected if measurements are only made within 10 or so K from the critical temperature (see below). S. Young stated in his book *Stoichiometry* [18-you], "it is impossible, by any method yet devised, to make direct experimental determination of the critical volume (or density) with sufficient accuracy", and in his 1910 paper [10-you-1] he recalculated his previously published directly observed values from the following equation for the rectilinear diameter:

$$(\varrho_1 + \varrho_g)/2 = \varrho_0 + at + bt^2 \qquad (8)$$

Here t is the Celsius temperature, a and b are constants, and ϱ_0 is the density at 0 °C.

However, although values of critical density are, in general, still obtained from the densities of liquid and vapor at lower temperatures by means of the rectilinear diameter, Moldover obtained the critical densities of carbon dioxide and ethylene by direct observation of tubes containing near-critical fillings, taking account of the density gradient by means of an equation of state [74-mol].

Cailletet and Mathias used an apparatus of variable volume [1869-cai, 1886-cai/mat]. S. Young introduced a method [1891-you-4] for determination of orthobaric densities in which two tubes of uniform bore are filled with different amounts of fluid and the positions of the two menisci at a series of temperatures are determined; from the volumes and masses of material the coexisting densities can be calculated. Values for vapor and liquid are obtained at each temperature in pairs, which simplifies obtaining the rectilinear diameter. A modern example of use of the method is the investigation by Cornfield and Carr of the coexistence curve of xenon [72-cor/car]. Hebert *et al.* [58-heb/mcd] used multiple tubes, each filled to a different extent, for measurements on water, and their method was followed by Ambrose and Townsend [63-amb/tow] for measurements on alcohols.

Orthobaric densities may be determined by confining a known amount of fluid in a transparent vessel of known volume, often a glass tube, so that two phases are present: as the temperature is raised, the level of the meniscus will rise or fall, depending on the extent of filling, and at some temperature will disappear out the end of the cell so that the cell is completely filled with liquid or vapor. The density of this phase at the measured temperature is then obtained from the volume of the cell and the mass of material present. Each tube gives only one point on the coexistence curve, and the points obtained for vapor and liquid will not be, except by chance, at the same temperature. Eck [39-eck] used a series of silica tubes for determination of the orthobaric densities of water by this method, and Ambrose and Grant [57-amb/gra] used glass tubes in the same way for work on pyridine. Alternatively, the mass of material may be varied in a cell of fixed volume, *i.e.*, normally, the cell is filled to a high density, the observation is made, a measured amount of material is withdrawn, and the process is then repeated until only one phase is present. This method was used by Weinberger and Schneider [52-wei/sch] for measurements on xenon in which they demonstrated the effect of gravity by comparing results obtained in a cell of 9 mm i.d. and 19 cm height held vertically with those obtained in a cell of 12 mm i.d. and 14 cm length held horizontally.

Anselme and Teja [88-ans/tej, 91-ans/tej] obtained approximate critical densities by observing the position of disappearance of the meniscus in two tubes with slightly different loading densities. They estimated by linear extrapolation the density at which the meniscus would disappear exactly at the half-volume of the ampule. This was assumed to be the critical density of the substance. This technique is not of the highest accuracy but is quick and can be used if decomposition of the sample is a major problem.

Orthobaric densities may also be measured by use of floats. Maass and co-workers [37-maa/ged, 38-mci/maa, 39-mci/dac, 40-nal/maa] supported a float on a spring, a method that was also used by Goldman and Scrase [69-gol/scr, 69-gol/scr-1] and by Cockett *et al.* [68-coc/gol]. Grigor and Steele [66-gri/ste] and Hales and Gundry [83-hal/gun-1] used a magnetically balanced float. Naumenko *et al.* [67-nau/shi] used a series of floats of varying density. Wagner and co-workers [86-kle/wag, 92-han/kle] have described a two-sinker method for determining densities. This is described in the next section.

