Measurement of Critical Temperatures of Thermally Unstable *n*-Alkanes

A modified sealed-tube apparatus has been developed for the measurement of the critical temperatures of thermally unstable fluids. The apparatus has been used to measure the critical temperatures of the normal alkanes from *n*-octane to *n*-hexadecane. Since the higher alkanes (with more than 10 carbon atoms) decompose at temperatures well below their critical temperatures, a new method of analysis of the apparent critical temperature vs. time data has been developed. This method employs reaction kinetics based on an irreversible first-order reaction and is used to linearize the data and to perform an unambiguous extrapolation to the critical temperature of the undecomposed substance. The method is successful because the temperature history of the substance is recorded by computer, and ampoule contents are analyzed at the completion of the experiment. The critical temperatures of the *n*-alkanes reported in this paper have been compared with values found in previous studies.

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Introduction

The critical temperature of a substance is an important characterization parameter in many thermodynamic and transport property predictions. Knowledge of the critical temperature allows vapor pressure data to be extrapolated to the critical pressure. Entire phase diagrams may then be predicted using appropriate corresponding-states methods.

The techniques for critical temperature measurement have been reviewed by Kobe and Lynn (1953) and more recently by Hicks and Young (1975). The technique used in this work is commonly referred to as the sealed-tube method; it consists of heating a sample in a sealed glass tube or ampoule until the liquid-vapor interface is replaced by an opalescent band. It is a relatively simple technique and requires only that the amount of fluid enclosed in the ampoule be such that its volume at the critical temperature is approximately equal to the volume of the sealed ampoule. Since the critical volume of the substance is not necessarily known in advance, a modification of the ampoule is described below that enables precise volumes to be sealed. A limitation of the original sealed-tube method is that it cannot be used with thermally labile substances since these substances may not be heated to their critical temperatures. Mogollon et al. (1982) overcame this problem by using a rapid heating furnace and extrapolating the apparent critical temperature vs. time data to zero time to determine the actual critical temperature of the undecomposed substance. However, their extrapolation procedure was risky because the origin (zero time) was arbitrary and because the time interval over which the extrapolation was carried out was large. We present below a new method of data analysis based on the kinetics of decomposition. Our approach overcomes the limitations of the Mogollon et al. procedure. It is made possible because the temperature history of the substance is recorded by an Apple IIe microcomputer and the decomposition products are analyzed at the completion of the experiment.

Experimental

Apparatus

The rapid heating furnace used in our study was constructed by Ace Glass Co.; it consisted of a 55 cm long, 2.5 cm OD quartz tube plated with four layers of platinum metal. The metal coating served as the electrical resistor of the furnace. Three windows, 90° apart and 75 mm long by 3 mm wide, were left uncoated in the middle of the furnace to allow viewing of the sample. The furnace was rated at 85 VAC at 6 A and had a room-temperature resistance of 6.9 Ω. It could easily achieve the temperatures of interest in about 5 min. Current to the furnace was supplied by two 12 A autotransformers operated in series, giving very fine voltage control; the main power was regulated by a GE voltage stabilizer. The furnace was capped with an aluminum plug at the top and a Teflon plug at the bottom, with the plugs drilled in the center to act as guides for the ampoule holder assembly. A 50 mm OD outer tube made of borosilicate glass was used to insulate the furnace from the surroundings. Two 10 cm widths of Fiberfrax insulation were packed at the top and bottom of the furnace in the annular space between the outside glass tube and the furnace wall. The furnace was mounted on a trunnion assembly to allow rotation through 180°, which provided mixing of the sample during heating.

The ampoules used in this study, shown in Figure 1, were made from 10 mm standard wall borosilicate glass tubing and had a nominal internal volume of 1.5 cm^3. Each ampoule was provided with a thermowell made from 4 mm standard wall tubing. The thermowell ensured that a thermocouple placed in it would extend into the center of the ampoule and be surrounded by the fluid during the experiment, thus ensuring accurate temperature measurement. The thermowell design is similar to that used by Mogollon et al. (1982). An additional modification used successfully in our work was the joining of a 3 cm length of 1 mm capillary tubing to the ampoule. The existence of the capillary enabled reliable seals to be made and is further discussed in the section on experimental procedure. The ampoule holder (Figure 1) was made from stainless steel and had a minimum contact area with the ampoule surface.

