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FLAMMABILITY LIMITS OVER LIQUID SURFACES

James T. Dehn

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A test is described for determining the flammable limits of liquid fuels and for rating the relative effectiveness of soluble inerting agents. This "layere cup" test resembles the widely used tube flame-propagation test in certain respects and differs from it in others. It requires simple equipment and is especially suited to liquid fuels which are more difficult to handle in the tube flame-propagation experiment than gases. It brings out explicitly the role played by relative volatilities in the case of inerting agents in

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20. Abstract (Continued)

flammable liquids. Comparisons with tube flame-propagation results and the results of standard flash point methods are made. Possible mechanisms are also discussed.

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I. INTRODUCTION

A large body of literature exists on the ability of various inhibitors or inerting agents to suppress combustion in gaseous fuel-air-inhibitor mixtures and the field has been surveyed many times[1].* A widely used test for gases refined by the Bureau of Mines[2,3] determines the flammability limits of fuels in air (or other oxidizer) as well as the change of these limits with a number of factors. One of these factors is the addition of inert gases, and the volume per cent of inert which forces the rich and lean limits to meet in a non-flammable mixture is called the peak percentage. Since no homogeneous fuel-air mixture can support flame propagation under the specified conditions if it contains this much or more inert, the peak percentage can be taken as a measure of inhibiting power. Other tests such as reduction in flame speed or extinguishment of burner flames are also commonly used[1]. The addition of fire retardants to solids has recently become an intensely studied subject. A great variety of tests have been developed and reviewed in the literature[4]. A relatively neglected field is the addition of inhibiting agents to liquids in spite of the wide use and known dangers of flammable liquids. Since the pioneering paper of Burgoyne and Williams-Leir[5] the number of reports on this subject has been surprisingly small. Part of the reason perhaps is the fact that experiments with the gaseous state are easier to interpret and the knowledge gained there is applicable in part to fires involving the liquid or solid state. This is because almost all combustion occurs in the vapor phase. However, liquids and solids have their own problems centered largely around the vaporization (with possible decomposition) and mixing of fuel and oxidizer.

It is the main purpose of this report to describe an experimental procedure which may be used to study the inhibition of flammable liquids by the addition of non-flammable agents which are soluble in the liquid. This test measures rich and lean flammable limits and gives peak percentages like the gaseous tube flame-propagation test. However, it brings out explicitly the effect of relative volatilities which can change the ranking of agents based on peak percentages as determined in the gaseous or in the liquid state. A secondary purpose of this report is to comment briefly on the possible mechanisms by which inhibitors operate.

II. EXPERIMENTAL ARRANGEMENT AND PROCEDURE

Three cylindrical copper cups were made with diameters of 2.5, 5.1 and 10.2 cm respectively. The cup and bath dimensions of interest are shown in Figure 1. These are the distance, a, from the fuel surface to the lip of the cup, the fuel depth, b, the lip height, c, above the top of the bath, and the diameter d. A constant temperature

*References listed on page 66.

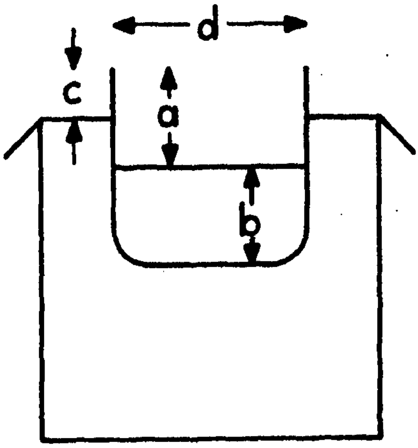

Figure 1. Cross Sectional Drawing of Cup and Bath Used in Layered Cup Experiments

bath (alcohol, water or oil) encloses most of the cup and keeps the temperature of the liquid and of the vapors just above the liquid the same to within a degree or two as determined by scans using a thermocouple connected to a digital readout. The whole apparatus was first cooled below the expected working range, then placed on a controlled heater and warmed at a rate of one degree centigrade per minute. Heating rates faster or slower than this by a factor of two or three did not make an appreciable difference in the results if ignition tests were carried out close to the liquid surface. The heater included a magnetic stirring device, but this was not used since even the slowest stirring speeds obtainable created too much disturbance at the liquid-gas interface. Instead, diffusion and natural convection were relied on to insure liquid homogeneity during an experiment.

A spark apparatus consisting of a 2,500 volt transformer charging a 0.1 microfarad condenser and creating a spark of about 300 millijoules between electrode tips one millimeter apart was used for ignition. Experiments with smaller sparks showed that this was well above the minimum ignition energy of the mixtures used. The electrodes were lowered into the cup to the height desired and sparked every few degrees rise in temperature of the liquid as indicated by a thermocouple tip placed 0.5 centimeter below the center of the liquid surface. By repeating experiments with fresh samples and sparking at temperatures between those of previous experiments accuracy could be improved and limits determined to within a couple of degrees centigrade.

Keeping the distance a in Figure 1 approximately equal to one half of d was found to be satisfactory. If a is much less than one fifth of d the fuel-air mixture is disturbed by slight air currents near the top of the cup. If a is as small as c it becomes difficult to maintain the vapor above the liquid at the same temperature as the liquid. If a is two or three times larger than d it becomes impossible to maintain a fire since the escaping product gases interfere with fresh air intake and the fire is self-extinguishing. This agrees with previous experiments in the laboratory on borderline conditions for sustained fires in which a critical height to diameter ratio, a/d, was found to be about 1.5 for d equal to 5 cm up to 2.5 for d equal to 60 cm for uncovered cups or cylinders. Smaller a/d ratios allow consistent ignition of sustained fires and reproducible results. Experiments showed that the fuel depth b is not critical if it exceeds a centimeter. Neither is the distance c important provided it is not zero or negative. If the cup lip lies below the top of the bath, the air flow is restricted and fires are more difficult to sustain, affecting the results.

