# The Critical Properties of *n*-Alkanes Using a Low-Residence Time Flow Apparatus

A low residence time flow method for the measurement of the critical temperatures and pressures of thermally-unstable fluids was developed in this work. The low residence time at elevated temperatures minimizes decomposition and other reactions, making it possible to measure the critical properties of many unstable fluids. An extrapolation procedure was developed to obtain the critical properties of rapidly reacting substances, based on the linear behavior of the apparent critical property with residence time. The measured critical properties of 14 *n*-alkanes (pentane through octadecane) using this method are reported in this paper. The results extend the available data on the critical properties of the higher alkanes and reveal a possible error in the literature value for the critical pressure of tetradecane.

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## Introduction

A knowledge of the critical properties of fluids is important in many thermodynamic and transport property calculations. In addition, critical points define the upper limit of two-phase behavior of fluids, which is of interest in a number of applications including oil drilling and supercritical extraction. In spite of these interests, however, measurements of critical properties have been limited to a small number of fluids and, moreover, some of these measurements are of doubtful accuracy because thermal decomposition or other reactions have apparently been ignored.

A major limitation of many experimental methods for the measurement of critical properties is that the substance under study must be kept at elevated temperatures for a substantial period of time. As a result, many thermally-unstable substances will have undergone decomposition or other reactions when the measurements are made. Smith et al. (1987) have recently described a rapid heating sealed ampoule technique which overcomes some of these limitations. The critical temperatures of the *n*-alkanes up to heptadecane (Smith et al., 1987) and the isomeric alkanols up to decanol (Anselme and Teja, 1988) have been measured using this approach. In addition, a modification of the method has been used to obtain the critical densities of the alkanols (Smith et al., 1986). It should be noted that only the critical temperature and density can be measured using the sealed ampoule technique. Moreover, the method is limited to substances which do not decompose or react to a significant extent.

Both these limitations can be overcome by the use of a flow method proposed by Roess (1936). Roess used his method to measure the critical temperatures and pressures of over 100 petroleum fractions with critical temperatures ranging from 560 K to 810 K. The method, however, suffered from several drawbacks. First, a large amount of fluid was required because of the size of the equipment and the flow rates employed. Secondly, several observers were used to control flow rates, set temperatures and pressures, and for detecting critical phenomena. Finally, critical temperatures were not measured directly, but by averaging temperatures at the inlet and exit to the apparatus. Nevertheless, the method showed promise and was selected for further study in this work.

A modified version of Roess' flow method is described below. The residence time of the substance under study at elevated temperatures is kept small in this method, so that decomposition or other reactions are minimized. The critical temperatures and pressures of the *n*-alkanes up to octadecane were measured and are reported below. The *n*-alkanes were selected for study because we have previously measured the critical temperatures and densities of these fluids using a rapid heating sealed ampoule technique (Smith et al., 1987). The critical temperatures obtained in the two different techniques can therefore be compared and checked for consistency.

## Experimental Studies

### *Apparatus*

In the flow method, the fluid of interest is pumped rapidly through a heated view cell at conditions (temperature, pressure, and flow rate) which yield critical opalescence and/or meniscus

disappearance in the cell. Thermal decomposition or reaction is minimized because the residence time of the fluid at high temperatures is kept low.

A schematic diagram of the apparatus used in this study is shown in Figure 1. An Aldex model 110A HPLC pump was used to pump the fluid through a heated view cell, where the pressure and temperature of the fluid were measured and any phase changes were noted. The pump had a pressure pulsation dampener and was capable of maintaining a constant flow rate of material in the range 0 mL/min to 10 mL/min. A check valve downstream from the pump was used to ensure unidirectional flow.