It is difficult to make the measurements just described very close to the critical temperature, and the question arises whether the critical density obtained by extrapolation of the rectilinear diameter is correct. Levelt Sengers [75-lev-1] stated that theoretically it is very unlikely that the mean density line is straight, but the most precise measurements have failed to reveal curvature within 10 K of the critical point. Levelt Sengers gave graphs of values for several compounds from the critical temperature to about 10 K below the critical temperature. The most detailed study is that by Cornfield and Carr [72-cor/car] on xenon. These authors obtained the critical density by Young's method applied over the range 1.5–81 K below the critical temperature and also by an NMR method over the range 1.4–15.5 K below the critical temperature. Both sets of measurements were fitted best by a linear function and gave values for critical density of 1.1121 and 1.1126 $g\cdot cm^{-3}$, respectively. These values were compared with that obtained by a method in which the heights of disappearance of the meniscus in tubes containing fillings of seven differing mean densities were related to the effect of gravity and, depending on the method of analysis, values of 1.1095 and 1.113 $g\cdot cm^{-3}$ were obtained. Cornfield and Carr concluded that although they could not detect any deviation from linearity of the rectilinear diameter, it was likely that if there was a deviation, the critical density would be less than the extrapolated values by not more than 0.5%.

Over a longer range, S. Young [00-you-1, 10-you-1] found for the 30 compounds he studied that away from the critical point the line was slightly curved (not always in the same direction). For the range from about 273 K to the critical temperature (nearly 600 K for acetic acid) it was necessary to use a second-order and, for alcohols, a third-order power series to represent the mean density line. According to S. Young the curvature has a significant effect only when the critical density is obtained by a long extrapolation from densities far from the critical point. Simon used a similar equation to that used by Young to represent the results he obtained for aromatic hydrocarbons [57-sim].

Van Poolen *et al.* [86-van/jac] compared the values for critical densities of oxygen and ethylene obtained in three ways. The first was by the conventional rectilinear extrapolation, the second by use of an equation that took account of curvature in the line, and the third by use of an equation based on the "critical liquid volume fraction" and taking account of scaling law exponents. They claimed that this last method was not extrapolative but interpolative in that the whole coexistence curve was fitted and the critical value was defined as that at the point where the critical liquid volume fraction is 0.5. Values obtained by the three methods differed by 0.15% or less when data for the full range of experimental measurements were used. If restricted ranges of data points away from the critical were used, values obtained from the new equation were closer to the accepted values than those obtained from the equations for the rectilinear diameters. Goodwin [70-goo-1] has also offered an equation providing an alternative method for calculation of critical density that avoids the conventional rectilinear diameter extrapolation.

Benson and Copeland [55-ben/cop] pointed out that near the critical temperature the means of the orthobaric volumes of liquid and saturated vapor also fall on a straight line, and a value for the critical volume can be obtained in a way analogous to that for critical density. The critical density obtained from the rectilinear density was about 4% higher than the reciprocal of this critical volume, and Benson and Copeland questioned whether the fact that the rectilinear density line is straight over a longer temperature range than the volume line is a compelling reason for assuming that the density line rather than the volume line gives the correct value at the critical temperature. However, their conclusion is a result of the method they used to fit the data. If the extrapolation is carried out correctly, both density and volume give the same result. The mean volume versus temperature is considerably more curved than the mean density when plotted against temperature. Data available to Benson and Copeland show such curvature. They chose to take data over a very limited range of temperature, and the curvature was masked by the experimental error.

Pressure–Volume–Temperature Measurements

Variable volume pressure–volume–temperature (*pVT*) measurements in an apparatus of the type used by Andrews [1869-and, 1876-and, 1887-and] employing a glass tube were made by Ramsay and Young [1885-ram/you-1, 1887-ram/you-1, 10-you-1], by Cailletet and co-workers [1869-cai, 1881-cai/hau, 1881-cai/hau-1, 1886-cai/mat, 1887-cai/mat], and by Cardoso [12-car-1]. In recent years they have been made by Kay and co-workers [36-kay, 47-kay, 65-mcm/kay, 67-kay/his, 80-kay/pak] and others [47-gor/ami, 48-die/sch, 62-con/kan]. Such an apparatus is suitable for determination of orthobaric densities. When it is possible to see the meniscus, critical points will inevitably be identified visually. In contrast, the apparatus developed by Beattie [34-bea] from one originally devised by Keyes for work on water [33-key] and subsequently used in numerous other investigations, for example [52-ben/fur, 73-dou/har, 76-dou/har], has a glass liner containing the sample in a steel bomb, isotherms are measured, and the critical point is identified from the *pVT* diagram so obtained. Isotherms at temperatures below critical show discontinuities at the dew and bubble points, whereas isotherms at critical and slightly higher temperatures are continuous and have points of inflection; for the critical isotherm only, the inflection occurs when the curve is horizontal. A modern *pVT* apparatus suitable for measurements in the critical region has been described by Wagner and co-workers [86-kle/wag, 92-han/kle, 94-gil/kle]. The most recent, the two-sinker apparatus, was specially designed for making accurate measurements of the saturated liquid and saturated vapor densities of pure sub-