Experiments were done by sparking at the liquid surface of pure fuels in the 2.5 cm, 5.1 cm and 10.2 cm diameter cups, keeping the same a/d ratio of 0.5. The 2.5 cm cup gave narrower limits displaced to higher temperatures, while the 5.1 cm and 10.2 cm cups gave identical results within the accuracy of the experiment. This agrees with analogous trends in the tube flame-propagation experiment. There it was found that for common fuels 2.5 cm tubes are too small to give results independent of diameter. However, only slight differences could be detected between the results of experiments in tubes 5.1 cm in diameter or larger. The Bureau of Mines[2-3] has adopted a 5.1 cm (two-inch) diameter tube as its standard. Even though the cup experiment described in this report is considerably different from the tube experiment, a 5.1 cm diameter cup also seems adequate to avoid undue dependence on this geometric factor. It has the further advantage of using less fuel and being less dangerous than a larger cup. Instead of using a special cup and bath it was decided to use the standard Tag Flash Point cup and bath as described in ASTM D56, but without the cover. This copper cup is 5.4 cm (2.125 inches) in diameter and when filled with 50 ml of test liquid gives a distance a of 2.86 cm (1.125 inches) so that the a/d ratio is 0.53. It meets the specifications determined for our experiment and is commonly available in other laboratories for comparison work. For these reasons it was used in all of the experiments described below.

If we spark at various heights above the liquid surface we obtain limit curves like those shown in Figure 2 for methylene bromide in n-octane. When sparking at the surface of a hydrocarbon (Figure 2a) it is possible to distinguish a region of flash-only and a region of sustained fire. The flash-only region is shown by dashed lines while the fire region is shown by solid lines. For pure n-octane the flash-only region lies between 14°C and 20°C. This compares with the standard closed cup flash point of 13.5°C[6] and the Tag open cup value of 22°C[7]. In this experiment we are dealing with something which lies between an open and a closed cup, a deep open cup. It differs from the usual Tag open cup in having the liquid surface 2.5 cm (1 inch) deeper below the lip and in using a spark ignition source at the liquid surface, that is, 2.86 cm below the cup lip instead of a flame ignition source above the cup lip. We will refer to it as a layered cup for reasons we will explain in the next section. For pure n-octane with sparking at the surface the fire region lies between the lean fire limit at 20°C and the rich fire limit at 45°C. As methylene bromide is added the limits approach each other. The flash-only peak percentage occurs at about 4.2 liquid volume per cent while the peak percentage for the fire region occurs at 2.5 per cent. If the sparking is done one centimeter above the liquid surface (that is, 1.86 cm below the cup lip) the flash-only region is hard to delineate and the fire region is shifted to higher temperatures with a peak of 5.5 per cent (Figure 2b). For sparking at two centimeters above the surface (that is 0.86 cm below the cup lip) we see a continued shift to higher temperatures with a further increase in peak percentage to 8.0 per cent (Figure 2c). This behavior is