A diagram of the experimental apparatus is shown in Figure 2. Temperature was measured with an iron-constantan thermocouple that was calibrated over the temperature range 500–770 K by comparison with a standard platinum resistance thermometer calibrated at the National Bureau of Standards. In addition, the standard thermometer was checked by comparison with the ice point, the freezing point of tin, and the freezing point of zinc. Thermocouple EMF was sensed by a Fluke 8840A digital voltmeter with a 1 μV sensitivity. The voltmeter was provided with an IEEE-488 interface for digital output of data. Since the temperature history and the apparent critical temperature as a function of time were desired, the EMF data were written to disk. This was done on an Apple IIe microcomputer having a 64K memory, an Applied Engineering Timemaster II real-time clock board, and an Apple IEEE-488 interface board. Time was read by the Applied Engineering quartz clock, which has negligible inaccuracy compared with the software constraints of the Applesoft BASIC used for the programming. An external switch was wired to the joystick port of the microcomputer to allow digital marking of the temperature and time when critical opalescence was observed.

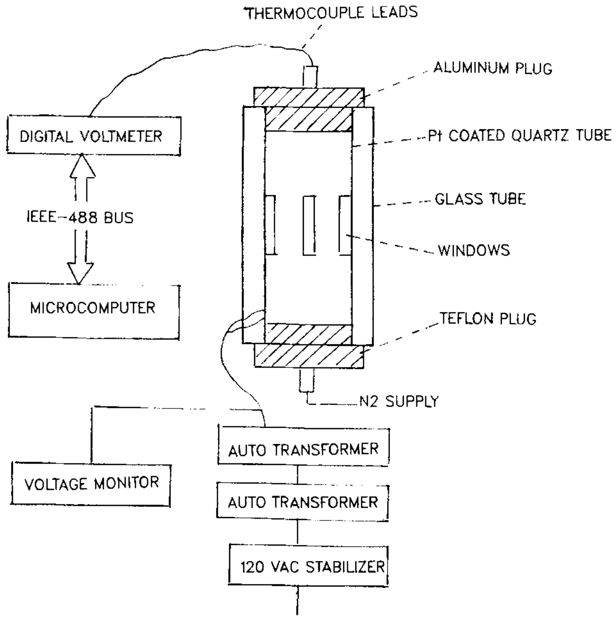

Figure 2. Diagram of apparatus.

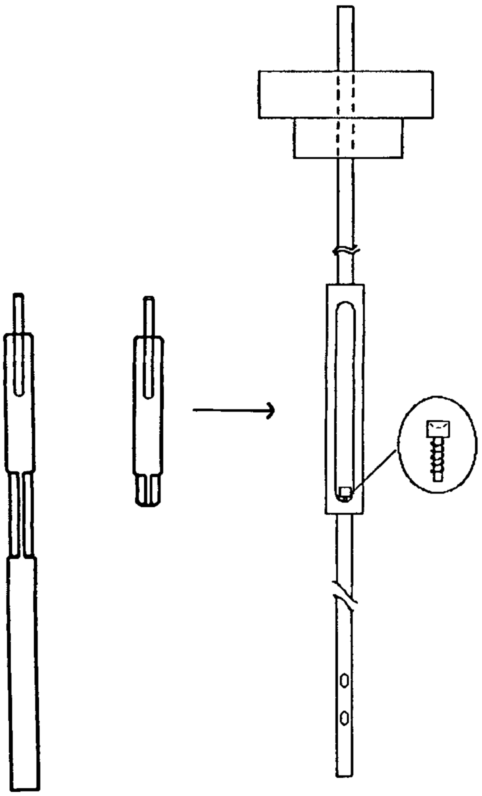

Figure 1. Ampoule and holder assembly.

Procedure

As a safety precaution each ampoule was tested to a pressure of 4,500–5,500 kPa. Bursting pressures of the ampoules were found to be between 9,000 and 10,500 kPa. The ampoules were etched with hydrofluoric acid on the capillary portion of the neck and cleaned by washing first with nitric acid, then with distilled water and acetone. The ampoules were allowed to dry in an oven and stored in a desiccator.