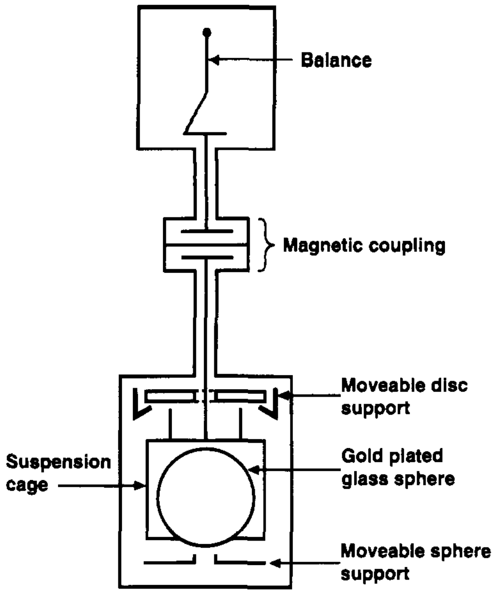

Figure 4. Schematic diagram of the density balance of Kleinrahm and Wagner [86-kle/wag, 92-han/kle].

stances, but it is suitable also for measurements over a wide range of temperature and pressure. The method is based on measuring the buoyancy of two sinkers of identical mass and surface area but with considerably different volumes. A simplified diagram of the apparatus is given in Figure 4. The sinkers can be independently placed in a cage suspended from a microbalance by a thin rod via a magnetic suspension coupling (without disturbing the cell in any other way). To measure the density, the sinkers are alternately put on the cage and the buoyancy is measured with the microbalance. With this apparatus the effects that require corrections in the single-sinker method, such as buoyancy forces on the whole suspension device, surface tension at the suspension wire when liquid densities are measured, and adsorption on the sinker, are automatically compensated. Values of the critical properties are obtained by computer-based analysis of both density and vapor–pressure measurements.

Measurements may also be made in a constant-volume apparatus. Cailletet and Colardeau [1888-cai/col] and Ipatieff and Monroe [42-ipa/mon] measured the pressure in a bomb containing the material as the temperature was raised—see ref 53-kob/lyn for some differences in detail between the two procedures. If the bomb was filled correctly, the vapor–pressure curve showed a break at the critical temperature, but it is an insensitive method. The expansion method proposed by Burnett [36-bur] is not suitable for use below the critical temperature but may be used for *pVT* studies above the critical temperature. Sorina and Efremova [66-sor/efr] described an apparatus using the method. The pressure vessel was of glass (i.d. 10 mm, wall thickness 4 mm), and the expansion measurements could be supplemented by visual observation at and below the critical temperature.

At the time Kobe and Lynn [53-kob/lyn] were writing their review, there was doubt whether the critical point determined by visual observation was the same as the critical point determined by *pVT* studies, and they stated that "the determination of the critical constants by *pVT* relations gives the true critical temperature". Despite the difficulty of identifying the isotherm with a horizontal point of inflection, the *pVT* value appeared to be unequivocal, whereas there was confusion about the significance of the visual phenomena—see ref 51-ata/sch for a summary of the consequences of, particularly, the work by Maass and coworkers [38-maa, 37-maa/ged, 39-mci/dac, 40-nal/maa], who defined several different temperatures distinct from the critical temperature. Today it is usual to prefer the recommendation by Kudchadker *et al.* [68-kud/ala] that "the critical temperature...observed visually should be preferred over the critical temperature determined from the inflection on the *pV* isotherm". As a test of the identity of the two values, Ambrose *et al.* [60-amb/cox] measured the critical temperature of fluorobenzene by the visual method using a sample from the same stock as that used by Douslin *et al.* [58-dou/moo], who obtained the critical temperature from *pVT* measurements. The agreement of the values obtained by the two methods using the same material, 286.95 and 286.92 °C, respectively, is within their estimated uncertainties. Moldover [74-mol] concluded that the temperature of disappearance of the meniscus did not differ from the thermodynamic critical temperature by more than 1 mK for many fluids.