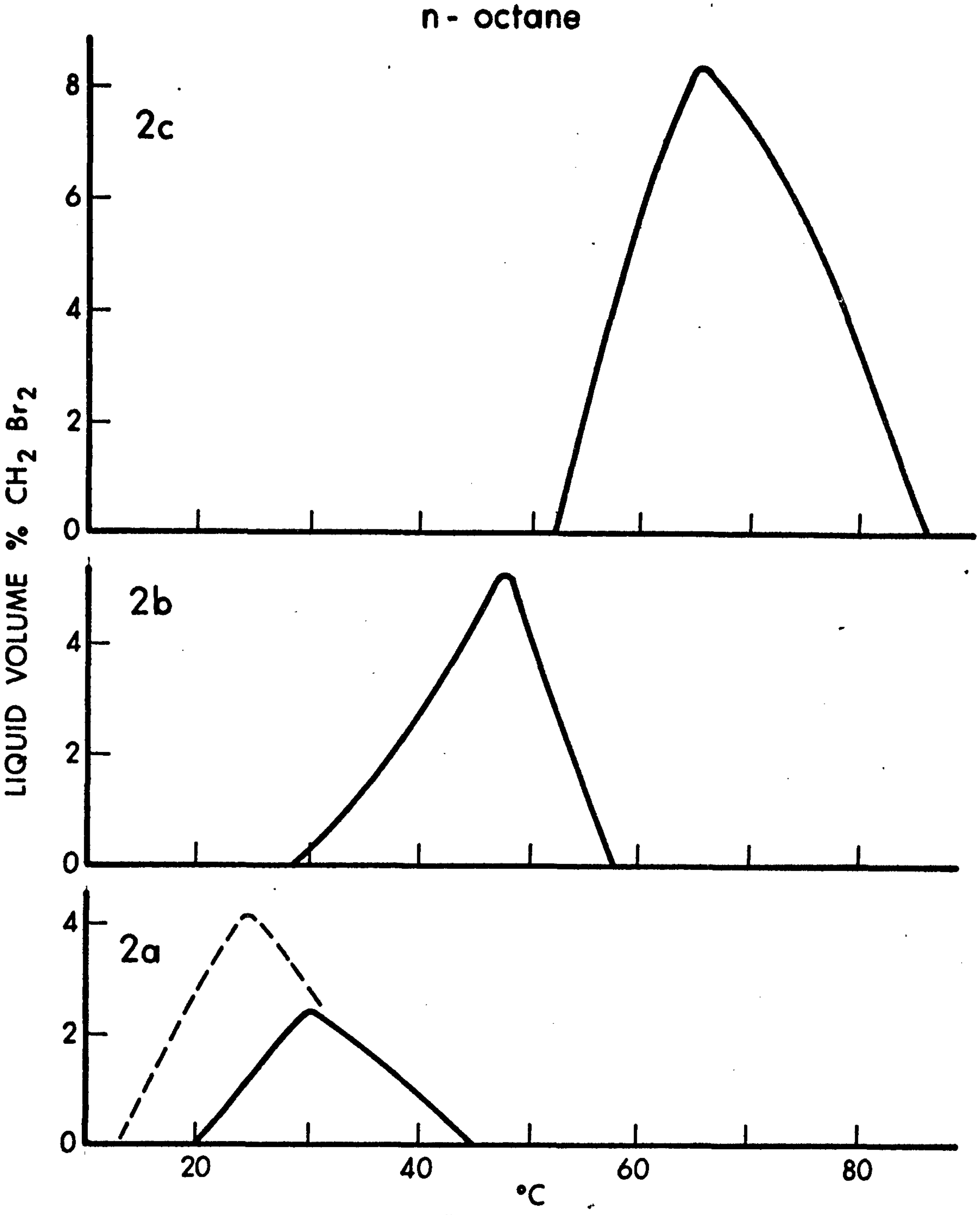

Figure 2. Liquid Flammability Curves for n-octane + CH_2Br_2 (Three Heights Above Liquid Surface in Layered Cup).

understandable because of the stratified or layered nature of the fuel-air mixture above the liquid. If sparking is done at or above the top of the cup it becomes harder to obtain consistent lean limits and very difficult to determine the rich limits. At the top of the cup gentle air currents (measured to be about 2 cm/sec) introduce too many uncertainties into the experiment. In addition, temperature differences between the vapor and the liquid and variations in diffusion and gravitational effects for different fuels and inhibitors make it difficult to interpret results found by sparking well above the liquid surface. Although such results could well be of practical importance, we will confine our attention here to results obtained by sparking at the liquid surface (2.86 cm below the cup lip) unless otherwise noted.

Several other procedures were adopted as standard. For example, care was taken to blow out of the cup the combustion products which remain after a flash or fire before proceeding to the next spark test at a higher temperature. Another procedure followed was scanning by raising rather than by lowering the temperature. Both methods seemed to give the same results within the accuracy of the experiment, provided sparking was done at the liquid surface where time and distance factors in the approach to a steady state are of minimal importance, so that the results depend essentially only on the liquid temperature. A third procedure adopted was leaving the cup uncovered throughout the test. Keeping the cup covered until a spark test was made gave the same results as leaving it uncovered, provided sparking was done at the liquid surface. Finally, the change in composition of binary liquid mixtures over the course of a temperature scan was determined by measuring the density before and after (with the liquid restored to its original temperature of $20^{\circ}C$). The composition change was typically about a tenth of a per cent. This is not surprising since the experiments were usually conducted well below the boiling points of the mixtures in reasonably short times of less than an hour.

The chemicals involved were used as received from commercial suppliers except for water which was once distilled. The fuels were ninety-nine per cent purity or better while the inerting agents were generally of ninety-eight per cent purity or better. Exceptions will be noted where appropriate.

III. LAYERING IN THE CUP

Let us consider the case of a pure liquid fuel in the cup experiment we are describing. If x is the mole fraction of fuel in the vapor above the liquid, z is the distance above the liquid surface and t is the time, then in the absence of any bulk vertical motion and under the assumption that the concentration at the surface is the equilibrium gas phase concentration[8] at a given temperature T ($x=x_o(T)$, $z=0$), with no fuel vapor present initially ($x=0$, $t=0$, $z>0$) and none present far from the surface ($x=0$, $z=\infty$) we have the well known solution to the one-dimensional diffusion equation for a semi-infinite medium[8]

$$x=x_o(1 - \mathrm{erf}(z/\sqrt{4Dt})) \tag{1}$$

where D is the binary diffusion coefficient of fuel in air, taking air to be a single component. This expression is too simple to give an adequate representation of the fuel vapor distribution in our cup which is of finite height with gentle air currents dispersing fuel vapors above it. Non-zero initial concentrations and gravitational effects are just two of the factors not represented in this model. Still, equation (1) can give us a qualitative model of the manner in which the fuel vapor is stratified in space and time. Obviously if we wish to minimize this dependence on space and time and study ignition as a function of liquid temperature only, we should conduct our tests as close to the surface as possible.