A diagram of the view cell is shown in Figure 2. The cell was made of stainless steel and consisted of a center piece and two compression plates. It had two windows made of borosilicate glass, 11-cm-long and 1.7-cm-thick. Two grafoil gaskets were used at the interface between the stainless steel and glass while two more were used to cushion the glass against the pressure plates. The pressure plates were made of 1.9-cm-thick stainless-steel flat plates, with fins added to prevent bowing. Two $\frac{1}{16}$-in. (1.6-mm) type-K thermocouples purchased from Marlin Manufacturing Company were inserted into the observation chamber at distances of approximately one-third of the length of the cell from each end. These thermocouples were sheathed and grounded to inconel 600 metal. The final dimensions of the cell are shown in Table 1. High-pressure NPT fittings, bonded to the cell with X-pando pipe joint compound, were used in the construction. The X-pando compound cements the bolt into the threads and withstands extreme conditions of pressure, vibration and temperature. It is also insoluble in hydrocarbons.

The cell was pressure-tested to 10 MPa at room temperature and 6.8 MPa at 673 K. The total volume of the chamber was slightly over 4.3 mL. Based on this volume and the volume of the tubing leading into the cell (ca. 0.5 mL), a flow rate of 10 mL/min of a liquid at room temperature results in a residence time in the cell of approximately 27 s. However, because the critical densities of the fluids are generally smaller than the densities at ambient conditions by a factor of three, the actual residence time of the fluid at elevated temperatures is of the order of 10 to 15 s at the highest flow rate.



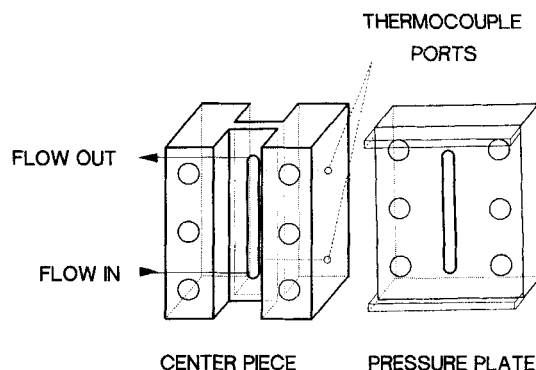Figure 1. Schematic diagram of apparatus.



Figure 2. View cell used in the experiments.

The visual cell was placed inside a thermostatted air bath, which consisted of an insulated metal cabinet, two Lindberg heating plates (Model 50026; rated up to 1,250 K), a circulating fan, and an Omega CN2010 PID temperature controller. The controller could maintain a setpoint temperature to ±1 K. The bath was provided with two windows 180° apart. One window was used for visual observation, whereas the second window was used to admit a source of light to the observation chamber. A plexiglass plate was securely fastened between the experimenter and the observation window for additional safety.

A Whitey flow control micrometering valve located downstream from the bath enabled the pressure in the cell to be manipulated. A digital Heise gauge was used to measure and display the pressure. The fluid was discarded when it exited the bath.

## Experimental procedure

The fluid was degassed separately in a vacuum system using a series of freeze-pump-thaw cycles. The degassed sample was then placed in the feed tank to the apparatus, which had previously been cleaned and evacuated. Next, the HPLC pump was started at the maximum flow rate setting, with the flow control valve shut and the air bath temperature set at a temperature approximately 20 K above the expected critical temperature of the fluid. As the liquid was pumped into the apparatus, it was initially seen to flash to vapor inside the chamber. When the pressure increased, this effect was no longer visible. As the system pressure approached the critical pressure of the fluid (approximately 45 s after starting the pump, and provided the temperature of the fluid in the cell was close to the critical temperature), a flat meniscus separating the vapor and liquid phases could be observed in the cell. The meniscus continued to move up the chamber until it disappeared with no observable differences between the vapor and liquid phases. If the temperature of the fluid inside the cell was lower than the critical temperature, then the meniscus had pronounced curvature because of the differences in density and surface tension between the
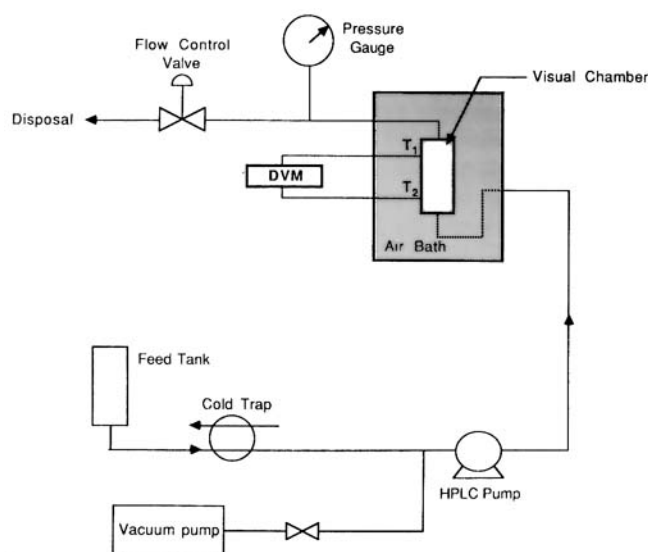
Table 1. Dimensions of View Cell