Physical Measurements in the Critical Region

Measurements of refractive index, light scattering, relative permittivity (dielectric constant), and velocity of sound have been used to study changes in density (and the effect of gravity) near the critical point, but the investigations, which were reviewed by Levelt Sengers [75-lev-1], have usually been aimed at the study of critical phenomena rather than at providing values of the critical temperature, pressure, and volume. However, W. G. Schneider [51-sch-1] showed that at the critical point there is a minimum in the velocity of sound in sulfur hexafluoride from which a value for the critical temperature may be obtained. The method was developed by Stepanov and Nozdrev [68-ste/noz], who combined ultrasonic measurements with *pVT* (including vapor pressure) measurement on chlorosilanes. Another physical measurement, of electrical resistivity, was used by Hensel and Franck [68-hen/fra, 72-hen] for mercury and by Hoshino *et al.* for selenium [76-hos/sch]. Bulavin *et al.* used neutron absorption measurements for the density of ethane [71-bul/ost-1]. Weinberger and Schneider investigated the variation of density in xenon by use of a radioactive tracer [52-wei/sch-1].

Effect of Impurity

The studies of critical phenomena in single-component systems that began with Andrews's work on carbon dioxide [1869-and, 1876-and, 1887-and] were soon broadened to include the behavior of mixtures. By 1880 Dewar had reported his observations on mixtures of carbon dioxide with numerous solvents [1880-dew] and Hannay and Hogarth their observations on the effects of the presence of solids [1880-han/hog]. (Accounts of Hannay's work have been given by Travers [39-tra] and by Flint [68-fli].) It became clear that the values of the critical properties for single-component systems were sensitive to the purity of the sample studied, and Pictet and Altschul suggested use of the critical temperature as a criterion of purity [1895-pic/alt]. The same suggestion was made later by Harand [35-har] and by Fischer and Reichel [43-fis/rei].

Use of impure samples is probably the main reason most 19th century observations could be correctly dismissed in ref 53-kob/lyn as of only historical interest. Conversely, one reason the values obtained by S. Young [10-you-1] have remained in serious consideration until recently is that, as a pioneer in the development of fractional distillation in the laboratory, he worked with purer samples. Today, the presence of differing amounts of impurity in the materials examined is a principal cause of the discrepancies that are found between results obtained by different investigators.

Typical of many studies on mixtures are two by Kay [64-kay] and by Pak and Kay [72-pak/kay], from which it may be seen that different binary mixtures behave in different ways that reflect the nonideality of solutions. In general, the critical locus curves as a function of composition are not straight, and in many instances the critical temperature and pressure of a slightly impure sample will differ from that of a pure sample by more than would be expected from linear interpolation between the values for the material and a supposed contaminant. An impurity that will always be present unless steps are taken to eliminate it is air. Samples are normally degassed and the air is removed, but in some investigations air-saturated samples have been used when, for example, the aim has not been to make the most accurate measurements possible but rather economy of effort in the study of mixtures [65-mcm/kay, 72-pak/kay].

Effect of Mercury

When mercury is present in the system, it is necessary to determine its significance for the property being measured. If mercury liquid was in equilibrium with the vapor phase at the experimental temperature, it has been customary to correct the measured value of the pressure by subtracting the mercury vapor pressure, possibly with account taken of its enhancement due to the superimposed pressure of the principal component [75-amb]. Doubt was cast on this procedure by the work of Rowlinson and his co-workers [55-jep/row, 57-jep/ric, 59-ric/row], who showed that mercury dissolved in compressed gases to a greater extent than would be calculated from its vapor pressure. A theoretical study taking account of this work was made by Haar and Levelt Sengers [70-haa/lev]. However, the results of experimental studies of the effect of mercury on critical properties are confusing.