If we take the data of Figure 2 for pure n-octane, convert liquid volume fractions to liquid mole fractions and use the known[21] vapor pressure versus temperature relationship, we can find the vapor mole fractions of n-octane at the liquid surface for any temperature. The values we shall use are $x_o(20^\circ C)=.013$, $x_o(45^\circ C)=.050$, $x_o(29^\circ C)=.024$, $x_o(58^\circ C)=.072$, $x_o(52^\circ C)=.066$ and $x_o(85^\circ C)=.270$. If we assume realistic values for the time between tests ($t=120$ sec) and the diffusion coefficient ($D=0.1$ cm^2/sec) then $\sqrt{4Dt} \approx 7$ cm and we can calculate the limits at various heights from equation (1). Table I shows rich and lean limits (x^L and x^R) for the three values of z used in Figure 2. As we see, equation (1) with experimental values of $x_o(T)$ predicts an increase in these limits with height which is especially noticeable between 1 and 2 cm. If $\sqrt{4Dt} = 2$ cm because of smaller D or t, Table I shows us that equation (1) predicts a decrease in both limits with distance. If $\sqrt{4Dt} = 20$ cm because of larger D or t, the increase of the limits with distance is more pronounced than for $\sqrt{4Dt} = 7$ cm.

If the cup was semi-infinite above the liquid surface and we were using flash limits instead of fire limits so air supply was not a problem we might expect the limits to be independent of height. Factors such as the non-zero initial fuel distribution in the cup as well as air dilution and temperature gradients near the top of the cup could well require more fuel at the surface (therefore a higher T and $x_o(T)$) in order to get sufficient fuel for limits at $z=2$cm. This might account for the apparent z dependence of the limits. The question could be settled by direct measurement of fuel concentrations as a function of space and time, but this has not yet been done. At present we are

TABLE I

Lean (x^L) and rich (x^R) limit fuel vapor mole fractions as a function of height above the liquid surface (z) and parameter $\sqrt{4Dt}$ as predicted by equation (1).

		z (cm)		
$\sqrt{4Dt}$ (cm)		0	1	2
7	x^L	.013	.020	.046
	x^R	.050	.060	.186
2	x^L	.013	.012	.011
	x^R	.050	.044	.043
20	x^L	.013	.023	.059
	x^R	.050	.068	.240

not in a position to judge the inadequacy of equation (1) or the manner in which our model should be corrected. Simple assumptions about bulk fluid motion or non-zero initial concentrations have been tried and do not improve the model.

Unpublished observations have been made in this laboratory[10] in a tube much taller than our cup where it is possible to reach a condition in which a flame can propagate from a lean mixture well above the liquid surface and die out before reaching the surface because of the richness of the mixture near the surface. However, this does not seem to occur over distances as small as 2 cm with the fuels we are using. This additional factor of a flame having to propagate through a rich mixture in order to establish itself on the liquid surface is also difficult to assess without further study. Our main purpose in this section is to point out some of the factors which can be important in the cup experiment. These become negligible if we spark at the liquid surface.

IV. A COMPARISON WITH A TUBE FLAME-PROPAGATION EXPERIMENT

It is worthwhile comparing this layered cup experiment with the tube flame-propagation experiment. In the tube we have a flame front propagating through a homogeneous gaseous mixture involving heat generation by the flame and heat losses dependent chiefly on gas parameters in a suitably wide tube. In the cup we have a flash in a pre-mixed, stratified vapor followed by a stationary diffusion flame. Heat is generated by the flash and the flame while heat losses depend not only on gas properties but also on liquid parameters (assuming minimal dependence on geometrical and wall factors).

If we compare the results of these two experiments we obtain Figure 3. Figure 3a shows the liquid volume per cent of bromochloromethane (BCM) in methyl ethyl ketone (MEK or 2-butanone) required to form a flammability limit curve in the cup experiment. MEK has no flash-only region, just a fire region. The temperature range involved is -13°C to 13°C with the peak percentage equal to 16.5. If we use the known vapor pressure versus temperature curves to calculate the volume percentages of BCM and MEK in the air at the liquid surface, we obtain the lower curve in Figure 3b which peaks at about 2% BCM. Superimposed on this curve is the curve obtained by Zabetakis[3] which peaks at about 7% BCM. The lean limits (1.3% and 1.9% MEK in air) of the two experiments are closer than the rich limits (8% and 10%). If we had chosen to spark higher above the liquid surface we might have improved agreement in the peak percentages. However, there is not much point to forcing agreement for one parameter in one case. If we did, then other parameters such as rich and lean limits and other fuel-inert

