Determination of the Thermal Stability of Perfluoroalkylethers by Tensimetry: Instrumentation and Procedure

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ABSTRACT

A computerized tensimeter and experimental procedure for determination of the thermal decomposition temperature (T_d) of perfluoroalkylethers have been developed and tested. Both the apparatus and the procedure are described in detail. Results of testing with bis(2-ethylhexyl) phthlalate and trimethylolpropane triheptanoate demonstrate that the reciprocal of the decomposition temperature is a linear function of the logarithm of the gas volume/heated liquid volume ratio. The T_d obtained for each compound at a gas volume/heated liquid volume ratio of one was similar to the value previously reported using an isoteniscope technique. Results of testing with a polymer of hexafluoropropylene oxide demonstate that this instrument and procedure can be used to determine the T_d of perfluoroalkylethers.

INTRODUCTION

Perfluoroalkylethers (PFAE) is a class of fluids which normally exhibits excellent thermal and oxidative stability (Refs. 1 to 3) and, when combined with good viscosity-temperature characteristics (Ref. 3), good elastohydrodynamic film forming capabilities (Ref. 5) and adequate boundary lubricating ability (Refs. 3, 4, and 6) make these fluids promising candidates for high temperature lubricant and hydraulic fluid applications.

In the past, only a few different PFAE chemical structures were available. One was a branched structure based on the polymerization of hexafluoropropylene oxide (HFPO) monomer (Refs. 7 and 8). Another was an unbranched structure prepared by the poly-

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merization of tetrafluoroethylene (TFE) in the presence of oxygen (Ref. 9). A third, also an unbranched structure, now commercially available, is made by polymerization of tetrafluorooxetane followed by direct fluorination (Ref. 10). Recently, a variety of new structures based on direct fluorination techniques have been prepared (Ref. 11).

This influx of new PFAE fluids has made it possible to correlate various properties with the different chemical structures. One of these properties, which is important in determining the maximum use temperature, is the thermal decomposition temperature.

In the case of hydrocarbons and most other fluid classes, thermal decomposition (i.e., processes occurring in the absence of oxygen) proceeds through a free-radical reaction yielding many products. Some of the products are volatile. Thus, in a closed system, a pressure rise accompanies decomposition.

A device which has been used for many years to measure this pressure rise and thus thermal decomposition is the isoteniscope (Ref. 12). It has been used to correlate thermal stability with chemical structure (Ref. 13 and 14) and is now used in a standard ASTM test procedure (Ref. 15) for measuring the initial thermal decomposition temperature of fluids.

Recently, a computerized tensimeter, based on the isoteniscope principle, has been developed which automates many of the tedious procedures. This computerized tensimeter was used to measure the isothermal rate of pressure rise from which the thermal

decomposition temperature can be determined. The purpose of this communication is to report the development and testing of this tensimeter, the procedure used to determine the thermal decomposition temperature of a perfluoroalkylether, and the determination of the significant dependence of the thermal decomposition temperature upon the gas volume/heated liquid volume ratio. The importance of this dependence has not been recognized previously, and is a principal finding, both experimentally and theoretically in this paper. It is anticipated that these new fluids and the computerized tensimeter will eventually aid in determining the ultimate thermal stability of perfluoroalkylethers in the absence of potential catalyzing agents such as metals, metal oxides, metal fluorides, and air.

Details of the tensimeter apparatus used in the present tests and its calibration that are relevant to its operation are given below.

APPARATUS

Tensimeter

A computerized tensimeter was used to measure isothermal rates of pressure rise from which thermal decomposition temperatures were determined. A schematic representation of this device is shown in Figure 1 and an isometric view appears in Figure 2. The device consists of a sample cell assembly, an oven, a temperature programmer, temperature and pressure measuring components, and a data acquisition system.

Pressure and Temperature Calibration

The pressure transducer had a resolution of 3 torr and was calibrated by measuring the millivolt output as a function of pressure for several known pressures ($\pm$ 2 torr) from 10 to 1450 torr (from an absolute pressure gage) and had a linear response (correlation coefficient=0.9999). The Type J iron-constantan thermocouple in the oven was precalibrated and had an accuracy of $\pm 3\,°C$. A check was made to determine if there was any significant difference between the oven temperature measured by the thermocouple and the fluid temperature in the bulb of the cell. The temperature of the fluid in the bulb of the cell was measured with a thermistor thermometer with an accuracy of $\pm 3\,°C$ while following the temperature program used to test fluids. Differences in temperature between the thermocouple and the thermistor were less than $3\,°C$.

Valve

A valve (constructed of 316 stainless steel) with two 6.3 mm (1/4") ferrule fittings was modified to accept a 1.7×10^5 Pa (0-25 psia) pressure transducer and one 6.3 mm (1/4") o-ring fitting for mounting the cell (Figure 3). The internal volume of the valve (excluding the transducer cavity, which was prefilled with test fluid) was determined (0.30 $\pm$ 0.02 mL) by weighing empty and reweighing filled with water.

Magnetic Stirring Bar

The volume (0.10 $\pm$ 0.02 mL) of a borosilicate glass covered magnetic stirring bar, with a small enough diameter to fit into the

stem of the cell, was determined by displacement of water in the graduated barrel of a 2 mL syringe.

Sample Cell

The 150 mm long sample cells with 23 mm diameter bulbs were made from 6.35 mm diameter borosilicate glass tubing with 1.2 mm walls and pressure tested to 1500 torr.

Sample Cell Assembly

The cell containing the magnetic stirring bar was mounted on the valve with the transducer and sealed with the o-ring fitting (Fig. 3). The cell assembly was vacuum tested for leaks with helium and a quadrupole residual gas analyzer at 10^{-7} torr with no helium detectable. It was pressure tested at 1400 torr for 1 hr. with the cell at 300°C with no reduction in pressure observable ($\pm$ 2 torr).

