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PROJECT ADMINISTRATION DATA SHEET

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Project No. E-19-658 GTRI/~~GIT~~ DATE 4 /2 /84

Project Director: Dr. A. S. Teja School/~~Lab~~ ChE

Sponsor: National Science Foundation

Type Agreement: Grant No. CPE-8314343

Award Period: From 3/15/84 To 8/31/85 * (Performance) 11/30/85 (Reports)

Sponsor Amount:

	This Change	Total to Date
Estimated:	$ 30,800	$ 30,800
Funded:	$ 30,800	$ 30,800

Cost Sharing Amount: $ 10,000 Cost Sharing No: E-19-314

Title: "Research Equipment: Critical Properties of High Boiling Hydrocarbons and Polynuclear Aromatic Hydrocarbons"

ADMINISTRATIVE DATA

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Defense Priority Rating: n/a

Military Security Classification: n/a

(or) Company/Industrial Proprietary: n/a

RESTRICTIONS

See Attached NSF Supplemental Information Sheet for Additional Requirements.

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Equipment: Title vests with GIT

COMMENTS:

* Includes usual 6-month unfunded flexibility period.

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date March 4, 1986

Project No. E-19-658 School/~~Lab~~ Ch. E.

Includes Subproject No.(s) N/A

Project Director(s) Dr. A.S. Teja GTRI ~~GIT~~

Sponsor National Science Foundation

Title "Research Equipment: Critical Properties of High Boiling Hydrocarbons and Polynuclear Aromatic Hydrocarbons"

Effective Completion Date: 8/31/85 (Performance) 11/30/85 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [x] Final Report of Inventions Patent Questionnaire sent to Project Director
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other

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FINAL REPORT

RESEARCH EQUIPMENT: CRITICAL PROPERTIES OF HIGH BOILING HYDROCARBONS AND POLYNUCLEAR AROMATIC HYDROCARBONS

By

Dr. Amyn S. Teja

Prepared for

NATIONAL SCIENCE FOUNDATION
Washington, D. C. 20550

Award Period from 3/15/84 to 8/31/85

Under

NSF Award Number - CPE 8314343

JANUARY 1986

GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
SCHOOL OF CHEMICAL ENGINEERING
ATLANTA, GEORGIA 30332

1986

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

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PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Tech Research Corporation Atlanta, Georgia 30332	Thermodynamics & Transport	CPE 8314343
	4. Award Period From 3/15/84 To 8/31/85	5. Cumulative Award Amount $30,800

6. Project Title
Research Equipment: Critical Properties of High Boiling Hydrocarbons and Polynuclear Aromatic Hydrocarbons

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

Critical properties of substances which decompose at high temperatures are required in petroleum and natural gas engineering and in the design of super-critical extraction prosesses. In spite of these interests, however, previous experimental studies of critical states have been confined primarily to thermally stable substances. Two apparatuses for the measurement of the critical properties of thermally unstable substances have been constructed in this work. A novel method of data acquisition and analysis has been developed and the critical temperatures of nine hydrocarbons and seven alcohols have been measured.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses		XX			
b. Publication Citations		XX			
c. Data on Scientific Collaborators	XX				
d. Information on Inventions	XX				
e. Technical Description of Project and Results		XX			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Dr. Amyn S. Teja		1/9/86

FINAL REPORT

NSF Grant No: CPE 8314343

Title: "Research Equipment: Critical Properties of High Boiling Hydrocarbons and Polynuclear Aromatic Hydrocarbons"

Principal Investigator: Dr. Amyn S. Teja

Graduate Research Assistants: Richard Lee Smith, Jr.
Marc Anselme

TECHNICAL DESCRIPTION OF PROJECT AND RESULTS

The critical properties (T_c, P_c and V_c) of a substance are important characterization parameters in methods for the calculation of thermodynamic and transport properties based on the corresponding states principle. It is not surprising, therefore, that the critical temperature (T_c) and critical pressure (P_c) of many organic compounds have been measured and the values reported in the literature (see, for example, the compilation by Reid et al. [1]). Most of these measurements, however, have been made on thermally stable substances; data on thermally unstable substances are much more difficult to measure and are, therefore, almost non-existent in the literature. Recent interest in heavy oil processing, coal conversion and in biochemical engineering - all of which involve the processing of thermally labile substances - has led to much interest in the development of methods for the measurement of the properties of such substances.

In the present work, an apparatus for the measurement of the critical temperatures and volumes of thermally unstable

substances has been constructed. A major component of the apparatus is a platinum-coated quartz tube furnace into which an open or sealed-tube containing the test substance can be inserted. Only "sealed-tube" experiments have been carried out to date. In these experiments, a sample of the substance in a sealed ampoule is successively heated and cooled in the furnace to observe the disappearance and reappearance of the vapor-liquid meniscus. If the substance decomposes, the temperature of the meniscus disappearance/reappearance (or the apparent critical temperature) will decrease with time; if the substance undergoes association reactions, the apparent critical temperature will generally increase with time. The rate of change of the apparent critical temperature depends on the rate of decomposition or association. A novel feature of the apparatus constructed in this work is the monitoring and recording of the temperature history of the sample (one data point per second for up to 3600 seconds) and of the apparent critical temperature versus time data. The extent of decomposition is also measured. This allowed us to develop a new method of data analysis based on the kinetics of decomposition. We have shown (Smith et al. [2]) that our data analysis leads to unambiguous extrapolation of the apparent critical temperature data to the critical temperature of the undecomposed substance.

A schematic diagram of the apparatus is shown in Figure 1 and details of the equipment and of the method of data analysis are given in Smith et al. [2,3].

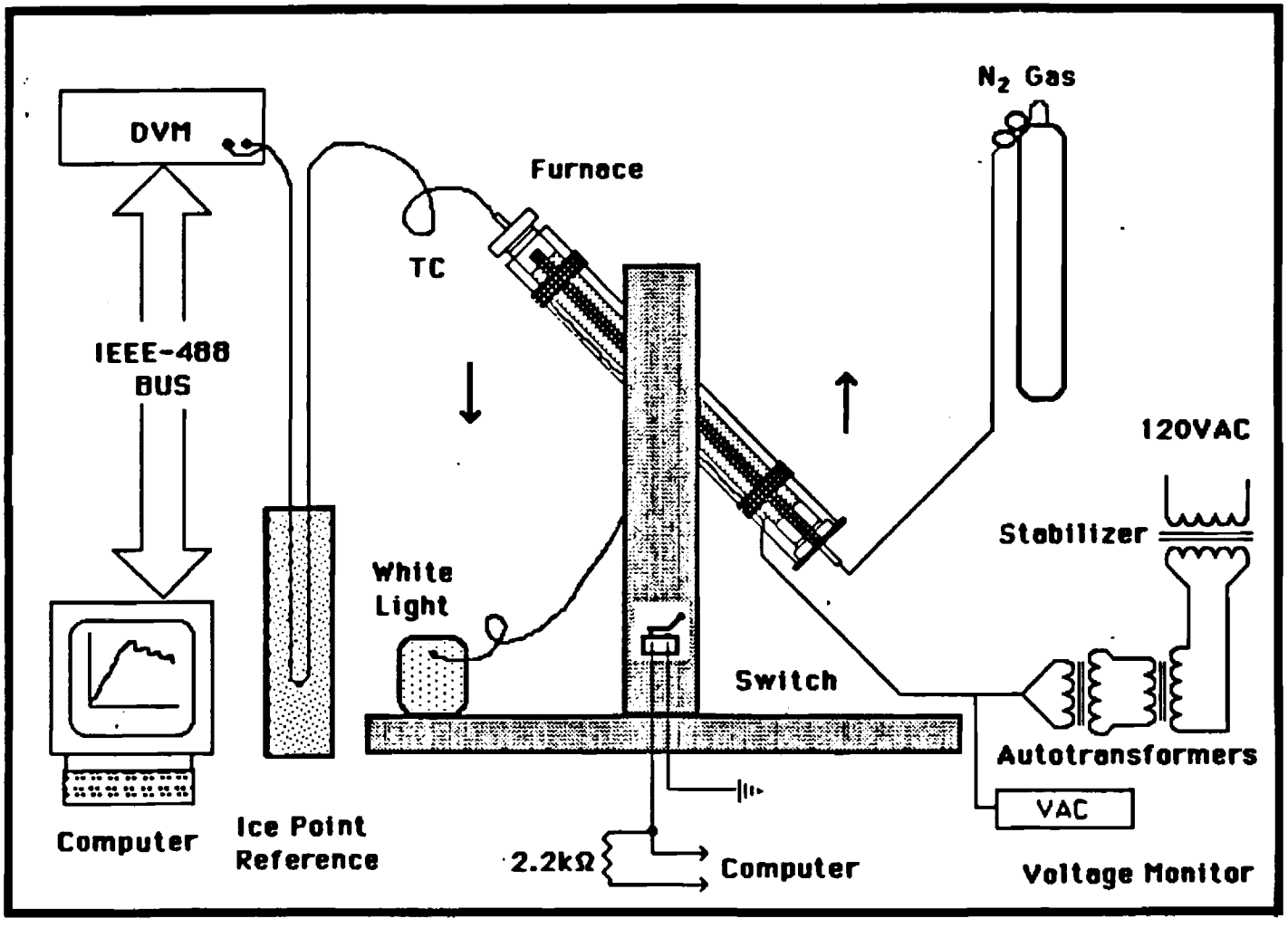

Figure 1. Schematic diagram of the critical point apparatus.