Richardson and Rowlinson [59-ric/row] found that the critical temperature of *o*-xylene measured in a sealed tube containing a visible excess of mercury, and therefore saturated with the metal, was 0.4 K lower than that of the pure compound, (356.2 ± 0.1) °C, whereas the critical temperature of cyclohexane, (280.20 ± 0.05) °C, measured under the same two conditions was unchanged. They concluded that when the vapor was saturated with mercury vapor, measurements of critical temperature above about 300 °C would be significantly affected. Kay and Pak [80-kay/pak] measured the critical temperatures and pressures of nonane, 1,2,4-trimethylbenzene, and naphthalene in an apparatus similar—but without the stirrer—to that normally used by Kay and his co-workers, with both mercury and gallium as confining fluids. (Gallium has a negligible vapor pressure but is experimentally difficult to work with, and Kay and Pak did not recommend its further use.) They also compared the critical temperatures and pressures of several hydrocarbons measured with the mercury−sample interface at the sample temperature and at ambient temperature. These experiments showed that the presence of mercury did indeed lower the observed critical temperatures, but the extent of the lowering did not much exceed the probable experimental error, except for naphthalene, which has a high critical temperature, 748.85 K. Contrary to the implication of the work by Rowlinson and his co-workers, the partial pressure of mercury in the critical pressure determinations was found always to be less than the vapor pressure. However, Kay and Hissong [67-kay/his] had previously found that although the effect of the presence of mercury on the measured critical temperatures of *o*-xylene and decane was negligible in comparison with the experimental error, the effect on the critical pressure was that it lowered one and raised the other.

The matter is still an open question since the uncertainties in measurements at the temperatures at which the mercury effect should be significant are larger than those at lower temperatures. S. Young made no correction for the presence of mercury, because he thought that its rate of evaporation through the long column of liquid in his apparatus was slow enough for equilibrium not to be reached [10-you-1]. In contrast, the height of the liquid in the apparatus designed by Beattie [34-bea] is relatively short, and it has been generally assumed that equilibrium is reached. No clear differences have been noted generally in published values for critical temperatures greater than 300 °C (and the associated critical pressures) that can be attributed to the presence of mercury.

Apparatuses using mercury for confinement of the fluid may not be suitable for some compounds because of the effect mercury may have on their decomposition or because of chemical reaction between the fluid and mercury; as has been mentioned, S. Young reported this problem in his work on carbon tetrachloride [1891-you-1]. Contact with mercury is avoided with the apparatus described by Rosenthal and Teja [89-ros/tej] that is referred to in the next section.

Unstable Compounds

Equilibrium is reached very slowly near the critical point, and the most precise values of the critical properties are those obtained in conditions of extreme stability of temperature and pressure. This cannot be achieved when the sample under study is unstable and it is necessary to make measurements quickly.

So far, except in the method developed by Nikitin *et al.* [93-nik/pav] described at the end of this section, the critical properties of unstable compounds have been determined by methods in which the critical point is identified visually. Decomposition leads to change in the observed values of the critical temperature with time, and to obtain the correct value, it is necessary to extrapolate the observations back to a hypothetical zero time at which the sample could be considered to have been at its critical point and no decomposition had occurred. Some compounds, such as alkanes, decompose into compounds with smaller molecules, and the apparent critical temperature falls while the pressure rises, whereas other types of compound, such as phenols, may condense with the formation of tars, and this causes a rise in the apparent critical temperature and a fall in the critical pressure.

Stability at the critical temperature is dependent on the chemical nature of the compound. Normal alkanes, for example, are stable up to decane, *i.e.*, decomposition is slow in comparison with the time required for determination of the critical temperature. Decomposition is detectable with undecane and dodecane, but its rate is sufficiently slow for there to be little difficulty in studying these compounds in apparatuses designed to be very stable in temperature and intended for use with stable compounds. Higher members of the series decompose rapidly, and the rate of decomposition increases rapidly with increase in molecular size. For these it is necessary for measurements to be made rapidly. The normal alkanes are the most stable aliphatic series; other types, such as halogen compounds other than highly fluorinated compounds, are generally unstable (and the decomposition may be catalyzed by the presence of mercury), and none of the fatty acids is stable at its critical temperature. Among aromatics, benzene and naphthalene are stable at their critical temperatures, and short chains can be added to benzene without diminishing the stability significantly, but 1- and 2-methylnaphthalenes are extremely unstable.