Test Fluids

Trimethylolpropane triheptanoate (TMPTH) and bis(2-ethylhexyl) phthalate ("dioctyl phthalate") (DOP) were vacuum distilled before use. The perfluoroalkylether (HFPO type) was used as received. Structures of these fluids appear in Figure 4. Some typical physical properties of the test fluids are tabulated in Table I.

OUTLINE OF BASIC TEST PROCEDURE

1. Fill transducer cavity with test fluid.

2. Determine volume of cell.

3. Clean and dry cell, then weigh cell assembly empty.

4. Inject fluid into cell.

5. Degas fluid, then weigh cell assembly with fluid.

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6. Mount cell assembly in oven.

7. Determine T_d' with tensimeter. (Symbols defined in Appendix B.)

8. Weigh cell with fluid.

9. Repeat steps 2-8 with a different V_g/V_l ratio.

10. Clean valve and transducer cavity.

DETAILS OF BASIC TEST PROCEDURE

Prefilling the Transducer Cavity

In order to minimize the volume of fluid in the cell during degassing, the transducer cavity was prefilled with test fluid. This was done by mounting a cell containing the type of fluid to be tested (approximately 2 mL), evacuating to 0.1 torr with stirring for several minutes to degas the fluid, closing the valve, and then inverting the cell assembly so that the fluid could flow into the evacuated transducer cavity.

Once filled, the cavity remained full due to the viscosity of the fluid and the small diameter (2 mm) of the transducer opening, as long as the transducer cavity was not inverted. After removal of the cell, the valve and transducer were ready for use.

Determining Volume of Cell

The total volume of each cell (approx. 5 mL) was determined ($\pm$ 0.002 mL) by weighing empty, filling with deionized water, reweighing, and converting the net weight to volume by dividing by the density of water (0.997g/mL). The volume of the stem alone was also determined (1.60 $\pm$ 0.05 mL) and assumed to be constant for all cells.

Cleaning and Drying the Cell

In order to prevent nonreproducible pressure increases due to vaporization of moisture and thermally unstable material from the inside surfaces of the cell, each cell was cleaned and dried immediately before use. The cell containing the stirring bar was mounted on the o-ring fitting of the valve with the valve open. The stirring bar was moved into the valve to avoid heating the magnet. The bulb and stem of the cell were heated with a gas burner to a yellow flame temperature (approx. 800°K) in air at atmospheric pressure to oxidize or decompose any thermally unstable material on the glass. The cell was then evacuated to 0.1 torr while hot to remove adsorbed water from the glass. The valve was closed and the cell assembly was removed from the vacuum line and weighed (±0.002g).

One cleaned cell was tested for remaining traces of volatile and thermally unstable material by heating in the tensimeter from 573°K to 723°K (300°C to 450°C) following the temperature programming used to test fluids. The cell pressure remained constant (± 2 torr), indicating that the cell contained no material that would cause a pressure increase during the testing of a fluid.

Injecting Fluid Into the Cell

The evacuated cell assembly was placed in a dry box purged with cryopumped nitrogen. The cell was removed from the valve. The calculated volume of fluid (V_f) required to give a specific

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V_g/V_l ratio (see Discussion Section) was measured ($\pm$ 0.02 mL) in a 5 mL syringe and injected with a 16 cm long 3 mm diameter needle into the bulb of the cell. The cell was replaced on the valve and the assembly removed from the dry box and degassed.

Degassing Fluid

The fluid in the cell was degassed with the cell assembly in a vertical position by magnetically stirring at room temperature and 0.1 torr on a 6.3 mm (1/4") vacuum line equipped with a liquid nitrogen trap until bubbling ceased (approx. 30 min). If the fluid was too viscous to stir well, the temperature was raised to 80°C by heating with a hot-plate stirrer. Foaming of fluid into the stem was minimized by mild heating of the stem with a hot air gun (maximum hot air temperature: 548°K). This prevented entraining of fluid into the valve and loss through the valve into the vacuum system. Degassing is improved by stirring the fluid, increasing the degassing time and temperature, and decreasing the degassing pressure. However, care must be exercised in selecting degassing conditions so that composition and properties of the test fluid are not inadvertently changed during degassing.

After degassing, the cell assembly was again weighed ($\pm$ 0.002 g) and the exact volume of fluid present was calculated by subtracting the weight of the empty cell assembly and dividing the remainder by the density of the fluid.

Mounting Cell Assembly

The magnetic stirring bar was moved into the valve to avoid heating the magnet. Then the cell assembly was mounted in the oven

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in a reproducible position with approximately 10° upward tilt toward the bulb of the cell.

Tilting the cell assembly slightly when mounting in the tensimeter oven insures that the valve and stem of the cell always remain filled with fluid. This prevents any possible refluxing of volatile starting materials or decomposition products in the cell assembly, and the corresponding erratic pressure fluctuations, as well as reduction in fluid temperature due to the heat of vaporization and condensation of the refluxing material. It also insures that a known and reproducible volume of fluid will always be present in the heated bulb of the cell so that V_g/V_l can be calculated (Equation 1).