The critical temperatures of nine high molecular weight hydrocarbons and seven alcohols were measured and reported in Smith et al. [2,3]. A summary of the measurements is given in Table 1. The measurement and data analysis techniques should also be applicable to other thermally unstable substances such as polynuclear aromatic hydrocarbons and biochemicals.

Current research is concerned with extending the method to the measurement of critical volumes (by use of calibrated ampoules) and critical pressures (by use of open tubes containing the sample).

A second (flow) apparatus has also been constructed for the measurement of critical temperatures and pressures of thermally unstable materials. The apparatus consists of a high pressure Eldex liquid pump, a preheating circuit and a stainless-steel equilibrium cell. The sample is allowed to flow through the equilibrium cell and the pressure, temperature and flow rate are adjusted until the vapor-liquid transition is visually observed in the cell. This apparatus has been designed for higher temperatures and pressures than the apparatus shown in Fig. 1.

Because of the limited funds awarded under this grant (funds for only 1 year instead of the 3 years requested in the original proposal were awarded), this project was mainly concerned with the construction of two apparatuses for the measurement of the critical properties of thermally unstable substances. This task has been accomplished and, moreover, new data have been obtained for several alkanes and seven alcohols.

REFERENCES

1. Reid, R.C., Prausnitz, J. M. and Sherwood, T. K., "The Properties of Gases and Liquids", 3rd Edition, McGraw-Hill, 1977.

2. Smith, R. L., Kay, W. B. and Teja, A. S., "The critical temperatures of thermally unstable n-alkanes", paper submitted to A.I.Ch.E. Journal.

3. Smith, R. L., Anselme, M. and Teja, A. S., "The critical temperatures of isomeric pentanols and heptanols", paper submitted to Fluid Phase Equilibria.

Table 1. Critical temperatures measured in this study.

Substance	T_c/K	Comments
n-octane	568.65	Stable test substance
n-nonane	594.65	Stable test substance
n-decane	617.9	Slight decomposition
n-undecane	637.1	" "
n-dodecane	657.4	Rapid decomposition
n-tridecane	674.0	" "
n-tetradecane	691.2	" "
n-pentadecane	706.4	" "
n-hexadecane	721.7	" "
1-pentanol	587.7	Slight Association
2-pentanol	560.4	" "
3-pentanol	559.6	" "
1-heptanol	632.3	" "
2-heptanol	611.4	" "
3-heptanol	605.4	" "
4-heptanol	602.6	" "

CONFERENCE PRESENTATIONS

1. Smith, R. L., Anselme, M., Kay, W. B. and Teja, A. S., "The measurement of the critical temperatures of thermally labile substances", presented at the AIChE meeting, Chicago, November 1985.

2. Smith, R. L., Anselme, M., Teja, A. S., "Critical properties of thermally unstable substances", to be presented at the World Congress of Chemical Engineering, Tokyo, Japan, September 1986.

THESIS COMPLETED UNDER THIS GRANT AWARD

MEASUREMENT AND CORRELATION OF CRITICAL STATES

A THESIS

Presented to

The Faculty Of The Division Of Graduate Studies

By

Richard Lee Smith, Jr.

In Partial Fulfillment

Of The Requirements For The Degree

Doctor Of Philosophy In The School Of Chemical Engineering

Georgia Institute Of Technology

December, 1985

SUMMARY

A modified sealed tube method has been developed for the measurement of the critical temperatures of fluids. The method has been used to obtain the critical temperatures of normal alkanes from n-octane to n-hexadecane, diphenylmethane, two normal alcohols, and five isomeric alcohols. Since alkanes decompose starting with n-decane, a new method of analysis has been developed. This employs reaction kinetics based on an irreversible first order unimolecular reaction and is used to linearize the apparent critical temperature versus time curve and perform a more certain extrapolation to 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 experiment completion. The approach is general since many hydrocarbon decompositions can be described empirically by a first order rate expression. New critical constants are reported and compared with previous experimental values and with available correlations from the literature.

From the analysis of our method it may be concluded that for the determination of critical points: (1) standard methods may be used if the substance is not thermally sensitive (2) an extrapolation to zero time may be used if the substance decomposes very slightly and (3) the temperature history must be known and the time in the hot zone minimized, if the substance decomposes rapidly.

A two fluid generalized corresponding states principle (GCSP) has

extended to the prediction of enthalpies, entropies, and critical loci. The method is applicable to nonpolar, nonpolar-polar, and polar-polar mixtures. The merit of the GCSP lies in the way the model can adapt to the mixture of interest by a judicious choice of refereence fluids. Accurate predictions have been obtained for mixtures of (1) simple spherical molecules, (2) large quasispherical molecules, (3) both spherical and nonspherical molecules, and (4) molecules exhibiting strong dipole moments.

The best predictions are made by using the most accurate reference fluids. Extrapolations in acentric factor about a reference fluid whose properties are not well known are shown to lead to high errors. The calculations are more sensitive to errors for critical pressure prediction with the temperature and the volume being much less effected.

The pseudocritical mixing rules used in the calculations had the advantage that the critical volumes of the components of interest were not required. It is shown how the use of inaccurate critical properties in the mixing rules can lead to large errors, especially in the region of a highly dilute solute.

PAPERS SUBMITTED UNDER THIS GRANT AWARD

The measurement of the critical temperatures of thermally unstable n-alkanes.

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ABSTRACT

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. The new 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.

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" and 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 which 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 versus 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 and 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., and consisted of a 55 cm length, 2.5 cm o.d. quartz tube plated with four layers of platinum metal. The metal coating served as the electrical resistor of the furnace. Three diametirically opposed 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 85VAC at 6 amperes and had a room temperature resistance of 6.9Ω. It could easily achieve the temperatures of interest in about five minutes. Current to the furnace was supplied by two 12A autotransformers operated in series, giving very fine voltage control, and with the main power being 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 a guide for the ampoule holder assembly. An outer tube 50 mm o.d. 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 (Fig. 1). The furnace was mounted on a trunion assembly to allow rotation through 180° which provided mixing of the sample during heating.

The ampoules used in this study (shown in Fig. 2) 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 (Fig. 2) was made from stainless steel and had a minimum contact area with the ampoule surface.

Temperature was measured with an iron-constantan thermocouple that was calibrated over the temperature range 500-770K 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 e.m.f. 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 e.m.f. 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 Enginering 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. A schematic diagram of the apparatus is shown in Fig. 3.

Procedure

As a safety precaution each ampoule was tested to a pressure of 4500 - 5500 kPa. Bursting pressures of the ampoules were found to be between 9000 and 10,500 kPa. The ampoules were then etched with HF on the capillary portion of the neck and cleaned by washing with nitric acid and 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 such that the critical density is achieved upon heating. To do this requires the ampoule volume and an estimate for the critical density. Critical densities were estimated using the group contribution method of Ambrose (1980). 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 slightly less sample. A wad of glass wool was placed in the neck afterwards 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 using the apparatus shown in Fig. 4. 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 Mogollen 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 due to the use of the 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, much more reproducible and precise results are 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 intial 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 in this case, reappearance is much more abrupt and easier to locate even when the apparent critical temperature is changing rapidly (>0.25K/minute).

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 in approximately one minute intervals with rates of a few tenths of a degree increase or decrease of temperature per minute. Experimental runs usually lasted from 20 to 40 minutes depending on the decomposition rate. Typical temperature histories of a stable substance (n-octane) and an unstable substance (n-hexadecane) are shown in Figs. 5 and 6. Note that the critical point is defined as the average of the adjacent disappearance and reappearances of the meniscus. This average is constant with time for the stable n-octane and decreases with time for the unstable n-hexadecane.

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 with TCD and

reporting integrator. A 2 m by 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 323.15K for 3.3 minutes increasing at a rate of 6.5K/minute until 453.13K was reached was found to be sufficient for the separation. UHP Helium at a flowrate of ≈20 cm^3/minute was used as the carrier gas.

Purity of the Samples

The purest commercially available grade of 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 372.39K. The measured boiling point of n-octane was 398.83K, compared with a literature value of 398.82K (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 Fig. 5, 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) which 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.

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 versus time data to zero time. This extrapolation may only be made with confidence for moderately-sized 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 versus time curve can

be linearized. However, the slope of the curve can be very steep (2.5K/min in the case of n-hexadecane) and since it can take five to ten minutes 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 which point the extrapolation must be carried out to (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 shown to be quite complex, [Murata et al., (1973); Tanaka et al., (1976)] many deocmpositions are first-order in nature [Burke, (1931); Greensfelder and Voge, (1945); Voge and Good, (1949)].

The detailed kinetic behavior of many n-paraffins has been examined by Murata (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 which focusses on the amount of substance remaining after a heating experiment.

The decomposition equation for a first order irreversible unimolecular reaction is given by

$$A \overset{k}{\rightarrow} R \tag{1}$$

with the rate expression and temperature dependence expressed as

$$dC_A/dt = -k \cdot C_A \tag{2}$$

and

$$k = k_o \cdot e^{(-E_V/RT)} \tag{3}$$

Here k_o is the rate premultiplier, E_V the activation energy, R the gas constant and T the absolute temperature, respectively. The rate expression (2) defines the rate of disappearance of A per unit volume per unit time at a constant temperature, and is written in terms of the number of moles of A reacted. 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 $\pm$ 500 calories/mole, 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 2000 calories 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_0 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 final experimental weight fraction. By guessing k_0, 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 interation, 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_0, generally in three iterations.

Once k_0 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 versus X, where X is the fraction of moles remaining and is defined by

$$X = C_A/C_{Ao} \tag{4}$$

where C_A is the number of moles of A at any time t and C_{Ao} is the initial number of moles.