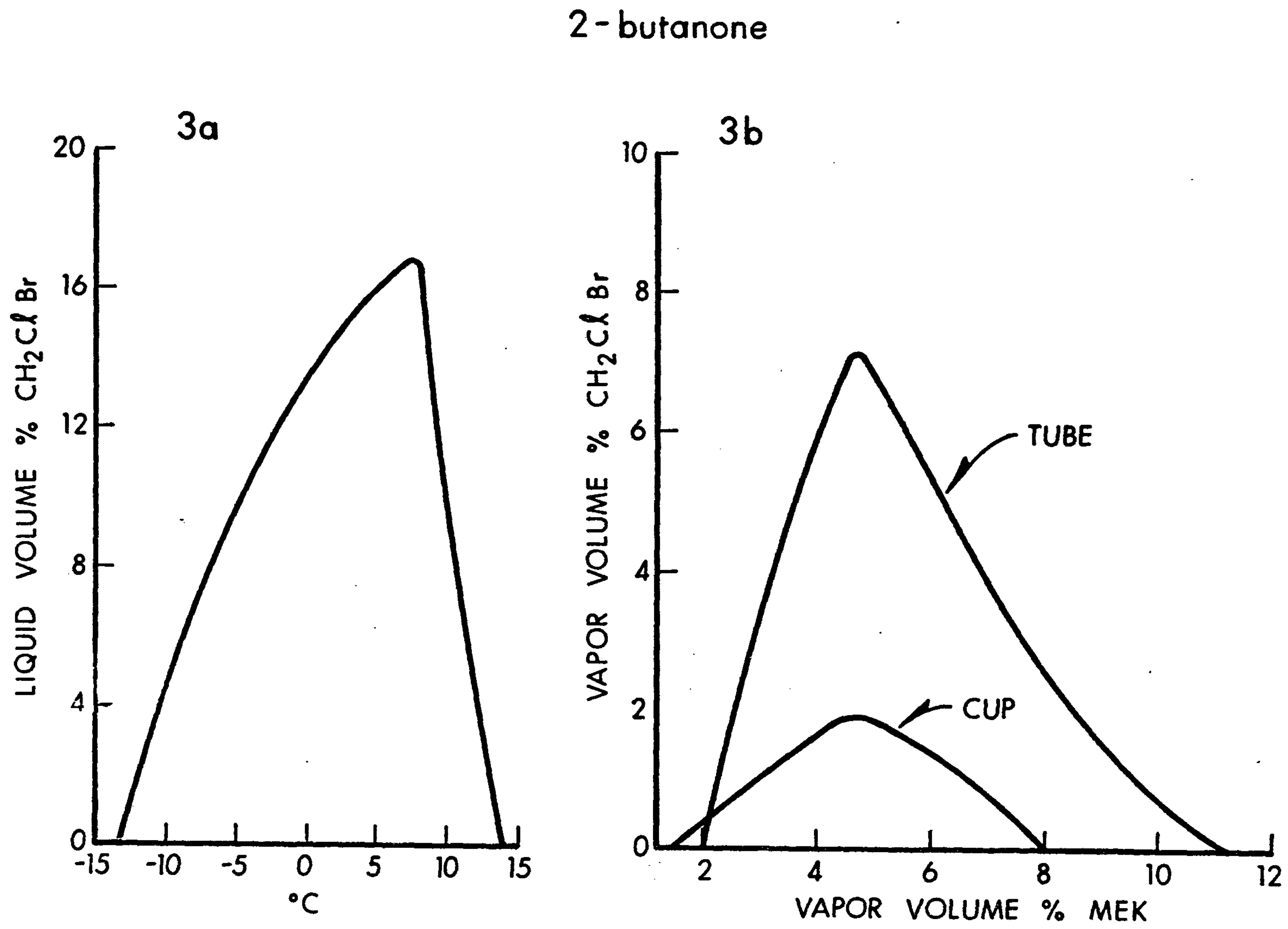

Figure 3. Liquid and Vapor Flammability Curves for Methyl Ethyl Ketone + CH_2ClBr.

combinations would not necessarily give agreement between tube and cup experiments under similar conditions.

It would seem wise to keep in mind the differences between the cup and tube experiments as well as their similarities. Besides the ones already mentioned, we note that every point on the lower curve in Figure 3b represents a different temperature (in the range -13°C to 13°C) while every point on the upper curve corresponds to 25°C. Other differences depending on departures from Raoult's law and so characteristic only of the cup experiment will be discussed later in this report together with similarities and differences in interpretation. We compare these curves here in order to point out the fact that there are differences as well as similarities between the two experiments.

V. ALCOHOLS

Let us begin to illustrate the use of this layered cup experiment with the lighter alcohols as fuels since both water and many inert halogenated hydrocarbons are completely soluble in these materials. For these alcohols it is not possible to observe a flash-only region. Figure 4 plots the temperature of the liquid mixture versus the liquid volume percentage of three non-flammable materials dissolved in methanol (boiling point 64.6°C), giving flammability limit curves. Methylene bromide (boiling point 98.2°C) appears to be more than twice as effective as water (boiling point 100°C) on a peak percentage basis, although large percentages of both are required to render the liquid mixture non-flammable since both are involatile compared to methanol. The difference is due not just to the slightly greater volatility of methylene bromide but includes contributions from a number of other factors. These will be discussed in section VIII of this report. The curve for methylene chloride (boiling point 40.1°C) has a lower peak percentage than that for methylene bromide showing that it is more effective for methanol in this experiment on a liquid peak percentage basis. This is due to its greater volatility since chlorinated compounds are usually poorer inhibitors than brominated compounds of the same type in a homogeneous gaseous mixture[11].

Let us calculate the percentages of fuel and inert which exist in the vapor phase just at the liquid surface. In order to do this let us assume that the binary mixtures involved behave ideally and follow Raoult's law. This is probably not a bad assumption as we can judge from various pieces of experimental evidence. For methanol-water mixtures vapor-liquid equilibrium curves have been determined[12-13] for all compositions at the boiling point of the mixtures and calculations show that Raoult's law is followed fairly closely over most of the composition