The sealed-tube method requires a sample to be loaded at room temperature so that the critical density is achieved upon heating. To do this requires knowledge of the ampoule volume and an estimate for the critical density. Critical densities were estimated using the group contribution method of Ambrose (1978). Ampoule volumes were determined from the weight and density of freshly distilled mercury required to fill the ampoule to the etched mark. The weighing was done using a balance with a sensitivity of 0.1 mg. A 1 cm^3 hypodermic syringe with a 15 cm long needle was used to introduce the sample into the ampoule. Some ampoules were loaded with slightly more and some with

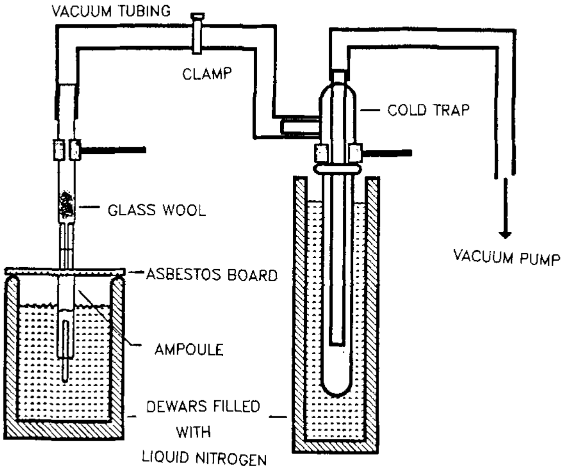

Figure 3. Degassing apparatus.

slightly less sample. A wad of glass wool was placed in the neck afterward to prevent debris from entering during degassing.

Since vapor pressure is sensitive to dissolved gases, the substances in the ampoules underwent successive freeze-melt cycles under vacuum to remove noncondensable gases. Each substance was frozen with liquid nitrogen and a vacuum was pulled with a roughing pump capable of 10^{-3} mm Hg (0.133 Pa) using the apparatus shown in Figure 3. The successive freeze-melt cycles were continued until no gas formed upon melting. The ampoules were then sealed off at the etched marks.

One problem with the ampoules used by Mogollon et al. was that they were difficult to seal reliably. In addition, it proved difficult to determine the volume once the seal had been made. The ampoule design used in our work allows for very reliable sealing by the use of 1 mm capillary tubing where the seal is to be made. The tube was typically collapsed with a gas-oxygen torch above the etched mark and the glass was melted exactly to the mark. Since the seal could be made exactly at the etched mark, highly reproducible and precise results were possible.

The sealed ampoule was then placed in the ampoule holder and the thermocouple was secured in the well. The assembly was placed in the furnace and the structure was fastened in the furnace support. A nitrogen gas line was connected to the bottom of the ampoule holder so that an inert atmosphere could be maintained and cooling could be enhanced for cases where the temperature was overshot. The gas was used sparingly, however, since it causes temperature fluctuations. Once the file and initial program parameters had been input to the microcomputer, the heater was switched on and the entire assembly rocked rapidly through 180°. When critical opalescence was observed, the switch was depressed. A tone was generated by the computer, signaling that the data had been recorded. Visual feedback was provided on the monitor, giving the operator a plot of the temperature profile, the heating time, the temperature, and the rate of heat increase or decrease.

The temperature of the fluid in the ampoule is seldom constant, due to the varying rate of heating and because of the changing nature of the substance being measured. This led us to define the critical point somewhat differently from the more common case when the substance is stable. As the temperature approached the critical temperature, it was observed that the lack of density gradients made separation of the mixed phases increasingly difficult. Upon each rocking of the furnace, therefore, a note was made whether or not a meniscus between the two phases could be found. When the meniscus was replaced by a band of opalescent fog, the point was noted as the critical point of disappearance of the meniscus. A similar procedure was used for the meniscus reappearance, although reappearance is much more abrupt and easier to locate even when the apparent critical temperature is changing rapidly (>0.25 K/min).