Determining T_d with Tensimeter

Instrument temperature control and data acquisition was handled automatically by the data acquisition system. The oven was preheated to a temperature about 20°C below the expected decomposition temperature of the fluid. The oven temperature was held constant for 360 sec. for the fluid to reach thermal equilibrium and constant vapor pressure. Then the temperature was recorded. Any change in pressure due to decomposition was measured during a 144 sec. interval at that temperature and also recorded. Finally, the actual cell pressure was recorded. Then the oven temperature was raised 5° during the next 60 sec. and the process repeated. When the pressure reached 1500 torr, or the change in pressure reached 100 torr in 144 sec., or the temperature reached 723°K (450°C), data acquisition was terminated and the oven was turned

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off. The data were tabulated and a plot of the log of the isothermal pressure change (log dP/dt) vs. the reciprocal absolute temperature was prepared as shown in Figure 5 for bis(2-ethylhexyl) phthalate.

That 360 sec. was adequate time to reach thermal equilibrium was demonstrated by increasing the equilibration time to 600 sec. in one test and observing no change in results.

Weighing Cell with Fluid

At the end of the test, the cell assembly was cooled. The fluid and stirring bar in the valve and stem were allowed to flow back into the bulb of the cell. The cell was removed from the valve and, after removal of the stirring bar, was weighed ($\pm$ 0.002g) with the fluid in it to confirm the volume of fluid actually in the cell during the test.

Cleaning the Valve

The valve and transducer unit was disassembled and cleaned whenever the type of fluid was changed by rinsing thoroughly with 1,1,2-trichloro-1,2,2-trifluoroethane or acetone, blowing out with nitrogen, and drying at room temperature and 0.1 torr.

RESULTS AND DISCUSSION

Experimental Procedure

In order to evaluate the computerized tensimeter and the corresponding experimental procedure used to determine thermal decomposition temperatures, two esters and one perfluoroalkylether were tested under a variety of experimental conditions. The two

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esters were chosen in order to compare results with those obtained previously using an isoteniscope technique (Ref. 13). The PFAE was chosen to insure that the conditions selected for the experimental procedure would be suitable for analysis of perfluoroalkylethers. Experimental conditions investigated included the test fluid purity, cell cleaning procedure, degassing procedure, the gas volume/heated liquid volume ratio, and the mounting angle of the cell in the tensimeter oven.

Effects of variations in several of these experimental conditions have previously been mentioned (Refs. 12, 13, and 15). Presence of volatile or thermally unstable material in the test fluid or cell can result in erratic isothermal pressure increases before the actual thermal decomposition temperature of the test fluid has been reached. These in turn can produce a curved Arrhenius plot and a corresponding reduction in the calculated T_d'. These problems can often be minimized by purification of test fluids (e.g., drying and distillation), by flame cleaning of the cell followed by drying under vacuum while hot, by filling the cell in a dry atmosphere, and by thorough degassing of the test fluid, as described in the Experimental Section.

Data Analysis

After discarding any low temperature data (log dP/dt<0.7) which appeared to be due to volatile or thermally unstable impurities as discussed above, the log of the isothermal change in pressure (log dP/dt) was plotted as a function of the reciprocal of the absolute temperature (Figure 6). The temperature at which

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the line obtained from a linear regression of the data intersected the log 0.3 line was taken as the decomposition temperature (T_d') for the fluid at that particular gas volume/heated liquid volume ratio. The slope of the line was used to calculate E' (Figure 6 and Equation 4), a value related to the energy of activation (Ref. 13). Decomposition temperatures were reproducible to $\pm$ 2°C. E' was estimated to be accurate to 17 kJ/mol (4 kcal/mol) and reproducible to 8 kJ/mol (2 kcal/mol).

Calculation of the Gas Volume/Heated Liquid Volume Ratio

A major observation in the study of the reproducibility of the data was that the measured decomposition temperature (T_d') of a given fluid depended significantly upon the ratio of the gas volume to the heated liquid volume (V_g/V_l) in the cell assembly. This ratio was calculated from the following equation, where all units are in mL.

$$V_g/V_l = (V_t - V_f)/(V_f - 1.00) \qquad [1]$$

V_f is the fluid volume. V_t is the total internal volume of the cell assembly (excluding the transducer cavity). It is equal to the cell volume (V_c) plus the valve volume (V_v) (0.30 $\pm$ 0.02 mL) minus the magnet volume (V_m) (0.10 $\pm$ 0.02 mL) (Figure 3):

$$V_t = V_c + V_v - V_m \qquad [2]$$

The cell assembly constant (1.00) represents the total volume of unheated fluid in the valve (0.20 mL) and stem (0.80 mL) of the cell. Therefore, the gas volume is equal to the total internal volume of the cell assembly (excluding the transducer cavity) minus the volume occupied by the fluid ($V_g=V_t-V_f$). The heated liquid

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volume is equal to the volume of the fluid placed in the cell minus the volume of unheated fluid in the valve cavity and stem of the cell outside the oven ($V_l = V_f - 1.00$).

Equation 1 neglects the expansion of the fluid due to heating, as well as the solubility of the product gases in the fluid. Individually, these two factors could significantly affect the pressure in the cell, but they appear to partially cancel each other. A theoretical derivation of the relationship between T_d' and log V_g/V_l appears below, and supports the experimental observations.

Derivation of the Relationship Between T_d' and Log V_g/V_l

The rate of thermal decomposition usually varies with temperature according to the Arrhenius rate law (Ref. 13) as shown in the following equation:

$$k = Ae^{-E/RT} \qquad [3]$$

where k is the rate constant, A is the frequency factor, E is the activation energy, R the gas constant, and T the absolute temperature. According to this equation, a straight line should be obtained when log k is plotted as a function of the reciprocal of the absolute temperature. It has been shown experimentally (Ref. 13) that for many organic compounds, log dP/dt versus 1/T is also a straight line. Then, by analogy,

$$\frac{dP}{dt} = A'e^{-E'/RT} \qquad [4]$$

Using this equation, one can determine the rate constant for thermal decomposition by measuring the isothermal rate of pressure

rise (dP/dt) at several temperatures. However, it is more convenient to have a single parameter for thermal decomposition rather than to tabulate values of A' and E' which actually define the rate constant for different fluids.