A comparison between T_C versus time and T_C versus X for n-pentadecane is shown in Figure 7. 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 8. 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). The same effect can also be seen in the n-hexadecane measurements of Figure 9 .

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

Two observations are worth noting. One, for substances that decompose slightly, the differences between extrapolation by the zero time method and the zero reaction method are small. Two, 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-time, the two methods yield almost the same calculated critical temperatures, and well within the uncertainty of both methods. The extrapolations compare well for n-pentadecane, yielding a critical temperature of 706.3K by the T_C-X curve and 706.7K 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 temperatures 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 (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, therefore, 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 SPRT is $\pm$0.01K, while the fitted accuracy of the thermocouple is $\pm$0.02K. The absolute measurement can be made within $\pm$0.03K, provided a complete calibration is done. A one-second error in temperature reading, or time lag, would cause an error of $\pm$(rate of change). Normally this is small, 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 $\pm$0.03K; while for the

reappearance, the precision is about $\pm$0.02K. With the temperature gradients in the furnace, the average of the two can vary by about 0.06K. The accuracy for the n-octane measurement is then $\pm$0.06K based on error propagation. For rapidly decomposing substances, it is not possible to obtain the reapparance 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. The best accuracy possible is then $\pm$0.1K.

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 error in the higher alkanes to be low by four or five degrees 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 low, being off by eight degrees for n-hexadecane. The method of Twu (1984), using Pade approximates, also shows good agreement with the present measurements.

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 to generally be lower than current literature values, but agree closely with predictions based on lower member alkanes.

ACKNOWLEDGEMENT

Financial support for this work was provided by a National Science Foundation grant CPE 8314343.

LITERATURE CITED

1. Ambrose, D., and D. G. Grant, "The Critical Temperatures of Some Hydrocarbons and Pyridine Bases," Trans. Faraday Soc., 53 (1), 771-778 (1957).

2. Ambrose, D., "Critical Temperatures of Some Phenols and Other Organic Compounds," Trans. Faraday Soc., 59 (2), 1988-1993, (1963).

3. Ambrose, D., "Correlation and Estimation of Vapour-Liquid Critical Properties: I. Critical Temperatures of Organic Compounds," NPL Report Chem 92, September, 1978.

4. Arai, Y., M. Murata, and S. Tanaka, "Simulation of Product Distributions from Pyrolysis of Normal and Branched Alkane Mixtures Over a Wide Range of Conversions," J. Chem. Eng. Japan, 10 (4), 303-307 (1977).

5. Burk, R. E., "The Thermal Decomposition of Straight Chain Paraffins," J. Phys. Chem., 35, 2446-2460 (1931).

6. Burk, R. E., L. Laskowski, and H. P. Lankelma, "Kinetics of the Thermal Decomposition of Straight Chain Paraffins," J. Am. Chem. Soc., 63, 3248-3250 (1941).

7. Genco, J., Kay, W. B. and Teja A. S " A Study of the Critical and Azeotropic Behavior of Binary Mixtures," J. Chem. Eng. Data, 25, 350-360 (1980).

8. Greensfelder, B. S., and H. H. Voge, "Catalytic Cracking of Pure Hydrocarbons," Ind. Eng. Chem., 37 (6), 514-520 (1945).

9. Hansford, R. C., "Mechanisms of Some Hydrocarbon Reactions," Chapter 6 in "Physical Chemistry of Hydrocarbons," Vol. II, A. Farkas ed., Academic Press Inc., New York, 1953.

10. Hicks, C. P. and C. L. Young, "The Gas-Liquid Critical Properties of Binary Mixtures," Chem. Rev. 75 (2), 119-175 (1975).

11. Kobe, K. A., and R. E. Lynn, Jr., "The Critical Properties of Elements and Compounds," Chem. Rev. 52, 117-236 (1953).

12. Lydersen, A. L., R. A. Greenkorn, and O. A. Hougen, "Generalized Thermodynamic Properties of Pure Fluids," University of Wisconsin, Engineering Experiment Station, Rept. 4, 1955.

13. Mogollon, E., W. B. Kay and A. S. Teja, "Modified Sealed-Tube Method for the Determination of Critical Temperature," Ind. Eng. Chem. Fundam., 21, 173-175 (1982).

14. Murata, M. S. Saito, A. Amano, and S. Maeda, "Prediction of Initial Product Distributions from Pyrolysis of Normal Paraffinic Hydrocarbons," J. Chem. Eng. Japan, 6 (3), 252-258 (1973).

15. Murata, M. and S. Saito, "Prediction of Initial Product Distribution from n-Paraffin Pyrolysis at Higher Temperatures by Considering Ethyl Radical Decomposition," J. Chem. Eng. Japan, 7 (5), 389-391 (1974).

16. Pak, S. C., and W. B. Kay, "The Critical Properties of Binary Hydrocarbon Systems," Ind. Eng. Chem. Fundam., 11 (2), 255-267 (1972).

17. Tanaka, S., Y. Arai, and S. Saito, "Simulation of Initial Product Distributions From Pyrolysis of Branched Alkanes," J. Chem. Eng. Japan, 8 (4), 305-309 (1975).

18. Twu, C. H., "An Internally Consistent Correlation for Predicting the Critical Properties and Molecular Weights of Petroleum and Coal-Tar Liquids," Fluid Phase Equilibria, 16, 137-150 (1984).

19. Voge, H. H., and G. M. Good, "Thermal Cracking of Higher Paraffins," J. Am. Chem. Soc., 71, 593-597 (1949).

Table 1. Purity and Sources of Substances Studied

Substance	Mol% Purity	Supplier
n-octane	99.85	Philips 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	Philips Petroleum Co.

Table 2. Critical temperatures of n-alkanes

Substance	T_c/K^*	T_c/K^{**}	T_c/K^+	T_c/K^{++}
n-octane	568.65 ± 0.06	568.56	568.80	---
n-nonane	594.65 ± 0.06	594.56	593.61	593.8
n-decane	617.9 ± 0.1	617.6	617.6	616.8
n-undecane	637.1 ± 0.2	638.7	638.7	---
n-dodecane	657.4 ± 0.2	658.3	657.7	659.0
n-tridecane	674.0 ± 0.3	---	676.2	674.9
n-tetradecane	691.2 ± 0.3	694.2	692.8	696.9
n-pentadecane	706.4 ± 0.3	---	709.2	---
n-hexadecane	721.7 ± 0.3	717.2	723.0	---

* This work

** Ambrose (1960)

\+ Mogollon et al. (1982)

++ Pak and Kay (1972)

Table 3. Initial Decomposition Rates Based on T_c Measurement

Substance	Rate of Decrease (K/min)
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

Table 4. Comparisons with predictive methods

Substance	T_b/K^{++}	T_c/K^{***}	T_c/K^{*}	T_c/K^{**}	T_c/K^{+}
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	721.7	722.3	713.8	721.7

*** This work

++ Boiling points used in predictions

* Ambrose (1978)

** Lyderson (1955)

+ Twu (1984)

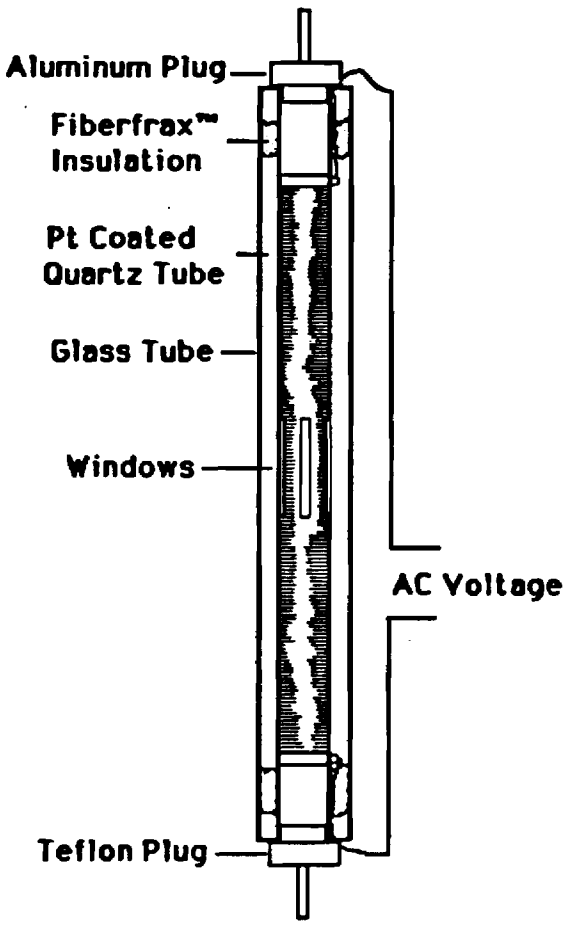


Figure 1. Details of the furnace.