| Length | 9.3 cm |
|---|---|
| Depth | 0.735 cm |
| Width | 0.635 cm |
| Internal Volume | 4.36 cm³ |
| Distance between Thermocouples | 2.9 cm |

vapor and liquid. This meniscus entered at the bottom of the cell and travelled up the cell until it exited at the top without disappearing. In this case, the oven temperature was raised and the procedure repeated.

After the disappearance of the meniscus inside the chamber, the flow control valve was adjusted so that a slow decrease in the pressure could be obtained. At pressures slightly above the critical pressure, a faint band of orange-red color could be observed in the fluid, together with a fine mist or fog. Further pressure reduction led to a very distinct band of red color, and finally to separation into liquid vapor phases. The pressure was recorded when the red color was the most intense. The position of the red band in the chamber could be altered by changing the flow rate of the fluid. When the red color appeared near one of the thermocouples, the temperature measured by that thermocouple was assumed to be the critical temperature. The size of the band varied in length from about 1 mm to 8 mm depending on the flow rate and hence the temperature gradient in the cell.

## Calibration

*Temperature.* The thermocouples were calibrated in the experimental setting using four fluids whose critical temperatures are well established, *viz.* pentane (469.7 K), heptane (540.3), cyclohexane (560.9 K), and toluene (591.5 K). This approach follows that of several previous investigators of critical phenomena (Ambrose, 1963; Trejo and McLure, 1983), who calibrated their thermocouples in this fashion. Direct calibration of the thermocouples was not possible because a PRT could not be inserted into the view cell. The agreement of the measured critical temperatures obtained in the present study for other stable alkanes (octane, nonane) with literature values attests to the validity of the calibration procedure.

The error in the measured critical temperatures were due to the calibration procedure and the precision of the measuring devices. We estimate that the accuracy of the critical temperatures measured in this study to be $\pm 0.6$ K for stable substances. The errors were larger for unstable substances because of the use of an extrapolation technique (as described below).

*Pressure.* Two Heise model 710A pressure gauges were used to measure the pressure. One gauge (serial # S7-19175) could measure pressures between 0–6,000 psi (0–41 MPa) with a precision of 1 psi (6.89 kPa), while the other (serial # S714510) could measure pressures in the range 0–200 bar with a precision of 0.01 bar. Both gauges were calibrated against a Budenberg model 380-H dead-weight tester (serial number 16685). The dead weight standards were certified by the National Physical Laboratory, and the apparatus had a basic accuracy of 0.05%. Since the pressure gauges tended to drift from day to day, they were calibrated after every experimental run.

The accuracy of the pressure measurement is estimated to be $\pm 0.02$ MPa (3 psi) for stable substances. The error is a function of the accuracy of the dead-weight gauge and the precision of the Heise gauge. The errors were larger for unstable substances because of the need for extrapolation of the data.

*Flow Rate.* The Aldex pump was calibrated with water and degassed ethanol. A flow rate was set and the fluid allowed to flow through the pump and into a container. After a set time, the container was weighed and the amount of fluid determined. The flow rate was found by dividing the volume of fluid by the time. Both fluids had approximately the same flow rate throughout the range of the HPLC pump.

## Criteria for detection of the critical point

The effect of changing the residence time was studied by altering the flow rate of the fluid. If no change in critical pressure occurred with varying flow rate, the substance was assumed to be thermally-stable. A change in critical pressure and/or critical temperature with flow rate indicated that the substance was thermally-unstable.