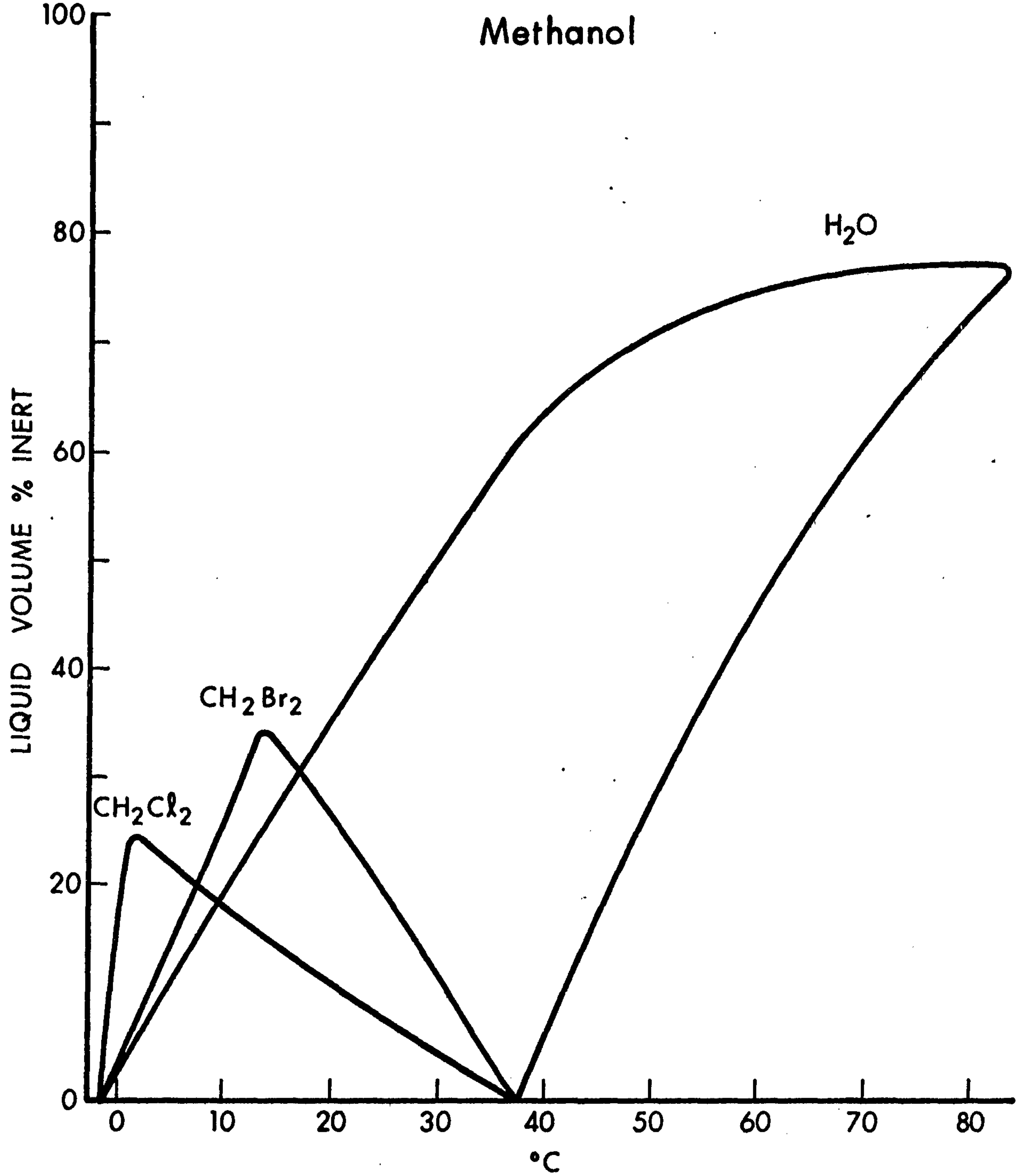

Figure 4. Liquid Flammability Curves for Methanol + Three Inerts.

range we are interested in even at temperatures which are higher than those we are interested in. Although there are no experimental measurements at lower temperatures such as we are concerned with, the expectation is that Raoult's law will be closely obeyed here also. Similar experimental evidence is also lacking for methylene bromide-methanol and methylene chloride-methanol. However, it is known[14] that methylene bromide-methanol does not form an azeotrope while methylene chloride-methanol exhibits only a slight positive azeotrope (boiling point 37.8°C) near ninety per cent methylene chloride, well beyond our region of interest. Consequently, we do not expect any large departures from ideal behavior especially at the temperatures and compositions of interest to us. Furthermore, the effects of slight differences for diffusion coefficients in air-methanol atmospheres are minimized by sparking at the liquid surface.

Under these assumptions we may use the known vapor pressure versus temperature curves of these compounds to transpose the data of Figure 4 and replot it as Figure 5 which shows the volume per cent of methanol in the vapor at the liquid surface versus the volume per cent of inert in the vapor at the surface, giving flammability limit curves. The volume per cent of air is then 100% minus the sum of the two previous percentages. In Figure 4 there was a difference between the two halons and water in that water raised both lower and upper limits on a temperature scale while the halons raised the lower limit and lowered the upper limit. In Figure 5 for the vapor phase where combustion occurs it is clear that all three non-flammable materials decrease the upper limit on a fuel volume percentage scale.

In Figure 5 we see that 44% water is needed (near 80°C) to make the limits meet. A second water-methanol curve determined by Zabetakis[3] in a tube experiment is also shown for comparison. This curve happens to have about the same peak percentage but with every point on the curve corresponding to an initial homogeneous mixture at 100°C. The tube peak percentage of course depends on initial temperature. The numbers from 50°C to 80°C on the cup experiment curve indicate how different points on this curve correspond to different temperatures. These temperatures do not increase monotonically from left to right since the original data in Figure 4 is double-valued in the ordinate because of the increase of both limits on the temperature scale. The pure methanol limits in the cup experiment are 4% and 34% while in the tube experiment they are closer to 6% and 37%, at least at 100°C.