Therefore, an arbitrary thermal decomposition temperature (T_d) is defined as the temperature at which the isothermal rate of vapor pressure rise is 1.85 Pa/sec (50 torr/hr) when the gas volume is equal to the heated liquid volume. An arbitrary pressure rise of 50 torr/hr was originally chosen because it represented the minimum pressure rise easily detectable experimentally. A gas volume equal to the heated liquid volume was originally used by Blake, et al. (Ref. 13) and is included in the definition here because of our experimental observation that T_d is significantly dependent upon this ratio. Then, the decomposition points for a series of organic compounds are the temperatures at which all have identical isothermal rates of pressure rise.

For the reaction $B_{liq.} \xrightarrow{\ k\ } b\ D_{gas}$, Blake, et al. (Ref. 13), have shown that the rate of pressure rise (dP/dt) due to formation of product (D) is related to the rate constant (k) by the gas volume/heated liquid volume ratio (V_g/V_B) and the constants b, n_B^α, R, and T:

$$k = \frac{V_g}{V_B b n_B^\alpha RT}\ dP/dt \qquad\qquad [5]$$

where b is the number of molecules of gas formed from one molecule of liquid B, n_B is the concentration of B, α is the order of the reaction, R is the gas constant, and T is the absolute temperature.

Setting equations 3 and 5 equal to each other gives equation 6:

$$Ae^{-E/RT} = \frac{V_g}{V_B \ b \ n_B{}^\alpha \ RT} \ \frac{dP}{dt} \qquad [6]$$

Taking logs of equation 6 gives:

$$\log A - (E/2.3RT) = \log V_g/V_B + \log 1/bn_B{}^\alpha R + \log 1/T + \log dP/dt \qquad [7]$$

Rearranging and solving for $\log V_g/V_B$ gives:

$$\log V_g/V_B = -E/2.3RT + \log T + \log A + \log bn_B{}^\alpha R - \log dP/dt \qquad [8]$$

For values of $\log V_g/V_B$ not equal to 1, when $\log dP/dt = 0.30$, $T = T_d'$. Substituting these into equation 8 gives:

$$\log V_g/V_B = -E/2.3RT_d' + \log T_d' + \log A + \log bn_B{}^\alpha R - 0.30 \qquad [9]$$

For decomposition of a specific fluid with various gas volume/heated liquid volume ratios, $\log V_g/V_B$ and T_d' will be variables while the other quantities are constant. Since $\log T_d'$ is small and nearly constant (for small changes in T_d') compared with $E/2.3RT_d'$ (Appendix A), it can be included in the other constants. Therefore, under these experimental conditions, equation 9 reduces to equation 10, which is the equation of a straight line. Theoretically, then, a plot of $\log V_g/V_B$ vs. $1/T_d'$ should be linear.

$$\log V_g/V_B = -E/2.3RT_d' + C \qquad [10]$$

This has indeed been found to be the case experimentally, as shown in Figures 7, 8, and 9, where $V_B = V_L$.

Furthermore, since the slope is equal to $-E/2.3R$, the Arrhenius energy of activation (E) can be calculated from this graph and compared with E' obtained from the $\log dP/dt$ vs. $1/T$ graph. Blake et al., (Ref. 13) have shown that $E = E' - RT_m$ where T_m is the

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mean temperature for the range of observations. Thus E' and E should be similar in magnitude. When the effect of the experimental error in dP/dt and T_d' on the magnitudes of E' and E are considered, the magnitudes of E' and E are indeed found to be similar. For TMPTH, E'=246±5 kJ/mol (Table III), E=283±31 kJ/mol (Figure 8). This places the instrument and method on a firmer mathematical basis and allows for more reproducible results.

Thermal Decomposition Temperature of Fluids

Since the T_d of the fluid is the temperature at which the rate of isothermal pressure rise is 1.85 Pa/s (50 torr/hr) at V_g/V_l=1, the T_d must be experimentally determined at this ratio, or read from a graph of log V_g/Vl vs. 1/T_d' where log V_g/V_l=0. The graphical method is probably the best.

The thermal decomposition temperatures (T_d) obtained for DOP (537.4°K, Table II and Figure 7)(264.2 ± 2°C, Lit. 263.3 ±2°C) and TMPTH (589.9°K, Table III and Figure 8)(316.7 ± 2°C, Lit. 317.2 ±2°C) are similar to values previously obtained (Ref. 13), demonstrating that the properties being measured with this computerized tensimeter and procedure are similar to those previously measured with the isteniscope technique.

Analysis of Perfluoroalkylethers

Although it is apparent that this computerized tensimeter works well under conditions necessary to determine the T_d of hydrocarbon esters, conditions necessary for analysis of perfluoroalkylethers are considerably more rigorous. The oven temperatures required may range as high as 723°K (450°C) and some

of the reaction products, such as carbonyl fluoride (COF_2) are known to be corrosive. Therefore, it was important to test the instrument under these conditions as well.

Tests with the HFPO perfluoroalkylether (Table IV and Figure 9) indicated that the instrument is capable of operating under these conditions as well, although etching of the inside surface of the pyrex cell occurred. The results were very similar to those obtained for the calibration fluids, indicating that nothing unusual was occurring under these conditions. Furthermore, the T_d obtained for the HFPO perfluoroalkylether of 628.4°K (355.2°C) demonstrates that this instrument and procedure can be used to determine the thermal decomposition temperatures of perfluoroalkylethers.