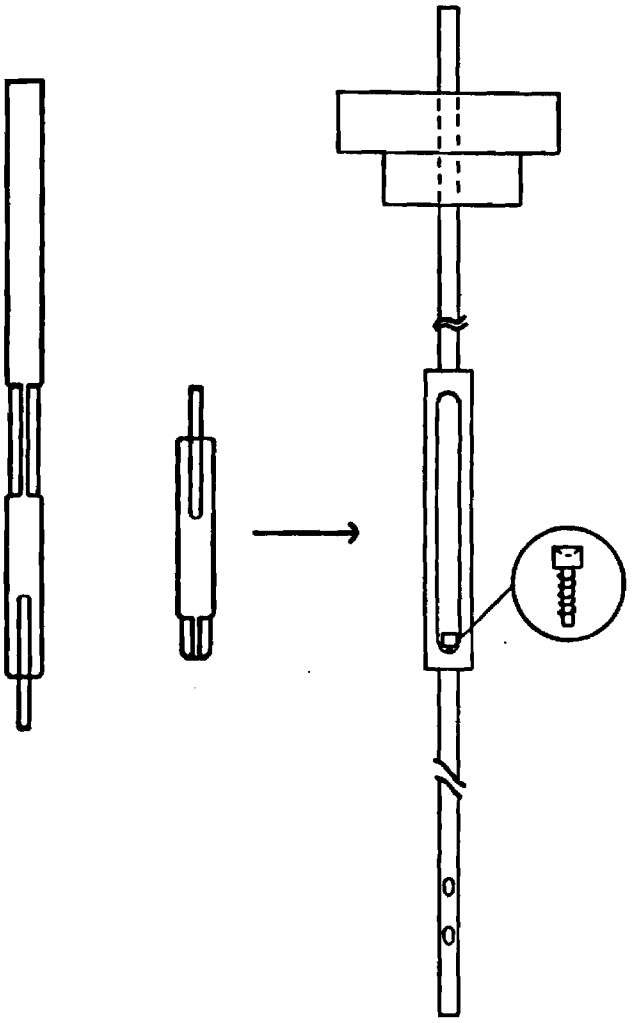


Figure 2. Ampoules and ampoule holder

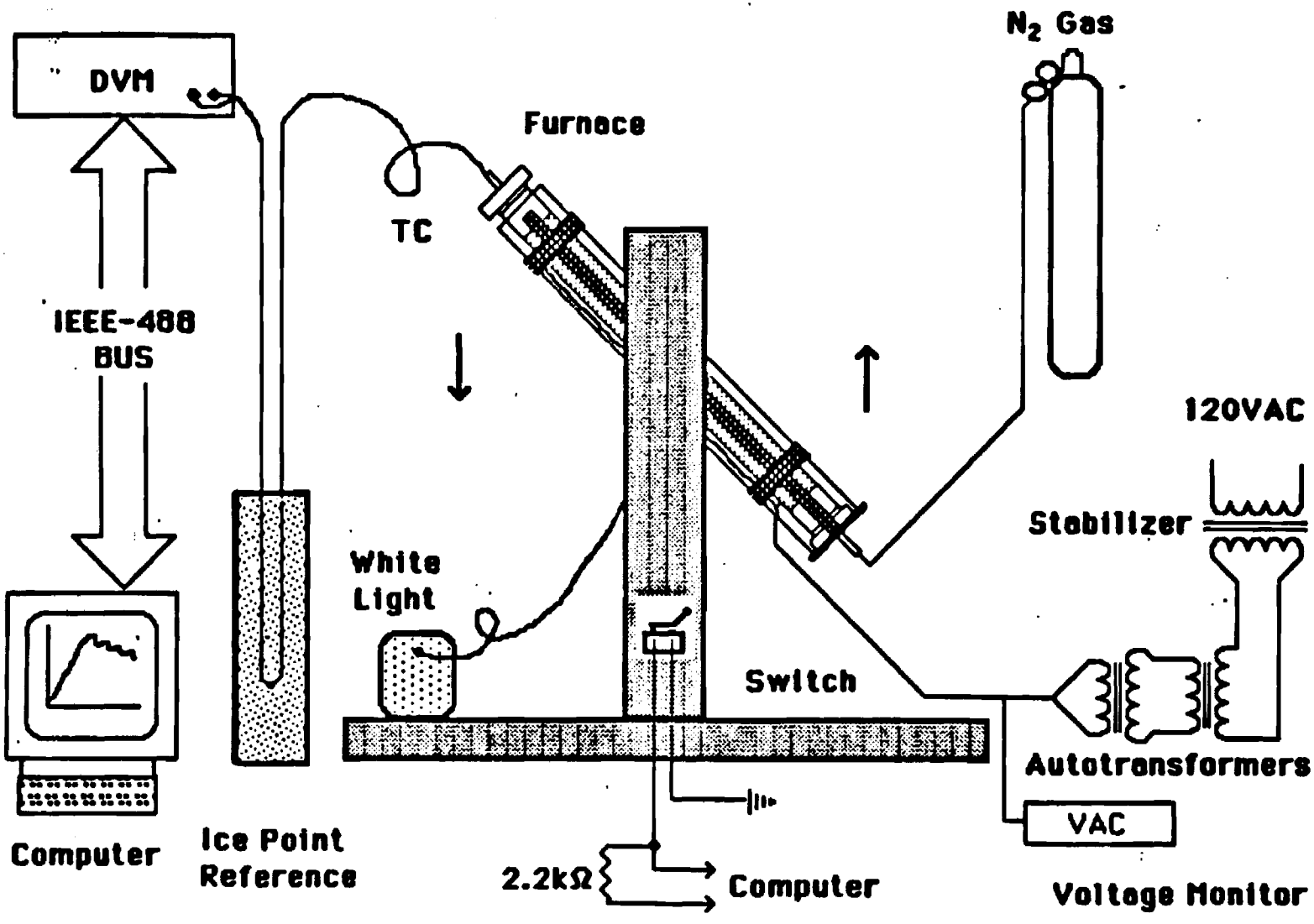


Figure 3. Schematic diagram of the critical point apparatus.

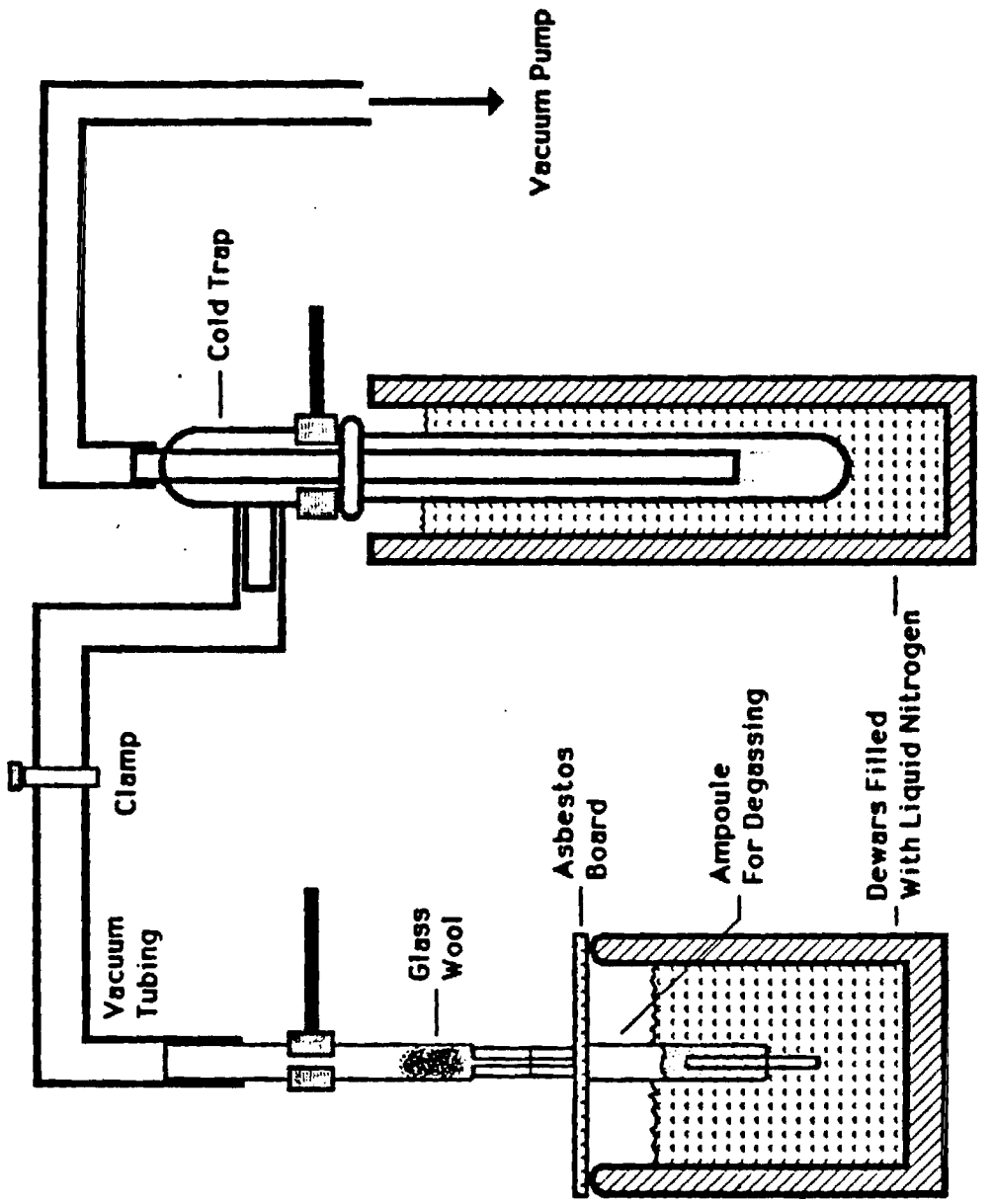
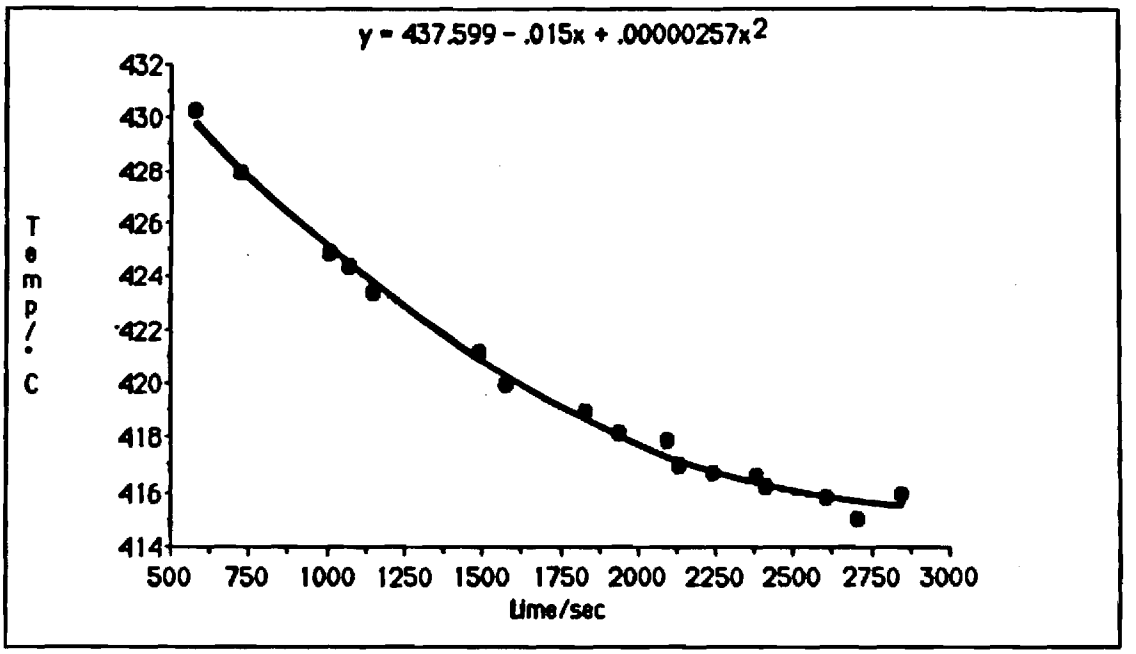