The peak percentage for methylene chloride in Figure 5 is about 3% (at 1°C) while for methylene bromide it is about 0.8% (at 13°C). Methylene bromide now appears to be more effective in the vapor phase than methylene chloride or water in agreement with tube experimental results. Its apparent ineffectiveness relative to methylene chloride

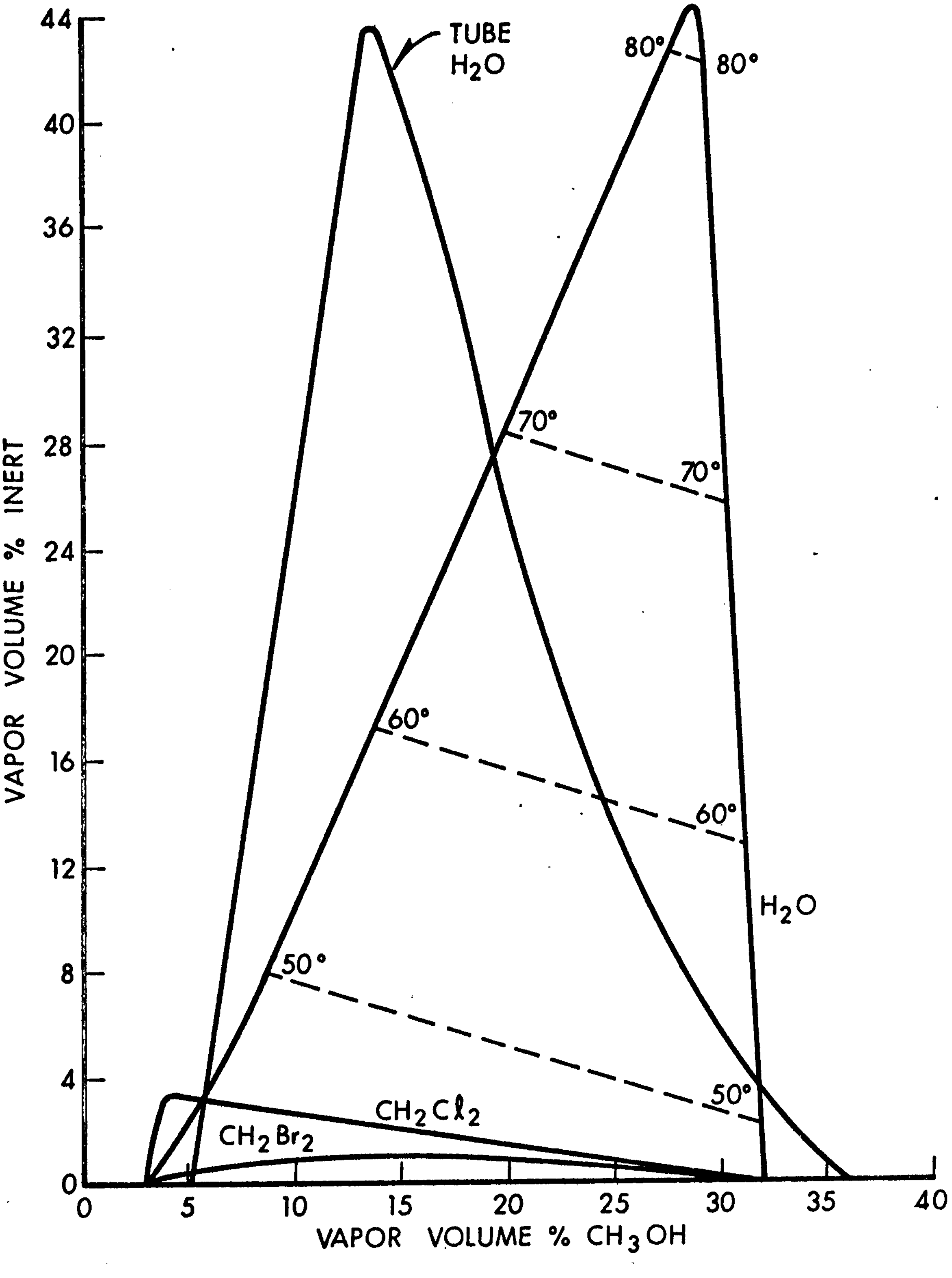

Figure 5. Vapor Flammability Curves for Methanol + Three Inerts.

in Figure 4 is due to its lack of volatility. Its effectiveness relative to water in the vapor phase is also considerably disguised in Figure 4 by the difference in peak temperatures (13°C versus about 80°C). This results in much less methylene bromide present at the peak than water since they have approximately the same vapor pressure at a given temperature. Figure 5 shows that methylene bromide is fifty times as effective as water in the vapor phase, on the basis of peak percentage, for this cup experiment. This is suggestive of a direct (chain-breaking) or indirect (blanketing) chemical mechanism which probably accompanies the effects of dilution and changes in the liquid and vapor properties of the system. Further discussion of this point will be deferred until section VIII of this report.

Figure 6 shows data similar to Figure 4 but for ethanol (boiling point 78.5°C), while Figure 7 gives data for 1-propanol (boiling point 97.4°C). The curve for an additional halon, bromoform (boiling point 149.5°C) is not shown to avoid crowding since it lies only slightly below the curve for methylene chloride. However, data for a very high flash point (221°C) silicone fluid, Dow Corning 704, is shown for comparison with water. At the temperatures used the silicone acts chiefly as a diluent in the liquid phase.