An apparatus was described by Ambrose [63-amb] with which it was possible to reach a temperature around 700

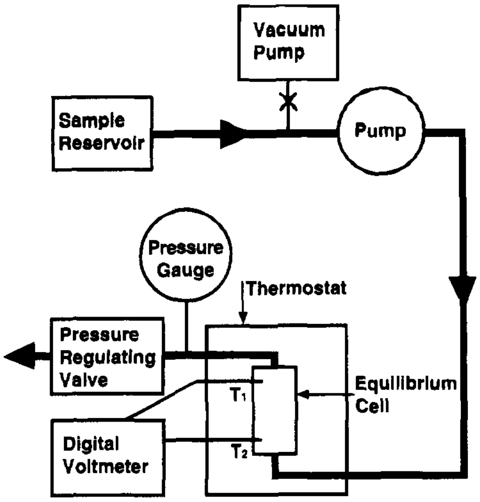

Figure 5. Block diagram of the flow apparatus of Rosenthal and Teja [89-ros/tej, 89-ros/tej-1].

K within a few minutes and to vary the temperature, measured by means of a thermocouple, up and down through a critical temperature very rapidly. The cold experimental tube was inserted into the hot oven, and the initial critical temperature was then obtained by a simple graphical procedure. There were inherent temperature gradients and uncertainties in the definition of the time zero. Mogollon *et al.* [82-mog/kay] improved the method by providing a thermocouple pocket inside the experimental tube itself and stirring the sample by rotating the apparatus. Smith *et al.* [87-smi/tej] developed the instrumentation so that the temperature could be recorded by the observer depressing a switch. The resultant curve was then interpreted on the basis that change in the critical temperature arises from a first-order reaction. Anselme *et al.* [90-ans/gud] used the same method to obtain critical densities in addition to critical temperatures.

Short exposures to high temperatures were achieved by Rosenthal and Teja [89-ros/tej, 89-ros/tej-1] in a different way. Their apparatus was designed so that critical conditions could be maintained in a viewing cell through which the fluid flowed. The fluid was not in contact with mercury, and by making the residence time in the hot zone short, decomposition was kept to a minimum. Critical temperature and critical pressures were measured. A block diagram illustrating the flow method used by Rosenthal and Teja is given in Figure 5. The method involves pumping the sample continuously through a cell in an air thermostat. Because of the need to heat the sample very rapidly, the temperature control is not as good as in conventional static equipment. The temperature gradient in the cell was of the order of 5 K.

A novel approach to the study of unstable compounds is the method used by Nikitin *et al.* [93-nik/pav], in which the temperature of the attainable superheat of a liquid is determined by means of an electrically pulse-heated thin wire probe. As the pressure is increased to the critical value, the temperature of the attainable superheat tends to the critical temperature, and whereas the methods just described allow measurements to be made in only a few minutes, this method exposes the material to high temperatures for only milliseconds and decomposition should be much reduced. The accuracy claimed for the critical temperature determined in this way is ±1% and for the critical pressure ±2%.

Classification of Methods

The classification of methods proposed by Kobe and Lynn [53-kob/lyn] was subsequently used in the reviews by Kudchadker *et al.* [68-kud/ala] and by Mathews [72-mat]. It seems appropriate now, however, to adopt for the reviews that will follow this introductory paper the revised classification given in Table 3 that reflects the advances in understanding and techniques made since 1953.

Table 3. Keys to Methods of Critical Point Determination

1.	visual—in glass tube
2.	visual—in cell with windows
3.	nonvisual—pVT measurements
4.	other nonvisual methods
5.	critical pressure measurements combined with vapor pressure measurements up to the critical point
6.	critical pressure by extrapolation of vapor pressure curve
7.	orthobaric density measurements
8.	equation of state, thermodynamic study
9.	calculation from another physical property
10.	literature survey
(a)	with stirring
(b)	instrumental detection of critical point
(c)	special feature of apparatus

Kobe and Lynn differentiated four different visual methods. Subsequent work has shown that the same results are obtained within experimental error by all methods if they are sufficiently refined. Certainly, the differentiation made in the review of Kobe and Lynn [53-kob/lyn] between disappearance of the meniscus and disappearance of the critical opalescence is only a differentiation between the closeness of control of conditions in different apparatuses: such differences as resulted from these two definitions of critical conditions arose because of the performance of control equipment available at the time. The performance of such apparatuses used about 30 years ago was much lower than that of modern equipment. With apparatuses controlled as exactly as is possible today, differentiation between disappearance of the opalescence and of the meniscus is alternatively an argument about the meaning of the words used to describe what is observed.