In the case of the thermally-stable substances, the temperature of maximum opalescence, that of the disappearance of the meniscus, and that of reappearance of the meniscus were identical within experimental error. Therefore, the critical point was determined by the criterion of maximum opalescence. On the other hand, maximum opalescence and reappearance of the meniscus were much more difficult to detect in the case of highly unstable substances because of condensation and retrograde behavior. Therefore, the disappearance of the meniscus was used as the criterion for the critical point. Although the meniscus separating the two phases is very faint near the critical point and therefore difficult to detect, disappearance of the meniscus was reproducible with $\pm 0.01$ MPa.

In the case of highly unstable substances, decomposition occurs even at the highest flow rate (or lowest residence time). Therefore, an extrapolation technique was used to determine the critical properties. Figure 3 shows the critical temperature-residence time behavior for hexadecane. A linear fit was used to extrapolate the data to zero time. The critical point reported is the average of the point at zero residence time $X_0$ and the first data point $X_1$, i.e., $X = \frac{1}{2}(X_0 + X_1)$ where $X = T_c$ (a similar procedure was used with $X = P_c$). The error was assumed to be $\frac{1}{2}|X_1 - X_0|$ with a minimum of 0.6 K in the case of the critical temperature with 0.02 MPa in the case of the critical pressure.

This procedure assumes that the original substance and its products of decomposition yield a critical locus for the mixture which is a linear function of the mole fraction of the impurities and therefore of the residence time. This assumption has been shown to be valid for dilute polydisperse fluids (i.e., mixtures composed almost entirely of one species, with the remaining
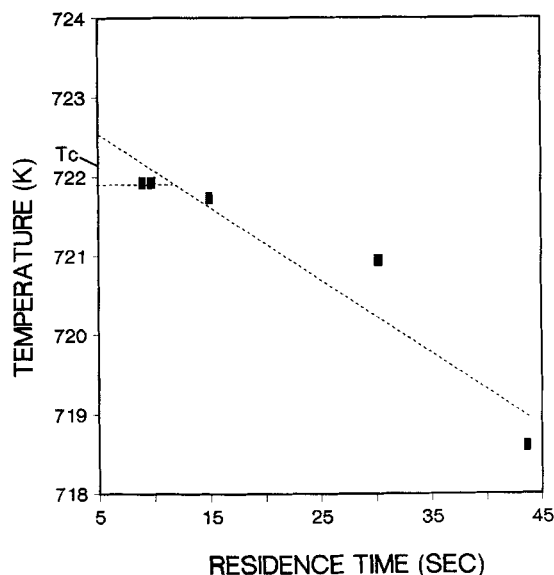


**Figure 3. Apparent critical temperature of *n*-hexadecane as a function of residence time.**

small fraction of the fluid consisting of an infinite number of components) by Gualtieri et al. (1982). We have also shown experimentally (Teja and Smith, 1987) that the critical locus of hydrocarbon mixtures is linear at high concentrations of one of the components. Since the extent of decomposition (and therefore the composition) is proportional to the residence time, it would appear that the linear extrapolation of the data with residence time is also valid. However, because of the uncertainty in the calculation of the residence time and other factors (such as the purity of the material, scatter in the data etc.), we have assumed that the extrapolated value ($X_0$) is an overestimate of the true value ($X$). Moreover, the experimental value $X_1$ at the lowest residence time provides the lowest estimate of the true value, since the least amount of decomposition will have occurred at the lowest residence time. The critical point is found by averaging these two values, as described above. The residence time, $\tau$, was calculated from the volume of the cell $V$, the volume of the oven inlet pipe $V_p$, the flow rate $F$ at the pump head, and the ratio of the critical density to the density at the pump head as follows:

$$\tau = \frac{V + V_p}{F} \cdot \frac{\rho_c}{\rho} \tag{1}$$

Because the time at which decomposition first occurs cannot be determined, the extrapolation procedure also assumes that decomposition occurs as the material enters the heated oven. This assumption is very conservative and also tends to overestimate the critical property. We have used an analogous extrapolation procedure in our sealed ampoule studies of critical properties and have obtained estimates which generally agree with literature values (Anselme and Teja, 1988).