Figure 4. Degassing apparatus.



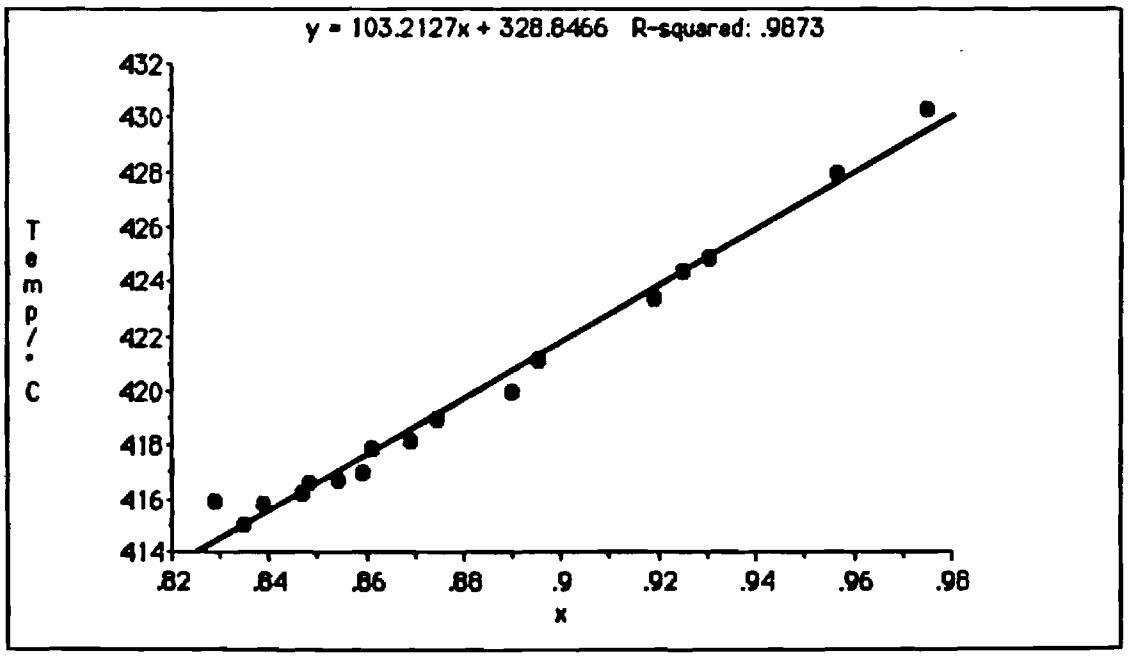
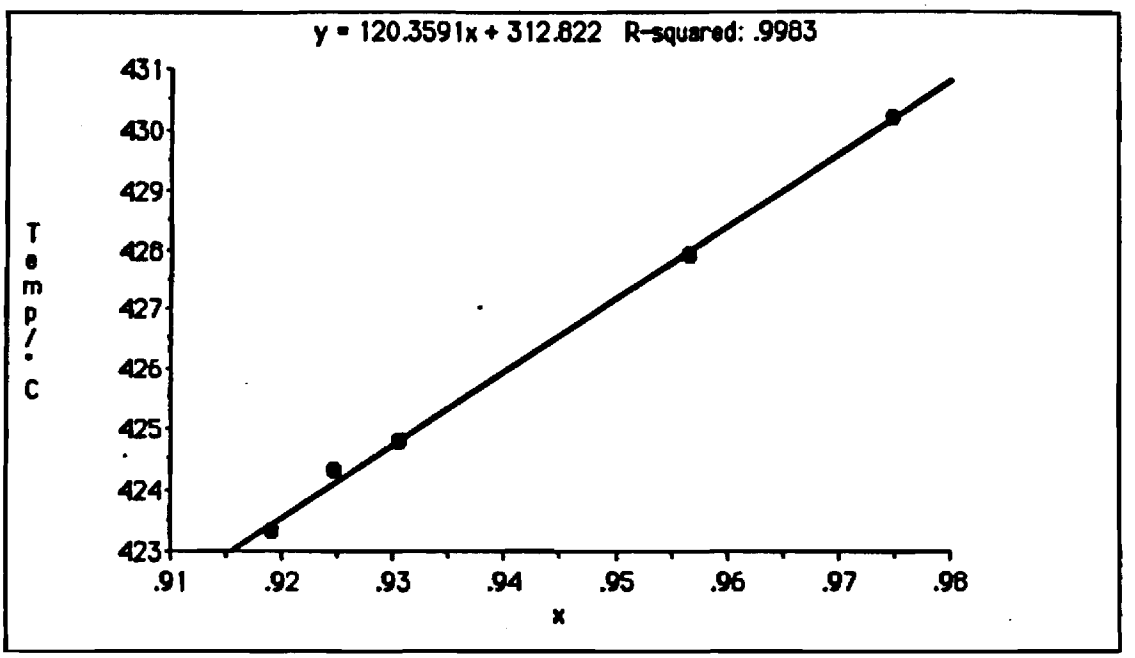


Figure 7. T_C Vs Time And T_C Vs X: n-Pentadecane



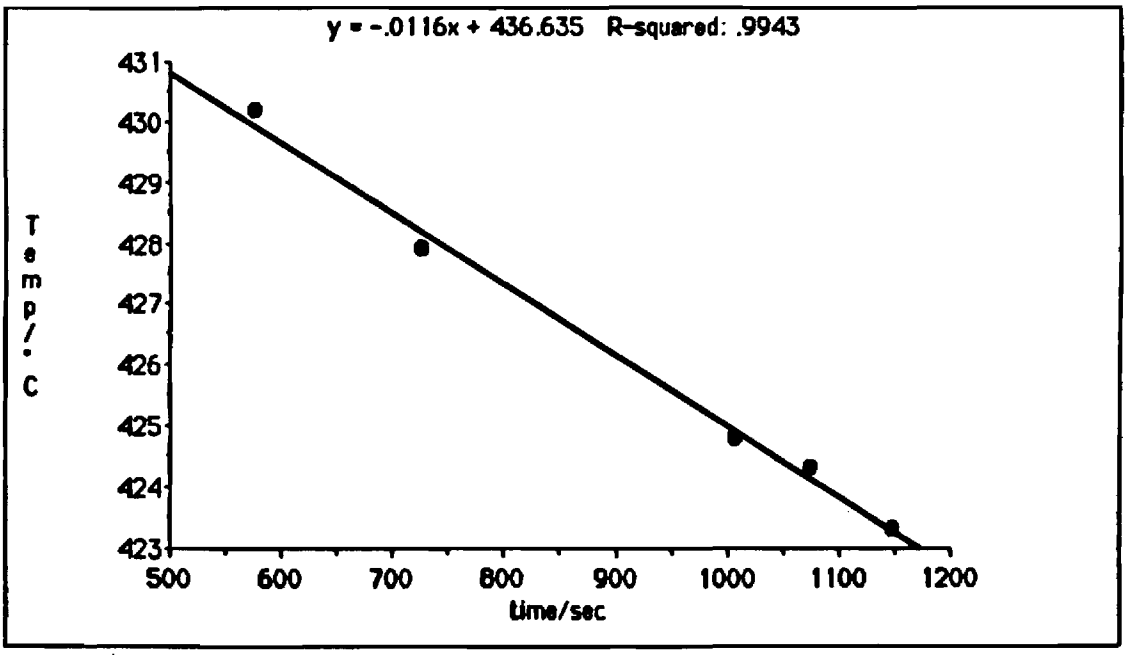
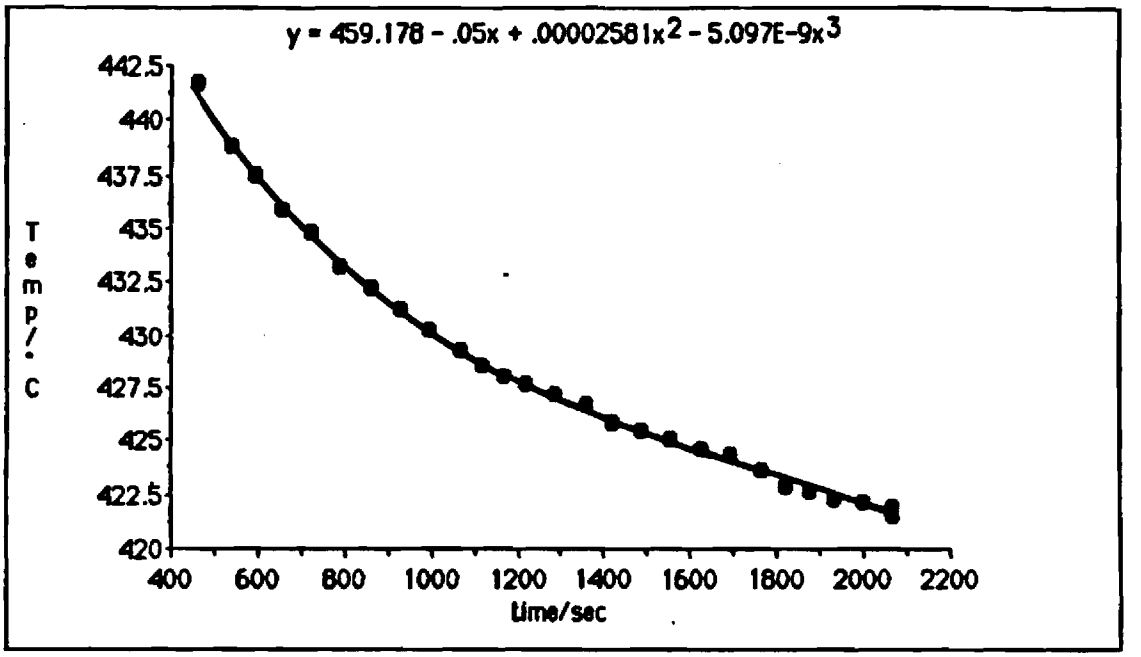