The classification adopted here is based on the view that there are two general classes of methods for the identification of the critical point. The first is observation of the optical phenomenon, either visually or instrumentally (methods 1 and 2). The second class depends on the interpretation of what can be measured without direct observation of the sample, primarily pVT measurement (method 3) or other measurements (method 4).

Method 4 includes various methods that have not yet been used sufficiently widely to justify classification into a special category. For example, Hoyer *et al.* [68-hoy/san] demonstrated the possibility of using differential thermal analysis as a method for determining the critical temperature, and this method has been used more recently by Chirico *et al.* [89-chi/kni] for alkanes. The accuracy attainable appears to be not better than ±0.5 K. Included in this category also is the method used by Nikitin *et al.* for unstable compounds that was described in the preceding section [93-nik/pav]. In addition, some substances, because of their properties, require special methods. For hydrogen fluoride, Bond and Williams [31-bon/wil] used a tube of a metal resistant to attack by the material. The tube was supported on pivots in an air thermostat and its balance changed as the temperature was allowed to fall through the critical value and the phases were separated. A similar method had been used by Nadejdine [1885-nad]. Burriel Lluna *et al.* [68-bur/cra] measured densities of bromine, iodine bromide and iodine by measuring gamma-ray absorption, obtaining the orthobaric densities and also the critical temperatures. Special methods are required at very high temperatures, and these were reviewed by Ohse and Tippelskirch [77-ohs/tip].

With most of the methods the sample may be stirred, and the table of methods includes qualifying letters that may be attached to the method number to indicate the use of stirring and some other features of the experiments. It is useful to record that the sample was stirred even though, for single-component fluids, there is no evidence to correlate stirring or not stirring with a more accurate result. Methods 1 and 2 are differentiated because of the very great difference in the apparatuses. Experiments by method 1 may have been performed in a sealed tube, when critical temperature only can be determined, or in a tube open at its lower end and sealed by mercury communicating with a pressure gauge, when critical pressure also may be determined. These two methods have not been differentiated since it will be clear from the properties reported whether a sealed or unsealed tube has been used.

Once the critical temperature has been determined, vapor−pressure measurements are useful for the determination of critical pressure (methods 5 and 6). Method 5 involves making vapor−pressure measurements close to the critical point and determining the pressure at the critical temperature from the pressure−temperature curve (equation). In contrast, method 6 involves determining the critical pressure by extrapolation of vapor pressures at lower temperatures. Obviously there is the possibility of methods borderline between 5 and 6, and these are denoted 5/6. Values obtained by extrapolation (method 6) are less exact than those obtained by what is essentially smoothing of experimental data (method 5). Critical volume or density (method 7) is obtained from orthobaric density measurements by the rectilinear diameter except when a comment indicates some modification of the normal method. Method 8 covers those methods in which the critical properties have been obtained by use of an equation of state fitted to experimental data including values obtained far from the critical point. Method 9 includes, for example, the calculation of critical temperature from velocity of sound data as proposed by Filippov [84-fil] and from surface tension by the Ramsay and Shields equation [1893-ram/shi-3] and also the calculation of the critical volume from the response of the thermal conductivity detector in gas chromatography as suggested by Barry *et al.* [72-bar/tra]. Method 10 covers values that have been recommended in previous major reviews. In a few instances such values have been quoted in the tables and discussed in the text even though they are suspect in the light of more recent measurements.

In the tables in subsequent parts indications according to the keys in Table 3 are sometimes amplified by footnotes.

It is not practicable to make a general assessment of the accuracy of the various methods as the accuracy obtained depends on the particular investigator, apparatus, and compound studied. In general, methods 4, 6, and 9 are expected to lead to less accurate values than those obtained from methods 1−3 and 5. Method 9, in particular, leads to values that are much less certain than those obtained by methods 1−3.

For most organic substances the visual method, using either an open-ended or a closed tube, is usually the best technique to measure the critical temperature. In general, the most suitable method to obtain the critical pressure involves measuring the vapor pressures close to the critical point and determining the pressure at the critical point from the vapor−pressure−temperature curve. In general, the most suitable method for determining critical densities is that which involves measuring densities of coexisting gas and liquid phases at the same temperature and extrapolating the rectilinear diameter to the critical point. There are situations where unique circumstances require the use of special methods to measure critical properties.