Finally, it is anticipated that thermal decomposition temperatures for several perfluoroalkylethers will be reported shortly, and that these will ultimately result in a correlation of thermal stability with chemical structure.

SUMMARY OF RESULTS

A computerized tensimeter and experimental procedure for the determination of the thermal decomposition temperature of perfluoroalkylethers have been developed. Testing of the tensimeter and procedure with standard fluids (bis(2-ethylhexyl) phthalate and trimethylolpropane triheptanoate) gave thermal decomposition temperatures which compared well with values previously determined by an isoteniscope technique. The thermal decomposition temperature was found both experimentally and

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theoretically to be significantly dependent upon the gas volume/heated liquid volume ratio in the cell assembly. Recognition of this relationship places the instrument and method on a firmer mathematical basis and allows for more reproducible results. Finally, the instrument and procedure were found to give satisfactory results under the more severe operating conditions required for the analysis of the PFAE hexafluoropolypropylene oxide.

CONCLUSION

The computerized tensimeter and corresponding experimental procedure are satisfactory for the determination of the thermal stability of perfluoroalkylethers.

Table I

Physical Properties of Test Fluids

Kinematic Viscosity, CS	Bis(2-ethylhexyl) Phthalate	Trimethylol-propane Triheptanoate	HFPO Perfluoro alkylether
@ 20°C	–	–	2717
38°C	–	15.2	–
50°C	–	–	444
99°C	–	3.5	–
100°C	–	–	63
Molecular Wt	390	470	11000[*]
Density, g/mL			
@ 20°C	–	–	1.92
25°C	0.981	0.963	–

[*]Average

Table II

Experimental Data: Bis(2-ethylhexyl) phthalate

Run No.	V_T (mL)	V_F (mL)	$1/T_d'$	LOG Vg/Vl	E' (kJ/mol.)
15	5.169	2.297	0.0018407	0.345244	201.3
19	5.189	2.538	0.0018492	0.236453	186.6
14	5.546	3.040	0.0018537	0.089350	195.4
17	5.724	3.498	0.0018648	-0.05006	190.4
16	6.676	4.514	0.0018731	-0.21094	186.6
					Mean 192±6

Table III

Experimental Data: Trimethylolpropane Triheptanoate

Run No.	V_T (mL)	V_F (mL)	$1/T_d'$	LOG Vg/Vl	E' (kJ/mol.)
26	5.401	2.488	0.0016782	0.291737	238.5
27	5.478	2.818	0.0016808	0.165287	246.4
24	5.664	3.256	0.0016959	0.028317	248.5
25	5.688	3.641	0.0017008	-0.11065	251.9
28	6.107	4.227	0.0017115	-0.23464	243.9
					Mean 246±5

Table IV

Experimental Data: HFPO Perfluoroalkylether

Run No.	V_T (mL)	V_F (mL)	$1/T_d'$	LOG Vg/Vl	E' (kJ/mol.)
15	5.223	2.40	0.0015719	0.304582	261.1
16	5.174	2.40	0.0015699	0.296978	263.6
22	5.304	2.90	0.0015821	0.102180	262.8
25	5.338	3.10	0.0015891	0.027640	254.0
21	5.586	3.50	0.0015965	-0.07862	255.6
32	5.817	3.74	0.0016003	-0.12031	251.0
26	6.074	4.01	0.0016034	-0.16385	254.4
27	7.259	5.08	0.0016112	-0.27240	241.4

APPENDIX A

Example calculations of $\log T_d'$ and $E/2.3RT_d'$ for DOP (where R = 8.31 J/mol °K):

T_d' (°K)	$\log T_d'$	E(kJ/mol)	$E/2.3RT_d'$
534	2.728	192.46	18.825
542	2.734	192.46	18.547

Note that $\log T_d'$ is small compared with $E/2.3RT_d'$ and that the change i $\log T_d'$ (0.006) is small compared with the change in $E/2.3RT_d'$ (0.278).

Appendix B

Symbol (Units)	Definition
T_d (K)	Thermal decomposition temperature at $V_g/V_l=1$
T_d' (K)	Thermal decomposition temperature at V_g/V_l not equal to 1
k (s-1)	Rate constant for a chemical reaction
A (s-1)	Preexponential factor
E (kJ/mol)	Energy of activation
E' (kJ/mol)	A value related to the energy of activation
R	Gas constant
T (K)	Absolute temperature
t (s)	Time
P (torr)	Pressure
V_g (mL)	Gas volume
V_l (mL)	Heated liquid volume
V_t (mL)	Total internal volume of the cell assembly
V_f (mL)	Fluid volume in cell
V_c (mL)	Cell volume
V_m (mL)	Magnet volume
V_v (mL)	Valve volume
B	Liquid reactant in a thermal decomposition
D	Gaseous product of a thermal decomposition
n_B (mol/L)	Concentration of reactant B
b	Number of moles of product gas D
V_B (mL)	Volume of reactant B
α	Order of reaction

REFERENCES

1. Gumprecht, W.H., "PR-143 - A New Class of High-Temperature Fluids," ASLE Trans., 9, pp. 24-30 (1966).

2. Sianesi, D., Zamboni, V., Fontanelli, R., and Binaghi, M., "Perfluoropolyethers. Their Physical Properties and Behavior at High and Low Temperatures," Wear, 18, pp. 85-100 (1971).

3. Snyder, C.E., Jr., and Dolle, R.E., "Development of Polyperfluoroalkylethers as High Temperature Lubricants and Hydraulic Fluids," ASLE Trans., 19, pp. 171-180 (1976).