Figure 8. . Linear Data- T_C Vs Time And T_C Vs X: n-Pentadecane



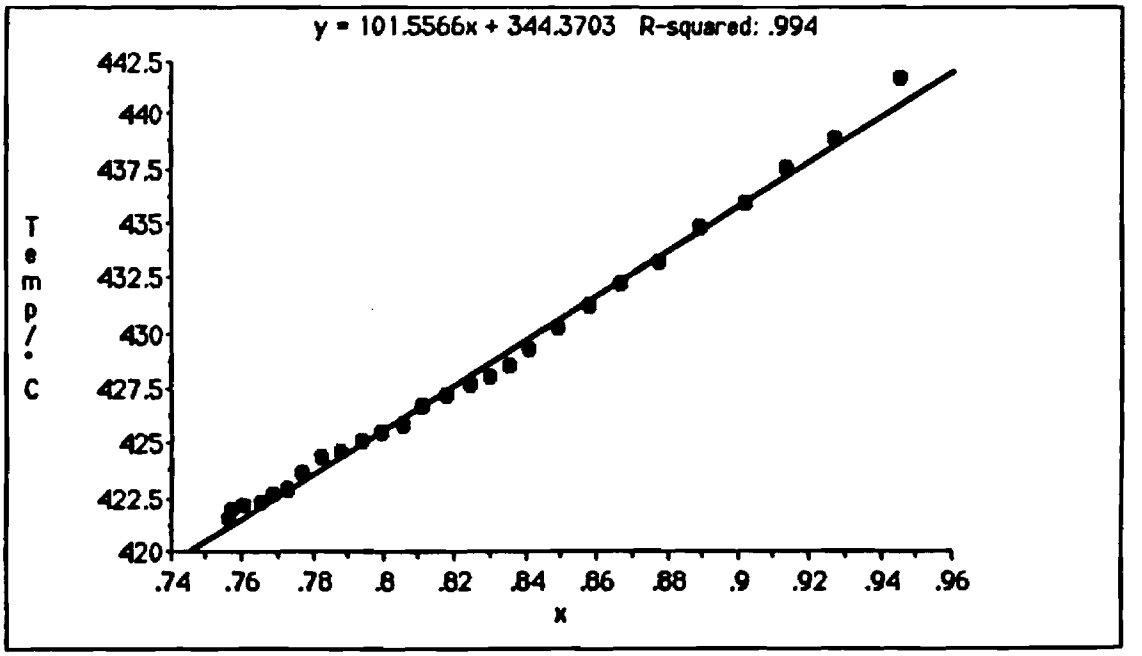


Figure 9. T_C Vs Time And T_C Vs X: n-Hexadecane

The critical temperatures of isomeric pentanols and heptanols.

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ABSTRACT

The critical temperatures of seven isomeric alcohols have been measured using the modified sealed tube method of Mogollon et al. The ampoule used in the Mogollon et al. method was modified to allow easier handling and reproducible results to be obtained. The addition of an Apple IIe microcomputer to the apparatus made possible the recording of the temperature history of the fluid and the monitoring of successive meniscus disappearances and appearances with time. The critical temperatures were obtained by averaging the temperatures of meniscus disappearance and reappearance.

INTRODUCTION

The critical temperature of a pure fluid is an important characterization parameter in methods for the calculation of thermodynamic properties based on the corresponding states principle. It is not surprising, therefore, that critical temperatures of many organic compounds have been measured and the values tabulated in compilations such as those of Reid et al. (1977) and Ambrose (1980). Data for polar fluids, however, are scarce and this is particularly true for the isomeric alcohols. In the latter case, the lack of data is partly due to the fact that alcohols undergo various degrees of association (hydrogen bonding) and therefore, the critical temperatures of the pure fluids are difficult to measure.

The simplest technique for the measurement of the critical temperature is by visual observation of the disappearance and/or reappearance of the vapor-liquid meniscus in a sealed ampoule containing a sample of the pure fluid. This technique is commonly referred to as the "sealed-tube method" and is capable of yielding data of high precision. A "modified sealed tube method" for the study of thermally unstable substances has been described recently by Mogollon et al. (1982). In this paper, we describe further modifications to the method of Mogollon et al. and present results of the determination of the critical temperatures of seven isomeric pentanols and heptanols.

EXPERIMENTAL APPARATUS

In the "sealed tube method", a sample of the fluid is

enclosed in an ampoule and the ampoule placed in a furnace where its contents can be heated through the vapor-liquid phase transition. In the Mogollon et al. "modified sealed tube method", a rapid heating furnace is used and the sample is successively heated and cooled to observe the disappearance and reappearance of the meniscus. If the substance decomposes, the apparent critical temperature will decrease with time; if the substance undergoes association, the apparent critical temperature will generally increase with time. The rate of change of the apparent critical temperature depends on the rate of decomposition or association. In the case of thermally stable substances, the critical temperature of the fluid does not change with time and is given by the average of the temperatures of meniscus disappearance and reappearance.

Ampoules. Several types of ampoules were used in this work. Figure 1 illustrates two of the more successful designs. The Mogollon et al. design is shown in Fig. 1a and was constructed from 10 mm standard wall 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 and which extended into the center of the ampoule. A modified design is shown in Fib 1b and consists of the Mogollon ampoule joined to a 3 cm length of 1 mm capillary tubing. The capillary neck facilitated reliable sealing of the ampoule and is further discussed below. Each ampoule was pressure tested to a working pressure of 5.5 MPa. The ampoule holder was made from stainless steel and had a minimum contact area with the ampoule surface.

Its design was similar, in principle, to the holder used by Mogollon et al.

Metal Film Furnace. The furnace is shown in FIgure 2 and was constructed by Ace Glass Co. Four layers of platinum were coated on a quartz tube of 2.5 cm o.d. x 55 cm long with three windows, 3-mm wide x 50-mm long, diametrically placed at 90° intervals. Power rating for the furnace was 85 VAC at 6 amperes and its resistance at room temperature was measured at 6.5Ω. The resistance was found to be relatively insensitive to temperature, increasing only 0.08Ω at a voltage drop of 41.73 VAC rms. The constant resistance characteristics of the metal film furnace, its low heat capacity, and the rapid response to voltage step inputs means that the furnace can provide rapid and constant heat input.

Test Furnace. For initial screening of chemicals to be studied, a small destructible furnace was constructed that would allow rough critical temperature determinations, but which could easily be reassembled if the substance under test exploded. Such a test furnace is shown in Figure 3 and consists of 20 gauge nichrome, 2.23 Ω/m wire tightly wound around a glass tube of 20 mm o.d. Resistance of the test furnace at room temperature was measured to be 9 Ω.

Temperature. Driver-Harris B & S 22 gauge iron constantan thermocouple wire with glass insulation was used to make the thermocouple for critical point measurements. The thermocouple was calibrated against a Leeds & Northrup standard platinum resistance thermometer (SPRT) using a Leeds & Northrup Speedomax

"Stull" type recorder capable of accuracies to $\pm$ 1m Ω, corresponding to a base accuracy of $\pm$ 0.01K. Thermal comparisons were made in a modified Leeds & Northrup calibrating furnace or in a modified Thermolyne oven.