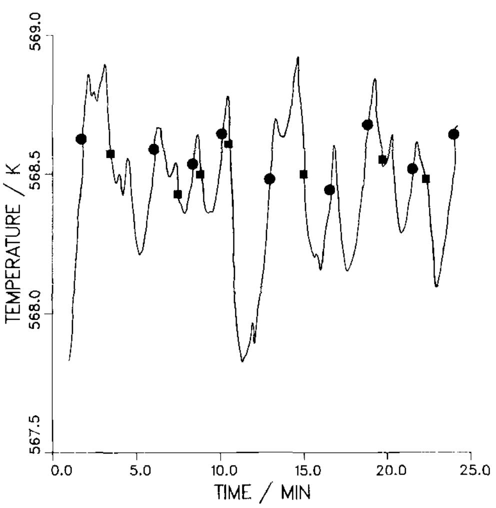

Figure 4. Temperature history of *n*-octane.
● meniscus disappearance, ■ meniscus reappearance.

After the disappearance of the meniscus had been noted, the voltage was reduced or shut off for a few seconds to allow the temperature to gradually decrease until a reappearance of the meniscus was observed. The voltage was then increased and the procedure repeated. In this manner, points could be redetermined at approximately 1 min intervals with rates of a few tenths of a degree increase or decrease of temperature per minute. These slow rates of temperature change also ensured that the thermocouple lag was not significant. Experimental runs usually lasted from 20 to 40 min, depending on the decomposition rate. The temperature history of a stable substance (*n*-octane) is shown in Figure 4. Note that the critical point is

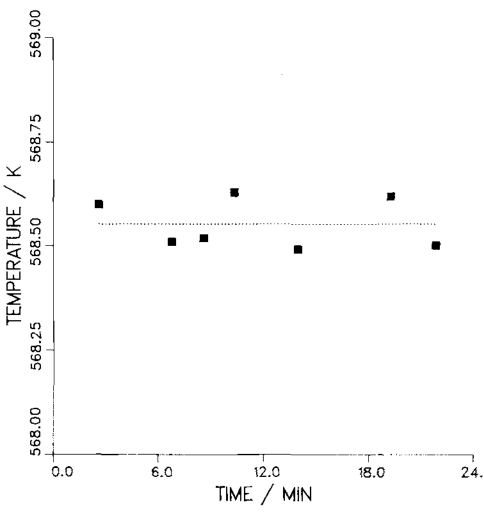

Figure 5. Average critical temperature of *n*-octane.

defined as the average of the adjacent disappearance and reappearances of the meniscus. This average is constant with time for the stable n-octane as shown in Figure 5. For substances that decompose, this average generally decreases with time.

Once the run had been completed, the ampoules were cooled and broken under a nitrogen atmosphere. Samples were taken and analyzed using a HP-5790A gas chromatograph (GC) with TCD and reporting integrator. A 2 m × 3 mm stainless steel packed column with 3% OV-101 on Chromasorb 80/100 mesh WHP solid support was used for the analysis. An initial temperature of 323.15 K for 3.3 min, then increasing at a rate of 6.5 $K \cdot min^{-1}$ until 453.13 K was reached, was found to be sufficient for the separation. UHP helium at a flow rate of 20 $cm^3 \cdot min^{-1}$ was used as the carrier gas.

Purity of the samples

The purest commercially available grade materials were used in this study. Trace quantities of water in the hydrocarbons were removed by percolation over freshly regenerated silica gel. GC analysis showed no detectable impurities in the samples. The substances studied and their stated purities are listed in Table 1.

Purity of the test substance (n-octane) was checked at the normal boiling point by standardizing a Swietoslawski ebulliometer with a standard reference sample of 2,2,4-trimethyl pentane having a normal boiling point of 372.39 K. The measured boiling point of n-octane was 398.83 K, compared with a literature value of 398.82 K (Ambrose, 1963).