4. Snyder, C.E., Jr., Gschwender, L.J., and Tamborski, C., "Linear Polyperfluoroalkylether-Based Wide-Liquid-Range High-Temperature Fluids and Lubricants," Lubr. Eng., 37, pp. 344-349 (1981).

5. Jones, W.R., Jr., Johnson, R.L., Winer, W.O., and Sanborn, D.M., "Pressure Viscosity Measurements for Several Lubricants to 5.5×10^8 Newtons per Square Meter (8×10^4 psi) and 149° (300 °F)," ASLE Trans., 18, pp. 249-262 (1975).

6. Jones, W.R., Jr., and Snyder, C.E., Jr., "Boundary Lubrication, Thermal and Oxidation Stability of a Fluorinated Polyether and a Perfluoropolyether Triazine," ASLE Trans., 23, pp. 253-261 (1980).

7. Gumprecht, W.H., "The Preparation and Thermal Behavior of Hexafluoropropylene Epoxide Polymers," presented at the Fourth International Symposium on Flourine Chemistry, Estes Parks, CO, July 1967.

8. DuBoisson, R.A., and Sellers, S.F., "Some Subtle But Significant Differences Among Perfluoropolyether Vacuum Pump Fluids," _Microelectronic Manufacturing and Testing_, July 1986.

9. Sianesi, D., Pasetti, A., Fontanelli, R., and Bernardi, G.C., "Perfluororpolyethers by Photooxidation of Fluoro-olefins," _Chim. Ind. (Milan)_, 55, pp. 208-221 (1973).

10. Ohsaka, Y., "Recent Advances in Synthetic Lubricating Oils. (8). Perfluorinated Polyethers," _Petrotech (Tokyo)_, 8, pp. 840-843 (1985).

11. Jones, W.R., Jr., Bierschenk, T.R., Juhlke, T.J., Kawa, H., and Lagow, R.J., "The Preparation of New Perfluoroether Fluids Exhibiting Excellent Thermal-Oxidative Stabilities," NASA TM-87284 (1986).

12. Fowler, L., and Trump, W.N., "A Recording Tensimeter and Decomposition Temperature Detector," _Analysis Instrumentation_, Vol. 7, B. Connelly, L. Fowler, and R. Krueger, eds., ISA, pp. 141-144 (1969).

13. Blake, E.S., et al., "Thermal Stability as a Function of Chemical Structure," J. Chem. Eng. Data, 6, pp. 87-98 (1961).

14. Jones, W.R., Jr., "Friction, Wear, and Thermal Stability Studies of Some Organotin and Organosilicon Compounds," NASA TN D-7175 (1973).

15. "Vapor-Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope," ASTM Standard D-2879-75, 1980.
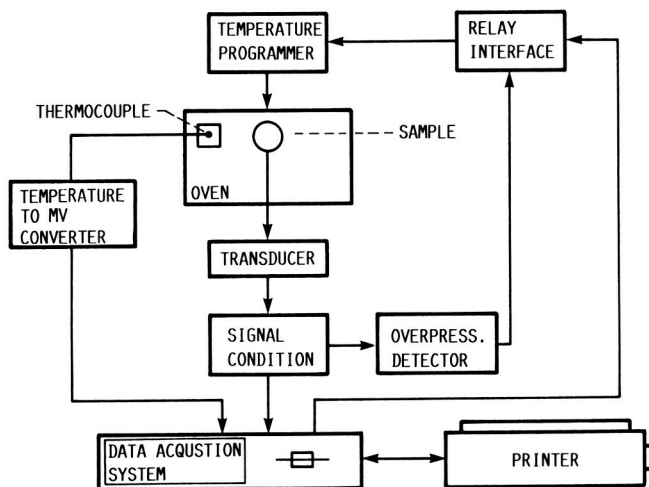
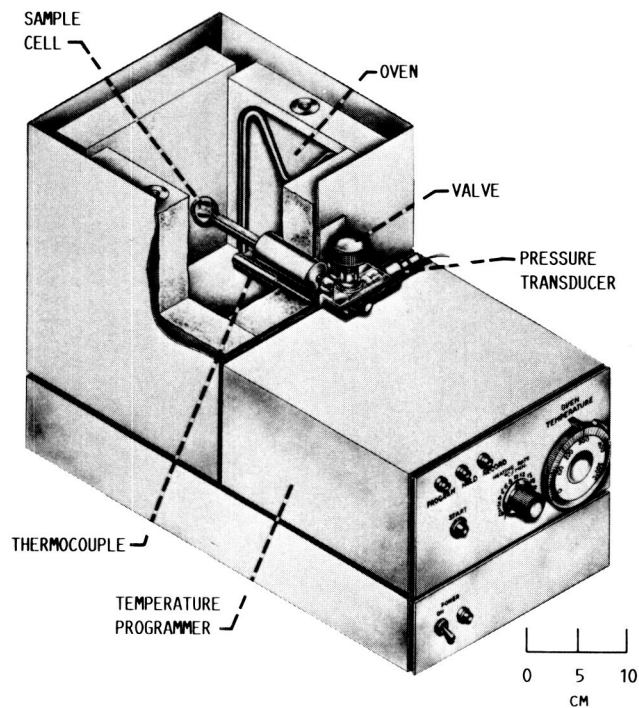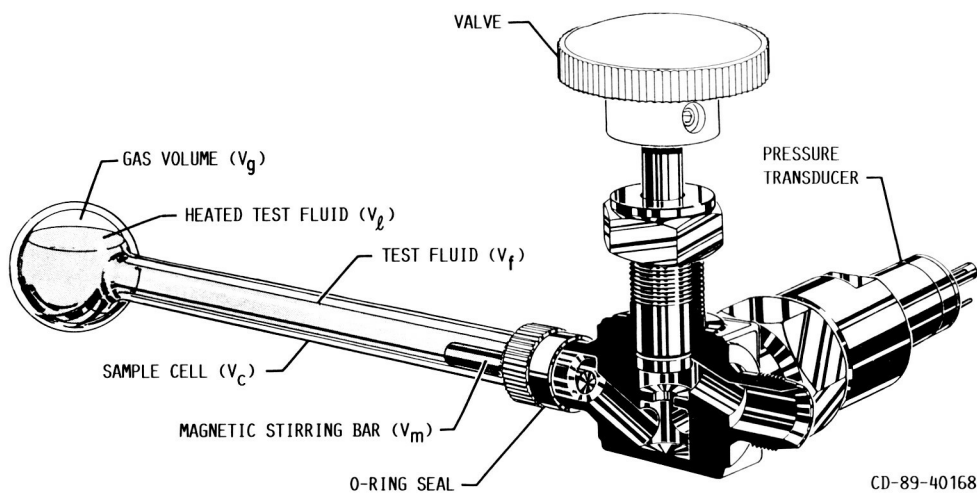FIGURE 1. - A SCHEMATIC DIAGRAM OF COMPUTERIZED TENSIMETER.