Other thermocouples used were compared similarly using the above SPRT or a Yellow Springs International SPRT. Two K-type thermocouples, custom manufactured by Omega engineering with an Inconel sheath proved disappointing, as they consistently read low by several degrees in the critical point apparatus - possibly due to heat conduction along the sheath. They were rugged, however, and found use in the test furnace. Freezing point traces of tin and zinc showed that the Leeds & Northrup SPRT was in calibration and within the limit of error of the freezing point furnace.

EXPERIMENTAL SETUP

The critical point apparatus is shown in Figure 4. Power to the metal film furnace was supplied by a General Electric voltage stabilizer with 2 KVA capacity to two 120/140V 12-ampere variacs connected in series. This arrangement allowed very fine temperature control. A Fluke 8840A digital multimeter with an IEEE-488 interface was used to detect the iron-constantan e.m.f. The e.m.f. information was collected and stored on disk by an Apple IIe microcomputer having 64K memory, an Applied Engineering, Inc., TIMEMASTER II real time clock board, and an Apple IEEE-488 interface board.

Operating in the slowest mode, the multimeter could sample

three readings per second using internal trigger. However, readings were rarely taken at a rate greater than 1 reading/second due to disk size limitations and real time clock operation. An external on/off switch was connected to the TTL level joystick port of the Apple IIe. For this case, the closure of the switch was sensed as a high-low transition. A small program in Applesoft BASIC was written to detect the switch sense, collect the data over the IEEE-488 bus, read the clock, and write the time, e.m.f., switch sense (0=open, 1=closed) information to the disk. Visual information was sent to the monitor giving a plot of e.m.f. versus time, the heating time, the temperature, and the rate of change of temperature in K/sec.

EXPERIMENTAL PROCEDURE

Ampoule Preparation. After pressure testing, the capillary portion of each ampoule was coated with a layer of beeswax and a fine line was scratched through the wax for etching with HF. Volume determination was done by filling with either freshly distilled mercury or triple distilled mercury, and weighing the ampoule before and after the filling. Knowing the density of mercury, and the buoyancy correction, enabled accurate volume determinations.

For the cases in which the expected temperature was greater than 573K, any possible traces of mercury were removed by rinsing with a 50/50 vol % solution of nitric acid. After volume determination, the ampoules were rinsed with several washings of acetone and distilled water and allowed to dry in an oven. They

were then stored in a desiccator until use.

Loading. The critical temperature, pressure, and density of the substance were first estimated using a group contribution method of Ambrose (1979). The correct amount of sample was then introduced into the ampoule with a 1-cm^3 hypodermic syringe having a 15 cm needle. The correct density was loaded by weighing on a Mettler analytical balance with a resolution of 0.1 mg. A small wad of glass wool was then put into the ampoule neck to prevent dirt or dust from contaminating the solution. To remove noncondensable gases, the samples were then subjected to successive freeze-melt cycles under vacuum as follows. Each sample was frozen by placing the ampoule in a liquid nitrogen bath and a vacuum was pulled on the ampoule with a pump capable of taking the pressure down to 10^{-4} kN/m^2. The successive freeze-melt cycles were continued until no gas formed on melting. The ampoules were sealed off at the etched marks. A difficulty with the Mogollon et al. design ampoules was that they were difficult to seal accurately. The ampoule design used in this work overcomes this problem by use of 1 mm capillary tubing where the seal is to be made. The capillary tube was typically collapsed with a gas-oxygen torch above the etched mark and the glass was melted to the mark. Accurate volumes could thus be sealed off.

Rapid Heating and Measurement. The ampoule was placed in the ampoule holder as in Figure 4 and the thermocouple secured in the thermowell. The assembly was loaded into the furnace and the maximum applied voltage was set on the first variac. This

ensured that the maximum voltage would never be exceeded. After the parameters in the computer were set, the current was turned on and the furnace allowed to heat up. The entire assembly was rocked vigorously during the heating cycle so that thermal gradients within the ampoule would be minimized. As the critical point was approached, the lack of viscosity and density differences was observed and less rapid rocking was used. In general, the current was shut off 20-30K away from the expected critical point, and the system was allowed to glide through the critical region. At each swing of the apparatus, a check was made whether the meniscus returned or not. If the meniscus did not return, the point was marked with the electronic switch as the point of meniscus disappearance. As the temperature gradually began to fall, and the system was just above the critical point, the current was switched on again. Before a rise in temperature occurred, the abrupt reappearance of the meniscus was observed and marked with the electronic switch. Throughout the run, the temperature and time were recorded on the computer every one or two seconds.

The rate of increase or decrease varied from point to point, but was frequently several hundredths of a degree per second. Larger rates of increase or decrease were recorded at the first disappearance or reappearance making it the most unreliable. As time went on, the critical point changed, and therefore heat input was either increased or decreased. Usually critical point readings could be taken at least once every minute. After a period of 20-60 minutes, the experiment was terminated and the

data collection stopped.

PURITY OF SAMPLES

The purest commercially available grade of alcohols were used in the experiment. The source of the materials and the stated purity are given in Table 1.

EXPERIMENTAL RESULTS AND DISCUSSION

Table 2 gives a summary of the critical temperatures of the substances studies. The test substance was n-octane since it is thermally stable. The octane data are plotted in Fig. 5, showing the temperature history as well as the temperatures of meniscus disappearance and reappearance. The (average) critical temperature of n-octane was found to be 568.65K compared with the literature value of 568.80K (Ambrose et al., 1960). It should be noted that the meniscus disappearances and reappearances did not differ by more than $\pm$0.03K from this value.

The alcohols exhibited a greater degree of hysteris in meniscus disappearance and reappearance. As the critical pressures are relatively high for alcohols, each was measured in the test furnace at least once. Overshooting the critical temperature by 20K or so generally caused a violent explosion, expanding the copper shield and destroying the inner glass tubing. For these measurements, the temperature approach was cautious.

The measured critical temperatures of the alcohols are compared with literature values (where available) and with the

predicted values of two group contribution methods. The measurements are close to the literature values for the two cases where literature values are available. The values also are in close agreement with the predictions of the Ambrose method. The predictions of the Lydersen method, however, were found to be low by 15-30K.

ACKNOWLEDGEMENT

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LITERATURE CITED

1. Ambrose, D., Cox, J. D., and Townsend, R., "The critical temperatures of forty organic compounds", Trans. Faraday Soc., 56, 1452 (1960).

2. Ambrose, D., "Correlation and estimation of vapor-liquid critical properties: I. Critical temperatures of organic compounds", National Physical Laboratory Report, Chem. 92 (1978).

3. Ambrose, D., "Correlation and estimation of vapor-liquid critical properties: II. Critical pressures and critical volumes of organic compounds", National Physical Laboratory Report, Chem. 98 (1979).

4. Ambrose, D., "Vapor-liquid critical properties", National Physical Laboratory Report, Chem. 102 (1980).

5. Efremov, Y. V., "Density, surface tension, vapor pressure and critical parameters of alcohols", Russian J. Phys. Chem., 40, 667 (1966).

6. Lydersen, A. L., Greenkom, R. A., and Hougen, O. A., "Generalized thermodynamic properties of pure fluids", University of Wisconsin Engineering Experiment Station, Report 4 (1955).

7. Mogollon, E., Kay, W. B., and Teja, A. S., "Modified sealed-tube method for the determination of critical temperature", Ind. Eng. Chem. Fundam., 21, 173 (1982).

8. Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., "The Properties of Gases and Liquids", 3rd Edition, McGraw-Hill, New York (1977).

Table 1. Purity and source of materials

Substance	Purity	Source
1-pentanol	99+	Fluka puriss p.a.
2-pentanol	98+	Fluka purum
3-pentanol	98+	Fluka purum
1-heptanol	99.5+	Fluka puriss
2-heptanol	99+	Fluka purum
3-heptanol	98+	Fluka purum
4-heptanol	98	Fluka purum

Table 2. Experimental results and comparisons

Substance	Experimental T_c/K		Predicted T_c/K	
	This work	Literature*	Ambrose (1979)	Lyderson (1955)
1-pentanol	587.7 ± 0.1	586.2	587.7	574.3
2-pentanol	560.4 ± 0.2	---	558.7	574.3
3-pentanol	559.6 ± 0.2	---	553.9	574.3
1-heptanol	632.3 ± 0.1	633.2	632.9	608.0
2-heptanol	611.4 ± 0.2	---	608.9	608.0
3-heptanol	605.4 ± 0.2	---	603.5	608.0
4-heptanol	602.6 ± 0.2	---	602.1	608.0

* Efremov (1966)

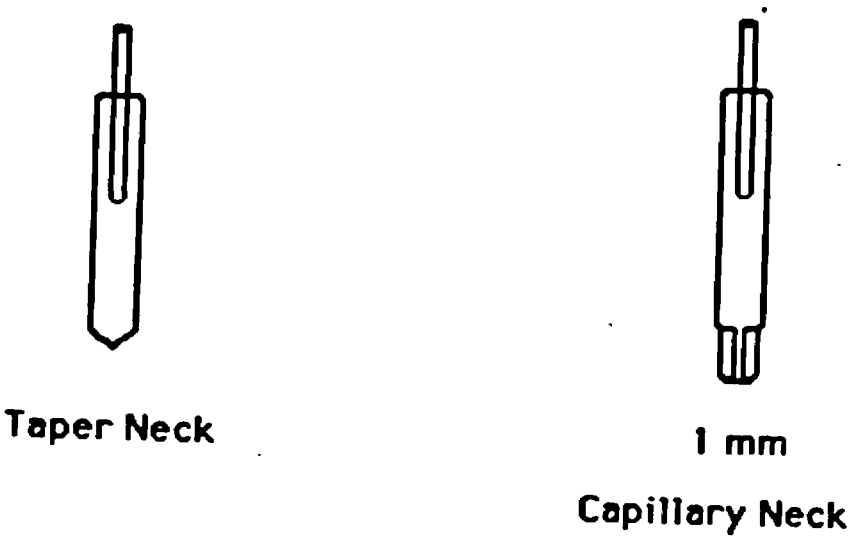

Figure 1. Types of sealed ampoules used.