Analysis of Experimental Results and Discussion

The critical temperatures of the n-alkanes studied in this work are listed in Table 2. Also listed are the measurements of various investigators reported in the literature. The measured critical temperatures of n-octane and n-nonane, which are known to be stable at their critical temperatures, show excellent agreement with the literature values. Sample data for n-octane are given in Figure 4, showing the magnitude of the heating rates as well as the scatter in the data. It should be noted that the critical temperatures recorded are the temperatures of meniscus disappearance and reappearance. They were, therefore, averaged to obtain the critical temperature of n-octane reported in Table 2. The critical temperature of n-octane was also determined in a Kay-type apparatus (Genco et al., 1980) that does not employ a radiant source of heat, and was found to be the same as that reported in Table 2, within experimental error. This shows that radiation effects in the present method were negligible.

Table 1. Purity and Sources of Substances Studied

Substance	mol % Purity	Supplier
n-Octane	99.85	Phillips Petroleum Co.
n-Nonane	99.68	↓
n-Decane	99.49	↓
n-Undecane	99.90	↓
n-Dodecane	99.70	↓
n-Tridecane	99.82	↓
n-Tetradecane	99.90	↓
n-Pentadecane	99.0	Aldrich Chemical Co.
n-Hexadecane	99.80	Phillips Petroleum Co.

Table 2. Critical Temperatures T_c of n-Alkanes

	T_c, K			
Substance	This Work	Ambrose (1960)	Mogollon et al. (1982)	Pak & Kay (1972)
n-Octane	568.65 ± 0.1	568.56	568.80	—
n-Nonane	594.65 ± 0.1	594.56	593.61	593.8
n-Decane	617.9 ± 0.3	617.6	617.6	616.8
n-Undecane	637.1 ± 0.3	638.7	638.7	—
n-Dodecane	657.4 ± 0.3	658.3	657.7	659.0
n-Tridecane	674.0 ± 0.6	—	676.2	674.9
n-Tetradecane	691.2 ± 0.6	694.2	692.8	696.9
n-Pentadecane	706.4 ± 0.6	—	709.2	—
n-Hexadecane	722 ± 1	717.2	723.0	—

In the case of the thermally labile higher n-alkanes, a noticeable decrease in critical temperature with time was observed. To obtain the critical temperatures of these substances, therefore, previous investigators (Ambrose, 1963; Mogollon et al., 1982; Pak and Kay, 1972) extrapolated the apparent critical temperature vs. time data to zero time. This extrapolation may only be made with confidence for moderate-size hydrocarbons such as n-decane, however, because the apparent critical temperature-time curve is linear only for these hydrocarbons. For hydrocarbons larger than undecane, the apparent critical temperature-time curves are nonlinear and therefore the extrapolation becomes uncertain. In addition, the zero extrapolation value is arbitrary and becomes a function of the type of curve and the choice of points. In some cases, the initial points on the critical temperature vs. time curve can be linearized. However, the slope of the curve can be very steep (2.5 $K \cdot min^{-1}$ in the case of n-hexadecane) and since it can take 5 to 10 min of heating to reach the critical point, large errors may arise in zero time extrapolations. Table 3 shows the rate of the critical temperature decrease for the normal alkanes. Beginning with n-tridecane, the rate of decrease, and therefore of decomposition, becomes significant. Moreover, it is not clear to which point the extrapolation must be carried out (i.e., the zero time coordinate is uncertain).

Unless a kinetic interpretation of the data is used, it is doubtful whether accurate determinations of the critical point can be made. For most hydrocarbon decompositions, the rate is well known to be represented empirically by a first-order unimolecular reaction (Hansford, 1953). Although the kinetics have been

Table 3. Initial Decomposition Rates Based on T_c Measurement

Substance	Rate of Decrease $K \cdot min^{-1}$
n-Decane	<0.01
n-Undecane	0.13
n-Dodecane	0.19
n-Tridecane	0.36
n-Tetradecane	0.31
n-Pentadecane	0.91
n-Hexadecane	2.30

shown to be quite complex, (Murata et al., 1973; Tanaka et al., 1975) many decompositions are first-order in nature (Burk, 1931; Greensfelder and Voge, 1945; Voge and Good, 1949).