FIGURE 2. - TENSIMETER.

FIGURE 3. - CELL ASSEMBLY DURING TEST.

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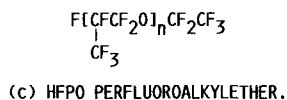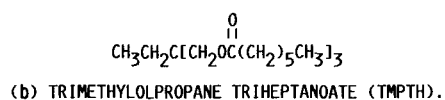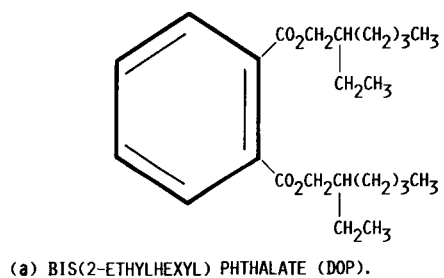27

(a) BIS(2-ETHYLHEXYL) PHTHALATE (DOP).

$$CH_3CH_2C[CH_2OC(CH_2)_5CH_3]_3$$

(b) TRIMETHYLOLPROPANE TRIHEPTANOATE (TMPTH).

$$F[CFCF_2O]_nCF_2CF_3$$
$$CF_3$$

(c) HFPO PERFLUOROALKYLETHER.

FIGURE 4. - CHEMICAL STRAUCTURES OF THE TEST FLUIDS.
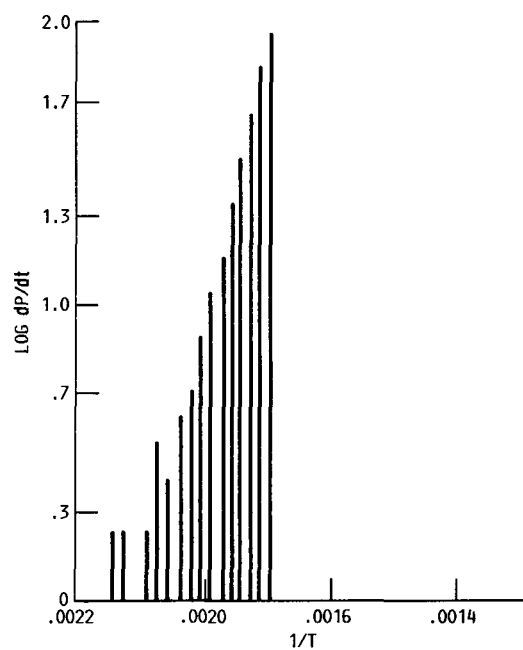
NUMBER	TEMPERATURE, °C	dP/dt	LOG(dP/dt)	TOTAL P, TORR
1	240.7	1.731	0.2383	30.56
2	245.0	1.731	.2383	37.48
3	249.8	1.000	.0000	42.68
4	255.0	1.731	.2383	50.47
5	259.6	3.462	.5393	60.85
6	265.1	2.596	.4144	74.70
7	270.2	4.327	.6362	95.48
8	275.4	5.193	.7154	120.58
9	280.2	7.790	.8915	156.93
10	285.2	11.252	1.0512	205.40
11	290.6	14.714	1.1677	277.25
12	295.4	22.504	1.3522	377.25
13	300.3	32.025	1.5055	516.14
14	305.1	45.875	1.6615	712.62
15	310.3	66.648	1.8237	988.74
16	315.5	88.287	1.9459	1379.11

FIGURE 5. - THERMAL DECOMPOSITION DATA FOR BIS(2-ETHYLHEXYL) PHTHALATE.

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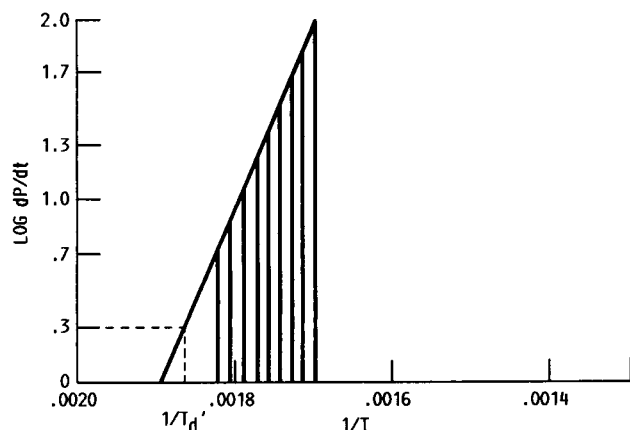
NUMBER	TEMPERATURE, °C	dP/dt	LOG(dP/dt)	TOTAL P, TORR
1	275.4	5.193	0.7154	120.58
2	280.2	7.790	.8915	156.93
3	285.2	11.252	1.0512	205.40
4	290.6	14.714	1.1677	277.25
5	295.4	22.504	1.3522	377.65
6	300.2	32.025	1.5055	516.14
7	305.1	45.874	1.6615	712.62
8	310.3	66.648	1.8237	988.74
9	315.5	88.287	1.9459	1379.11

SLOPE = -9957
Y-INTERCEPT = 18.87
T_d' = 263.08 °C = 536.2 K.
E' = 45.56 KCAL/MOL = 190.6±6.3 KJ/MOL.