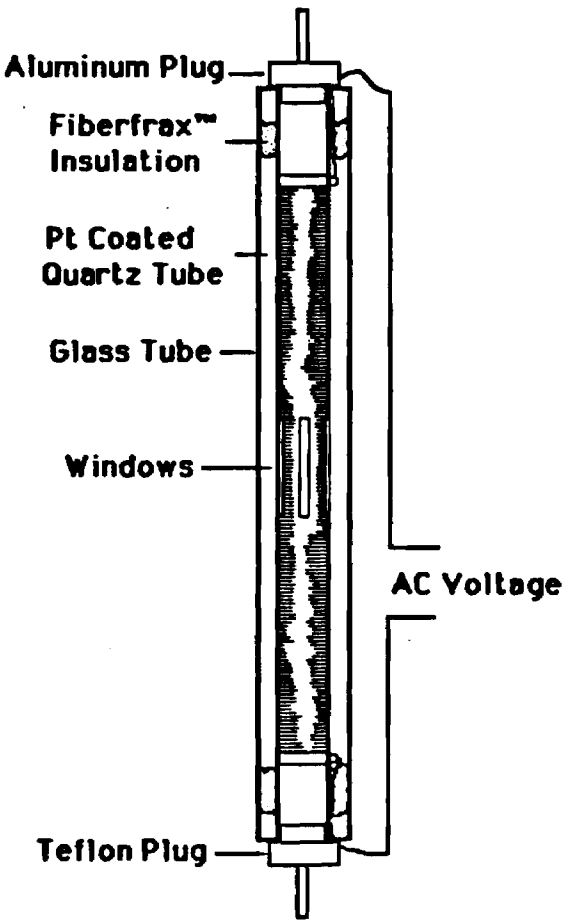

Figure 2. Experimental furnace.

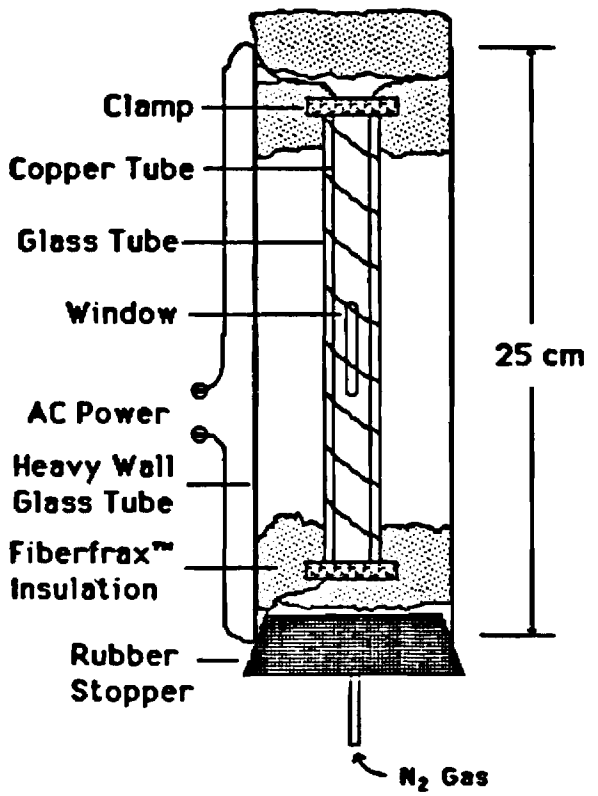

Figure 3. Test furnace.

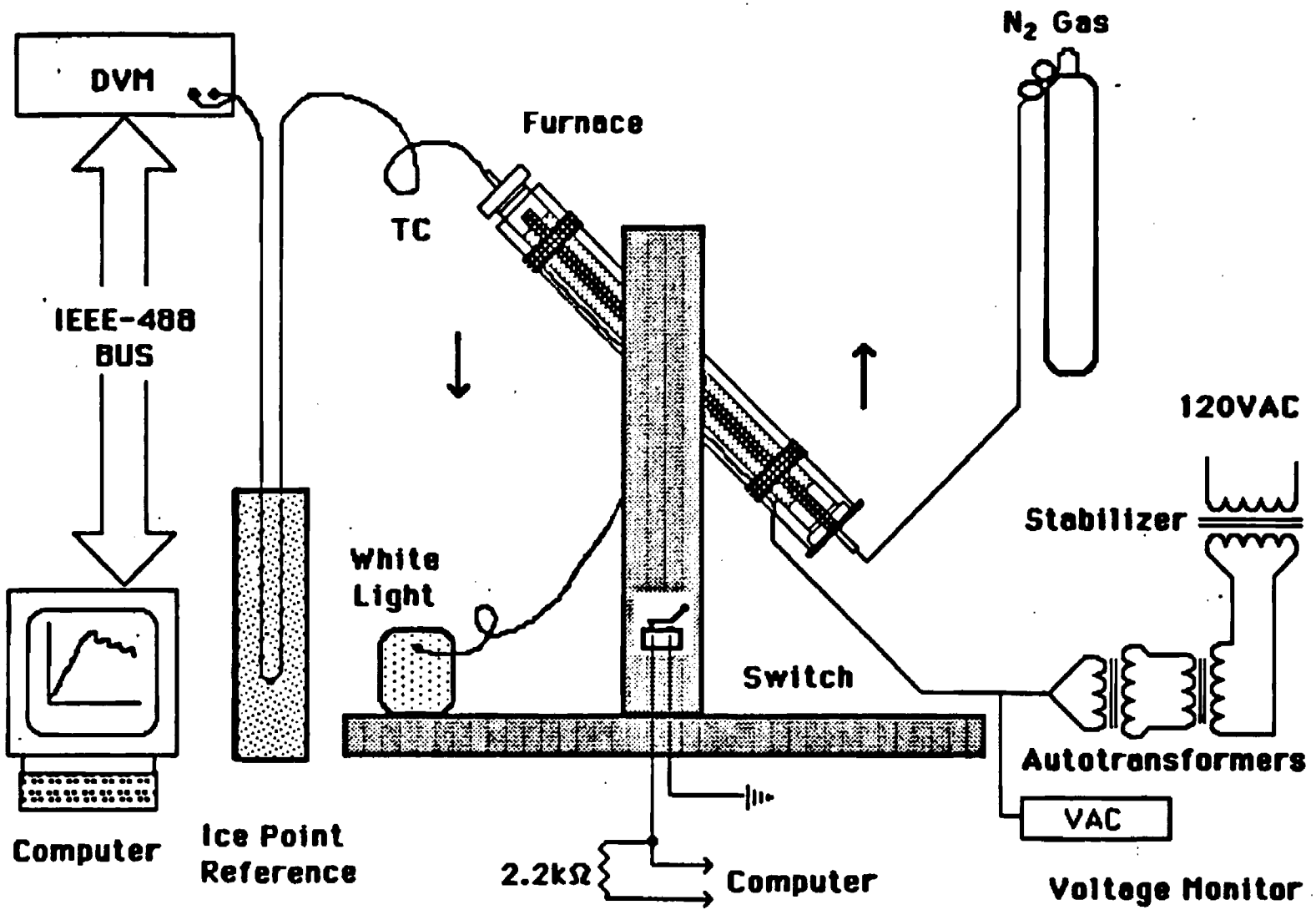

Figure 4. Schematic diagram of the apparatus.

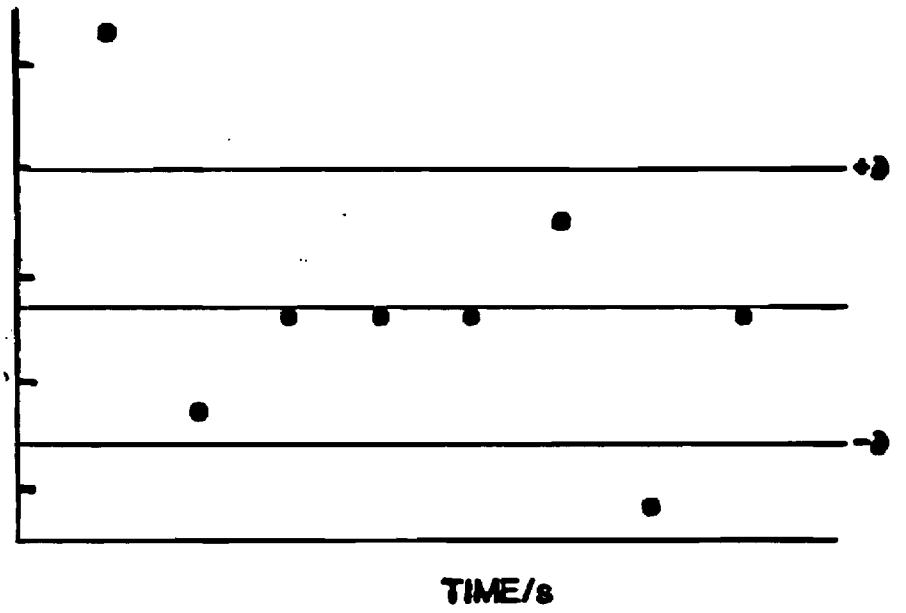

Figure 5. Critical temperature versus time data for n-octane.