The detailed kinetic behavior of many *n*-paraffins has been examined by Murata et al., (1973); Murata and Saito, (1974); Tanaka et al. (1975), and Arai et al. (1977), who showed that the mechanism becomes complex in molecules larger than *n*-decane. The assumption of a first-order decomposition is therefore only approximate in these cases. For these reasons our data analysis adopts a more pragmatic approach, one that focuses on the amount of substance remaining after a heating experiment.

The decomposition equation for a first-order irreversible unimolecular reaction $A \rightarrow R$ is given by

$$dC_A/dt = -k_o C_A \exp(-E_v/RT) \qquad (1)$$

Here k_o is the rate premultiplier, E_V the activation energy, R the gas constant, and T the absolute temperature. The rate expression defines the rate of disappearance of A per unit volume per unit time at a constant temperature, and is written in terms of C_A, the number of moles of A reacted per unit volume at time t. The temperature function is not known but the discrete data are, and the relation forms the basis of the procedure.

To analyze the data, the temperature history of the substance, the activation energy of the bond that is expected to be broken, and the final moles reacted or fraction reacted are required. For hydrocarbons, Burk et al. (1941) found that reasonable values for E_V lie in the range 63,000 ± 500 cal/mol (2,640 ± 2 kJ/mol), and this was confirmed by Voge and Good (1949), who studied the thermal decomposition of *n*-dodecane, isododecane and *n*-hexadecane. However, in our treatment, a variation of 2,000 cal (8.4 kJ) caused differences of only 0.0001 in the fraction of moles reacted.

The amount reacted was determined by gas chromatography. The temperature history of each ampoule is known from the digital data recorded onto disk. Therefore, the only effect not accounted for is the reaction pressure. Pressure affects decomposition by causing a larger distribution of higher molecular weight hydrocarbons to be formed. These effects are not accounted for in any of the theory, but are treated empirically.

The rate constant premultiplier k_o is a fitted constant that serves to account for some of the pressure effects and reaction behavior that are not first-order. The procedure is to minimize the differences between the predicted, simulated weight fraction reacted and the actual fluid experimental weight fraction. By guessing k_o, the discrete temperature data can be used to determine weight fractions reacted along the temperature profile. The procedure is iterative, as the differential equation must be solved for each Δt increment, and the new number of moles determined. At the end of each iteration the fraction of moles reacted is compared with the experimental value. Newton-Raphson iteration with numerical derivatives was used to converge to a solution for k_o, generally in three iterations.

Once k_o is known for the run, the fraction of moles reacted can be computed as a function of temperature. The time at which no moles have reacted corresponds to the time of zero reaction rate. The moles reacted can also be computed at the (critical) temperatures of disappearance and reappearance of the meniscus, and a plot can be made of T_C vs. X, where $X = C_A/C_{Ao}$ is the fraction of moles remaining and C_{Ao} is the initial number of moles.

A comparison between T_C vs. time and T_C vs. X for *n*-pentadecane is shown in Figure 6. A quadratic equation has been fitted to the T_C-time curve, since it is not linear. Extrapolation of the curve is risky due to the degree of the polynomial, and because the point to which the extrapolation must be made is arbitrary. In contrast, the T_C-X curve is linear, and since the moles ratio has a clear meaning, extrapolation may be done with a greater degree of confidence. Of course, one may choose to use the linear portion of the T_C-time curve so as to minimize the effect of curvature. A comparison of this type is shown in Figure 7. Although the data fit is almost the same for the T_C-X and T_C-time cases, the problem of which point to extrapolate to still remains for the T_C-time curve. Zero time extrapolation could therefore lead to a critical temperature that is too high, or a value that has a much higher error bound. The T_C-X curve is linear and extrapolation is easily made to zero reaction (i.e., $X = 1$).