### Effects of dissolved air

The critical properties of several stable substances were measured prior to and after degassing. No observable differences in the two measurements could be detected for any of the substances. Eaton and Porter (1932) also found no differences between degassed and air-saturated samples in their experiments using a sealed ampoule method. Pak and Kay (1972), however, found that the critical temperatures of air-saturated samples were lower by an average of 0.6 K and critical pressures were higher by an average of 0.02 MPa. It should be added that Pak and Kay only measured the critical properties of air-saturated substances and assumed that the literature values were for degassed samples. In conclusion, for stable substances, the small amount of air present in a hydrocarbon has little or no effect on the critical point.

In the case of unstable substances, air saturation had a detrimental effect on the pump flow rate. Air-saturated samples produced sporadic flow rates, and furthermore the presence of oxygen tended to increase the decomposition rate of the hydrocarbons. Increased decomposition lowers the apparent critical temperature and elevates the critical pressure. For these reasons, the samples of both stable and unstable substances were degassed prior to measurement.

### Source and purity of materials used

The experimental work in this study involved the determination of the critical temperature and pressures of the 14 alkanes

**Table 2. Source and Purity of the Materials Used**

| Substance | Supplier | Lot # | Purity |
|---|---|---|---|
| Pentane | Aldrich | 03003KT | 99.5% |
| Hexane | Fluka | 274065 | 99.5% |
| Heptane | Aldrich | 9809EL | 99.9% |
| Octane | Fluka | 262608 | 99.5% |
| Nonane | Aldrich | 00108HT | 99% |
| Decane | Aldrich | 00815HT | 99% |
| Undecane | Aldrich | 07225KT | 99% |
| Dodecane | Aldrich | 1224DZ | 99% |
| Tridecane | Aldrich | 02303HT | 99% |
| Tetradecane | Aldrich | 02604ET | 99% |
| Pentadecane | Aldrich | 04220KM | 99% |
| Hexadecane | Aldrich | 00523PT | 99% |
| Heptadecane | Aldrich | 1908EL | 99% |
| Octadecane | Sigma | 114f0288 | 99% |

**Table 3. Critical Temperatures and Pressure of n-Alkanes**

| Substance | $T_c$/K | | $P_c$/MPa | |
|---|---|---|---|---|
| | This Work | Lit. Value | This Work | Lit. Value |
| Pentane | 469.7 ± 0.6 | 469.7(a) | 3.369 ± 0.02 | 3.369(a) |
| Hexane | 507.4 ± 0.6 | 507.5(a) | 3.014 ± 0.02 | 3.012(a) |
| | | 507.3(e) | | |
| Heptane | 540.3 ± 0.6 | 540.3(a) | 2.734 ± 0.02 | 2.736(a) |
| Octane | 568.8 ± 0.6 | 568.6(a,e) | 2.495 ± 0.02 | 2.487(a) |
| | | 568.7(b) | | |
| | | 568.8(c) | | |
| Nonane | 594.7 ± 0.6 | 594.6(a) | 2.280 ± 0.02 | 2.288(a) |
| | | 594.7(b) | | 2.294(d) |
| | | 593.6(c) | | |
| | | 593.8(d) | | |
| Decane | 617.9 ± 0.6 | 617.6(a) | 2.099 ± 0.02 | 2.104(a) |
| | | 617.9(b) | | 2.139(d) |
| | | 617.6(c) | | |
| | | 616.8(d) | | |
| | | 617.5(e) | | |
| Undecane | 638.4 ± 0.6 | 638.8(a) | 1.948 ± 0.02 | 1.966(a) |
| | | 638.7(c) | | |
| | | 637.1(b) | | |
| Dodecane | 658.8 ± 0.6 | 658.3(a) | 1.810 ± 0.02 | 1.824(a) |
| | | 659.0(d) | | |
| | | 657.4(b) | | |
| | | 657.7(c) | | |
| | | 658.4(e) | | |
| Tridecane | 676.0 ± 0.6 | 676.0(a) | 1.679 ± 0.02 | 1.72(a) |
| | | 676.2(c) | | 1.73(d) |
| | | 674.0(b) | | |
| | | 674.9(d) | | |
| Tetradecane | 691.8 ± 0.7 | 696.9(d) | 1.573 ± 0.02 | 1.44(d) |
| | | 692.8(c) | | |
| | | 691.2(b) | | |
| Pentadecane | 707.5 ± 0.7 | 709.2(c) | 1.479 ± 0.02 | |
| | | 706.4(b) | | |
| Hexadecane | 722.4 ± 1.1 | 723.0(c) | 1.401 ± 0.05 | |
| | | 722.0(b) | | |
| Heptadecane | 735.9 ± 1.0 | 736.0(c) | 1.342 ± 0.16 | |
| Octadecane | 747.7 ± 1.0 | 748.0(a) | 1.292 ± 0.11 | |