Accuracy of Values

The accuracy with which the properties can be measured varies considerably from substance to substance. For example, the attainable accuracy of critical property measurement of many substances is severely restricted by decomposition.

For a stable compound with the best modern equipment it may be expected that the repeatability of measurements of critical temperatures identified by the visual method will be ±0.01 K or better. As stated earlier, it was suggested by Kudchadker *et al.* [68-kud/ala] that visual identification of the critical point was to be preferred to identification from the isotherms of a *pVT* study. This was the view of the present authors, whose experience has been predominantly with the visual method, but it now seems likely that the accuracy of values obtained from the best modern *pVT* studies, for example ref 94-gil/kle, will be as high as those obtainable by the visual method. An estimate of the corresponding figure for critical pressure is about ±0.005 MPa, though it is more usual for the best values of this property to be obtained from study of *pVT* or vapor pressure over a range of temperature extending close to the critical temperature, with the critical pressure obtained as the vapor pressure at the critical temperature calculated from an equation.

The figures for reproducibility are much larger than those for repeatability because the critical temperature (with the critical pressure moving accordingly) is sensitive to the presence of impurities in the sample, as has been discussed under Effect of Impurity.

It will also be noted that, even within laboratories, different investigations yield results differing by more than might be expected—for example, those on hexane by Kay and his co-workers given in part 2 of this series. While impurity may again be the reason for discrepancies, there is also, at least for the visual method, a personal effect to be considered: different observers may identify the critical point at different temperatures. In several investigations by Kay and co-workers that were not directed to measuring the critical properties with the highest accuracy, observations were made with air-saturated samples. Although the effect may not be great, the presence of air means that the investigation was made on a multicomponent mixture, albeit one that was very dilute. A more serious consequence of the presence of air with some compounds is that they may react with the oxygen.

Authors are recommended to give an uncertainty for their results, and in doing so quite properly wish to put the best possible interpretation on what they have done. They assess the accuracy of the readings given by the individual instruments used and, when more than one is involved, apply formulas for the propagation of errors to obtain an overall error. When, however, they report, for example, critical temperatures with uncertainties of ±0.01 K, or even ±0.001 K, these figures are to be interpreted as indications of the care with which the work has been done, but they can seldom be taken as the accuracy of the values reported, because values for one substance from different authors often differ by more than the sum of their estimated errors. The uncertainties for critical temperatures and critical pressures given in the tables of recommended values have to be, in general, larger than those for each separate investigation.

Values of the critical density depend on measurements made at temperatures below the critical, and a density, defined as the critical density, is obtained from them after taking account, when necessary, of the effect of gravity. However close the measurements are made to the critical temperature and however plausible the method used to interpret them, the value of the critical density is not a direct observation. Perhaps the earliest highly reliable results for this property were obtained by Beattie and his co-workers [39-bea/sim, 51-bea/lev]; they claimed an accuracy of ±1%, and this seems a reasonable figure for all except the best modern measurements which may attain ±0.2% (for example, refs 74-mol, 94-gil/kle]).

For all three critical properties the same problem arises for authors in this field as for the expression of other physical properties—how many digits should be given? One wishes not to lose precision and smoothness, and the present authors would admit instances when they may have given one more digit than is strictly justified. To go further, however, and give all of the digits delivered by computer or instruments belittles the work because it reveals ignorance of the measuring process; for example, expression of a critical pressure of 4 MPa to six decimal places implies an accuracy in measurement attainable only with difficulty in a standards laboratory.

Note on the Terms Repeatability and Reproducibililty

Definitions 3.06 and 3.07 in the "International vocabulary of basic and general terms in metrology" (ISO, Geneva, 1984) are as follows:

3.06 Repeatability of Measurements.

The closeness of the agreement between the results of successive measurements of the same measurand carried out subject to all of the following conditions:

the same method of measurement
the same observer
the same measuring instrument
the same location
the same conditions of use
repetition over a short period of time

Note: Repeatability may be expressed quantitatively in terms of the dispersion of the results.

3.07 Reproducibility of Measurements.

The closeness of the agreement between the results of measurements of the same measurand, where the individual measurements are carried out in changing conditions such as:

method of measurement
observer
measuring instrument
location
conditions of use
time

Note: 1. A valid statement of reproducibility requires specification of the conditions changed.
2. Reproducibility may be expressed quantitatively in terms of the dispersion of the results.

Acknowledgment

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