In spite of the linear nature of the T_C vs. X curve, it is still preferable to use only the points where the fraction of moles remaining is 0.90 or greater, because there is still a small curva-

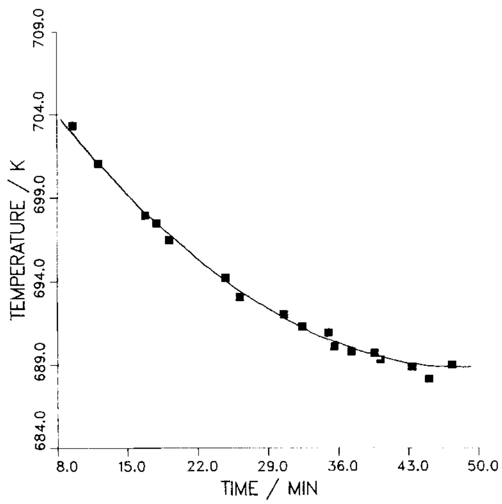

Figure 6a. Critical temperature vs. time for *n*-pentadecane.

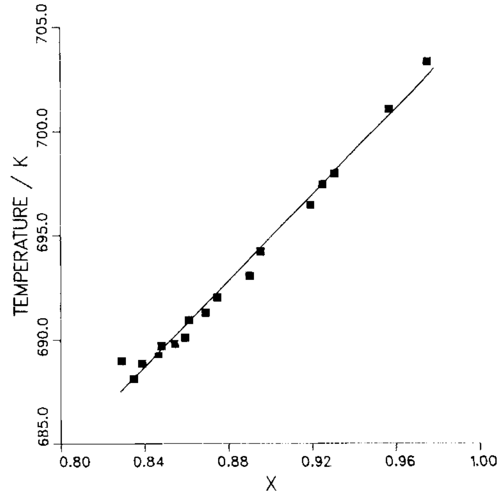

Figure 6b. Critical temperature vs. *X* for *n*-pentadecane.

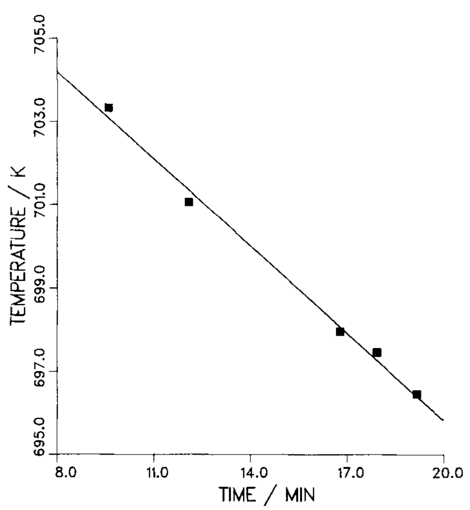

Figure 7a. Linear portion of critical temperature vs. time curve for *n*-pentadecane.

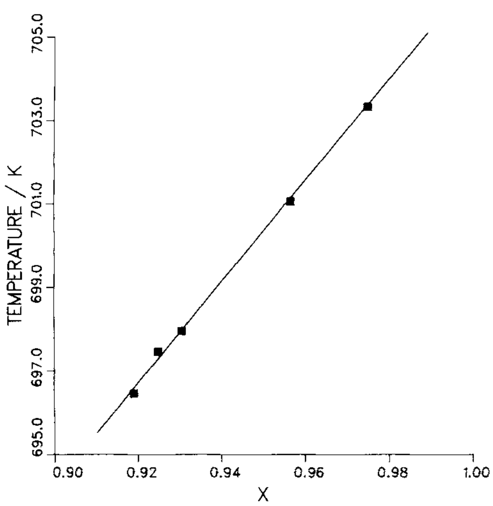

Figure 7b. Linear portion of critical temperature vs. *X* curve for *n*-pentadecane.

ture to the line. For *n*-pentadecane, the difference in using all the data as opposed to using the most linear portion, is only 1 K. For *n*-hexadecane, the difference is greater, being about 2.6 K, since 25% of the substance has reacted at the end of 20 min.

Two observations are worth noting:

1. For substances that decompose slightly, the differences between extrapolation by the zero time method and the zero reaction method are small.

2. If the time at which the substance begins to decompose (i.e., when $X = 1$) is substituted into the straight line curve of T_C vs. time, the two methods yield almost the same calculated critical temperatures, well within the uncertainty of both methods.

The extrapolations compare well for *n*-pentadecane, yielding a critical temperature at 706.3 K by the T_C-X curve and 706.7 K by the T_C-time curve. However, if the extrapolation is done to an arbitrary zero of time, then the critical temperature can be significantly different in the two cases. This suggests that the coordinates of the undecomposed substance have been correctly found and the data analysis is correct.