a – Ambrose (1980); b – Smith et al. (1987); c – Mogollon et al. (1982); d – Pak and Kay (1972); e – Anselme (1988).

listed in Table 2. The purest, commercially-available materials were used in the experiments. The purity was generally above 99%, and all the chemicals were used as received. Table 2 also gives the purity, supplier and lot number of the substances studied.

## Results and Discussion

The critical temperatures of the $n$-alkanes from octane to octadecane and critical pressures from pentane to octadecane ($C_5$ to $C_{18}$) were measured in this work and are presented in Table 3. Also reported are values of the critical temperature obtained from the literature and in our laboratory by Smith et al. (1987) and Anselme (1988) using a sealed ampoule technique.

Smith et al. and Anselme found that $n$-decane was the first $n$-alkane to decompose in their sealed ampoule experiments. In contrast, pentane through undecane were found to be "stable" in the flow apparatus. Starting with dodecane, lowering the flow rate produced a noticeable increase in critical pressure and a slight decrease in critical temperature with residence time. This

effect can be attributed to thermal decomposition. The cracking of the hydrocarbon yields a mixture of lower-molecular-weight hydrocarbons which have higher critical pressures and lower critical temperatures. In fact, the occurrence of thermal decomposition could also be deduced from the observation of the critical opalescence phenomena. A narrow, clear-cut, red-colored band was observed in the case of stable substances. This band became generally broader and less well defined for pentadecane and higher alkanes. Furthermore, a white cloud could also be observed with the orange-red opalescence band in the case of pentadecane and higher alkanes. This cloud was probably caused by condensation of the hydrocarbon from the vapor phase.

In the case of unstable substances ($C_{12}$ to $C_{18}$), extrapolation was used to obtain the critical properties as described above. The results of the extrapolation are shown in Figure 4. For the higher alkanes, the critical temperature decreases and critical pressure increases linearly with time. In general, the slope increases as the carbon number of the alkane increases. This is expected since the steeper slope indicates greater decomposition and a larger cracking reaction rate. The reaction rate has been shown to increase with carbon number by Murata and Saito (1974).

Figure 5 shows the critical pressure and critical temperature of the $n$-alkanes plotted against carbon number. A smooth curve is obtained from the homologous series of alkanes. Also, the critical properties of the stable alkanes (pentane through undecane) obtained in this work are in excellent agreement with literature values, including those measured in our laboratory using the
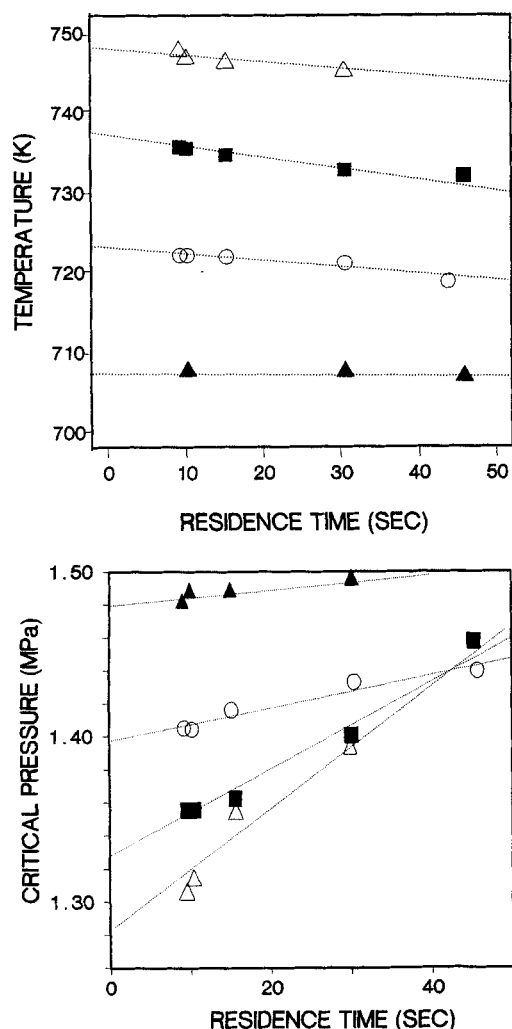