FIGURE 6. - TYPICAL THERMAL DECOMPOSITION CURVE, LOGARITHM OF RATE OF VAPOR PRESSURE RISE AS A FUNCTION OF RECIPROCAL OF ABSOLUTE TEMPERATURE. FLUID: BIS(2-ETHYLHEXYL) PHTHALATE.
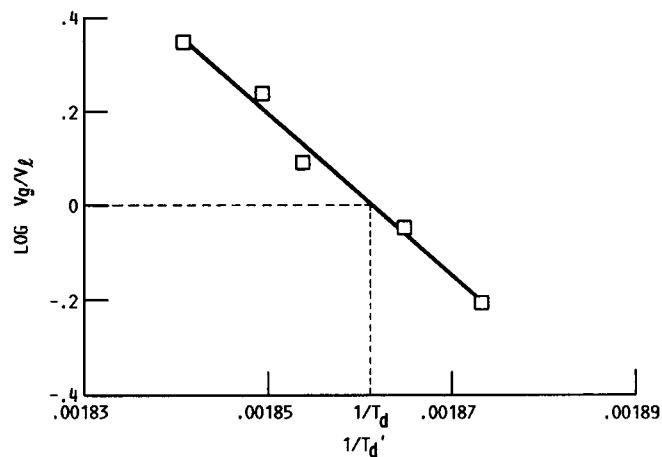

FIGURE 7. - DETERMINATION OF T_d FOR BIS(2-ETHYLHEXYL) PHTHALATE. LIT. T_d = 263.3±2 °C;

EXP. T_d = 264.2±2 °C (537.4 K), E = 329±23 KJ/MOL; COR. COEF. = 0.986.
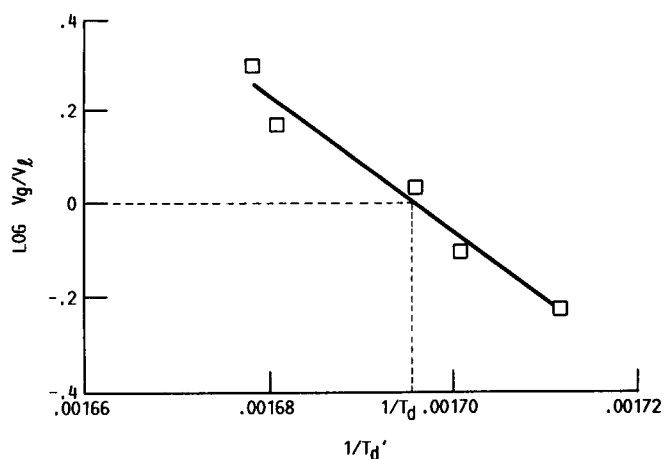
FIGURE 8. - DETERMINATION OF T_d FOR TRIMETHYLOLPROPANE TRI-HEPTANOATE. LIT. T_d = 317.2±2 °C; EXP. T_d = 316.7±2 °C (589.9 K), E = 283±31 KJ/MOL; COR. COEF. = 0.964.
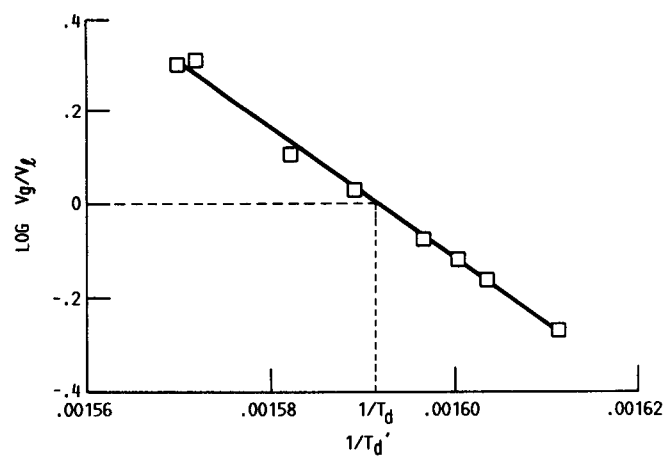

FIGURE 9. - DETERMINATION OF T_d FOR HFPO PERFLUOROALKYL-ETHER. EXP. T_d = 355.2±2 °C (628.4 K),

E = 269±9 KJ/MOL; COR. COEF. = 0.994.

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16. Abstract

A computerized tensimeter and experimental procedure for determination of the thermal decomposition temperature (T_d) of perfluoroalkylethers have been developed and tested. Both the apparatus and the procedure are described in detail. Results of testing with bis(2-ethylhexyl) phthalate and trimethylolpropane triheptanoate demonstrate that the reciprocal of the decomposition temperature is a linear function of the logarithm of the gas volume/heated liquid volume ratio. The T_d obtained for each compound at a gas volume/heated liquid volume ratio of one was similar to the value previously reported using an isoteniscope technique. Results of testing with a polymer of hexafluoropropylene oxide demonstrate that this instrument and procedure can be used to determine the T_d of perfluoroalkylethers.

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