The critical temperature obtained in this work are shown in Table 2, as are values obtained from the literature. A wide range of differences is apparent among the measurements, for several reasons. The criteria for the critical point are very subjective. Even with the same apparatus, different observers will report different critical temperatures for the same substance, as discussed by Ambrose and Grant (1957). The purity of all of the compounds in all the reported measurements is high, minimizing this source of error. The data of Ambrose (1963) were not extrapolated, but the rate of decomposition was taken as uncertain and the first critical point was reported. The work of Pak and Kay (1972) used air-saturated samples, and some differences may be attributed to this. Mogollon et al. (1982) reported their data based on extrapolation to zero time. We believe our critical temperatures are the most accurate of the values cited for the reasons stated above.

Accuracy and precision

Both the accuracy and the precision of the data measured in this work depend on the temperature range and the rate of thermal decomposition. The base accuracy of the standard platinum resistance thermometer is ±0.01 K, while the fitted accuracy of the thermocouple is ±0.02 K. The absolute measurement can be made within ±0.03 K, provided a complete calibration is done. A 1 s error in temperature reading, or time lag, would cause an error of ±(rate of change). Normally this is small (less than 0.01 $K \cdot s^{-1}$), and since the thermocouple mass is small and the thermocouple is surrounded by the substance, the error and time constants are low.

The largest error is perhaps due to the personal factor. This factor can be determined by the variation in critical temperature for the test substance. For meniscus disappearance, the scatter can be seen to be about ±0.03 K, while for the reappearance the precision is about ±0.02 K. With the temperature gradients in the furnace, the average of the two can vary by about ±0.06 K. The accuracy for the *n*-octane measurement is then ±0.06 K based on error propagation. Because of the personal factor involved, however, the error is likely to be larger. Although any estimate of this error will be subjective, we believe that our *n*-octane and *n*-nonane critical temperatures are accurate to ±0.1 K. For the higher *n*-alkanes, it was not always possible to obtain the reappearance and disappearance of the meniscus for every ascending and descending part of the temperature-time curve. In particular, reappearance was found to be more prominent due to phase separation and therefore was used to locate the critical point, even though the critical temperatures noted would be high by several hundredths of a degree. Additional errors arise because of the curve-fitting procedure. The error bands for the higher *n*-alkanes are therefore larger and are given in Table 2.

The data can also be compared to predictive methods of Ambrose (1978), Lydersen et al. (1955) and Twu (1984). This is shown in Table 4. The group contribution method of Ambrose is found to accurately predict the data. Claims in the report state that the temperatures of the higher alkanes were low by four or five degrees compared with the then-available literature. The present study shows that the Ambrose correlation is very close to our experimental values (being approximately one degree too high). The very popular Lydersen method is consistently lower, being off by eight degrees for *n*-hexadecane. The method of Twu, using Pade approximates, also shows good agreement with the present measurements.

Table 4. Critical Temperatures T_c, Comparisons with Predictive Methods

		T_c, K			
Substance	T_b* K	This Work	Ambrose (1978)	Lyderson et al. (1955)	Twu (1984)
n-Octane	398.82	568.65	568.82	568.61	568.70
n-Nonane	423.97	594.65	594.65	593.30	595.62
n-Decane	447.30	617.9	617.9	615.3	618.9
n-Undecane	469.08	637.1	639.0	635.1	639.9
n-Dodecane	489.47	657.4	658.4	653.2	659.1
n-Tridecane	508.62	674.0	676.2	669.8	676.6
n-Tetradecane	526.73	691.2	692.6	685.3	692.9
n-Pentadecane	543.80	706.4	708.0	699.9	707.8
n-Hexadecane	560.01	722.0	722.3	713.8	721.7

*Boiling points used in predictions

Conclusions

We have developed an apparatus together with a data collection technique and analysis method that can be used for the determination of the critical temperatures of thermally labile substances. The critical temperatures of the *n*-alkanes were found generally to be lower than current values, but they agree closely with predictions based on lower member alkanes.

Acknowledgment

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