**Figure 4. Extrapolation of the apparent critical temperatures and pressures of the $n$-alkanes.**

▲ $n$-pentadecane, O $n$-hexadecane, ■ $n$-heptadecane, △ $n$-octadecane
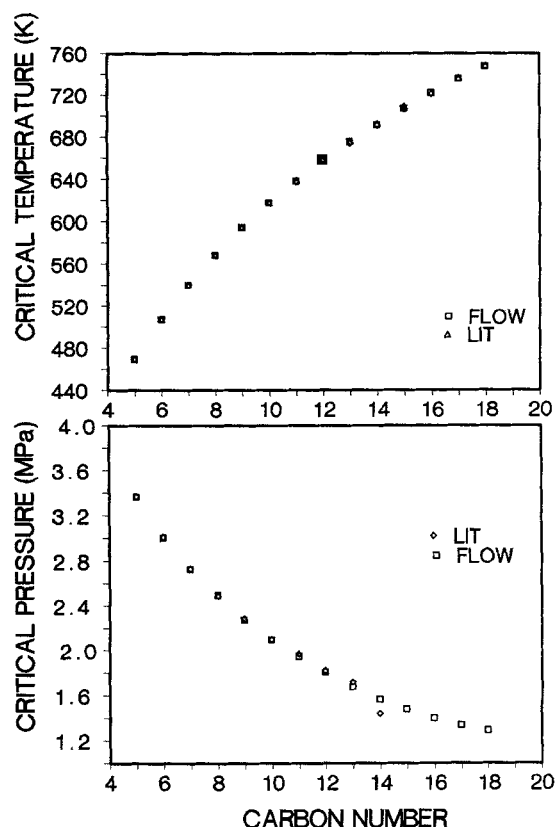


**Figure 5. Critical temperatures and pressures of the $n$-alkanes as a function of the carbon number.**

sealed ampoule method (Smith et al., 1987; Anselme, 1988). In the case of unstable n-alkanes, however, agreement between experimental values and literature values is generally only fair. Moreover, the literature values for the critical temperature do not agree with each other as can be seen in the case of tetradecane in Table 3. There is a 4.7 K difference in experimentally-measured critical temperatures of tetradecane reported in the literature. This difference is most likely due to the extrapolation procedure used (or not used) to obtain the critical temperature. The advantage of the flow method is that this extrapolation is done over a smaller time interval and over a smaller range of decomposition. Hence, the results from the flow method are likely to be more accurate than the other results.

The critical pressures of the n-alkanes obtained in this study are in excellent agreement with literature values, within experimental error. Figure 5 also shows that the critical pressure follow a smooth and consistent trend with carbon number. However, the literature value for the critical pressure of tetradecane does not lie on this curve and must be regarded as questionable.

## Conclusions

We have developed a dynamic apparatus to measure the critical pressure and temperature of thermally-labile substances. The substance is maintained at its critical temperature for a short period of time (ca. 10–50 s) so that thermal degradation is minimized. Critical temperatures and pressures of the n-alkanes from pentane to octadecane were measured and are reported in this paper. The measured critical properties were generally found to be in agreement with literature values, except for tetradecane where the literature value must be regarded as questionable. No literature data are available for the critical pressures of n-alkanes above tetradecane.

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