In Figure 6 methylene bromide appears to be more effective than methylene chloride, even before transposing to a vapor phase plot resembling Figure 5, since ethanol is not as volatile as methanol. Moreover, both halons are more effective than water. The same can be said of Figure 7 with bromoform being more effective than water in spite of its lack of volatility. A trend to lower methylene chloride and methylene bromide peak percentages can also be observed as we proceed from methanol to ethanol to propanol as we might expect because of the decreasing volatility of the fuels. The same is not true of water which seems to have a rising peak percentage for the three alcohols despite the decreasing fuel volatility relative to water. Another fact to be noted is the kink which develops in the water curves for ethanol and propanol at about 10-20% water. Both of these observations can be related to the non-ideal behavior of water-ethanol and water-propanol mixtures. Water-methanol mixtures behave approximately ideally and do not form an azeotrope. However, water-ethanol exhibits a slight azeotrope boiling at 78.2°C near 4 weight per cent water, while water-propanol has a strong azeotrope which boils near 88°C at about 29 weight per cent (about 59 mole per cent) water[14].

Liquid-vapor equilibrium curves have been determined for water+propanol by Fowler and Hunt[15] and for water+methanol in the work already referenced[12-13] at the mixture boiling points. Figure 8 replots their data as volume percentages of water in liquid and vapor for ease in comparing Figures 4 and 7. From these latter figures

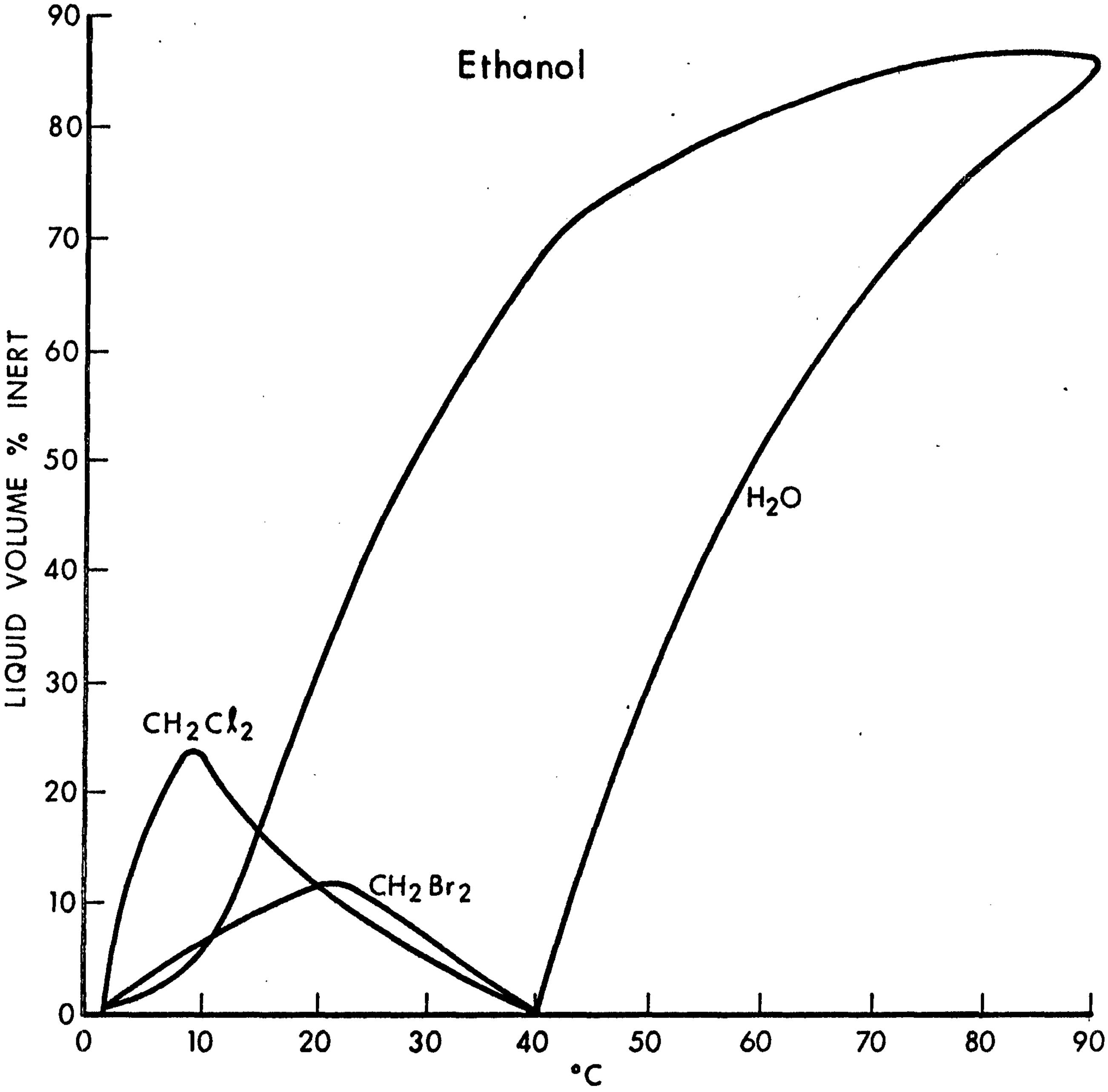

Figure 6. Liquid Flammability Curves for Ethanol + Three Inerts.

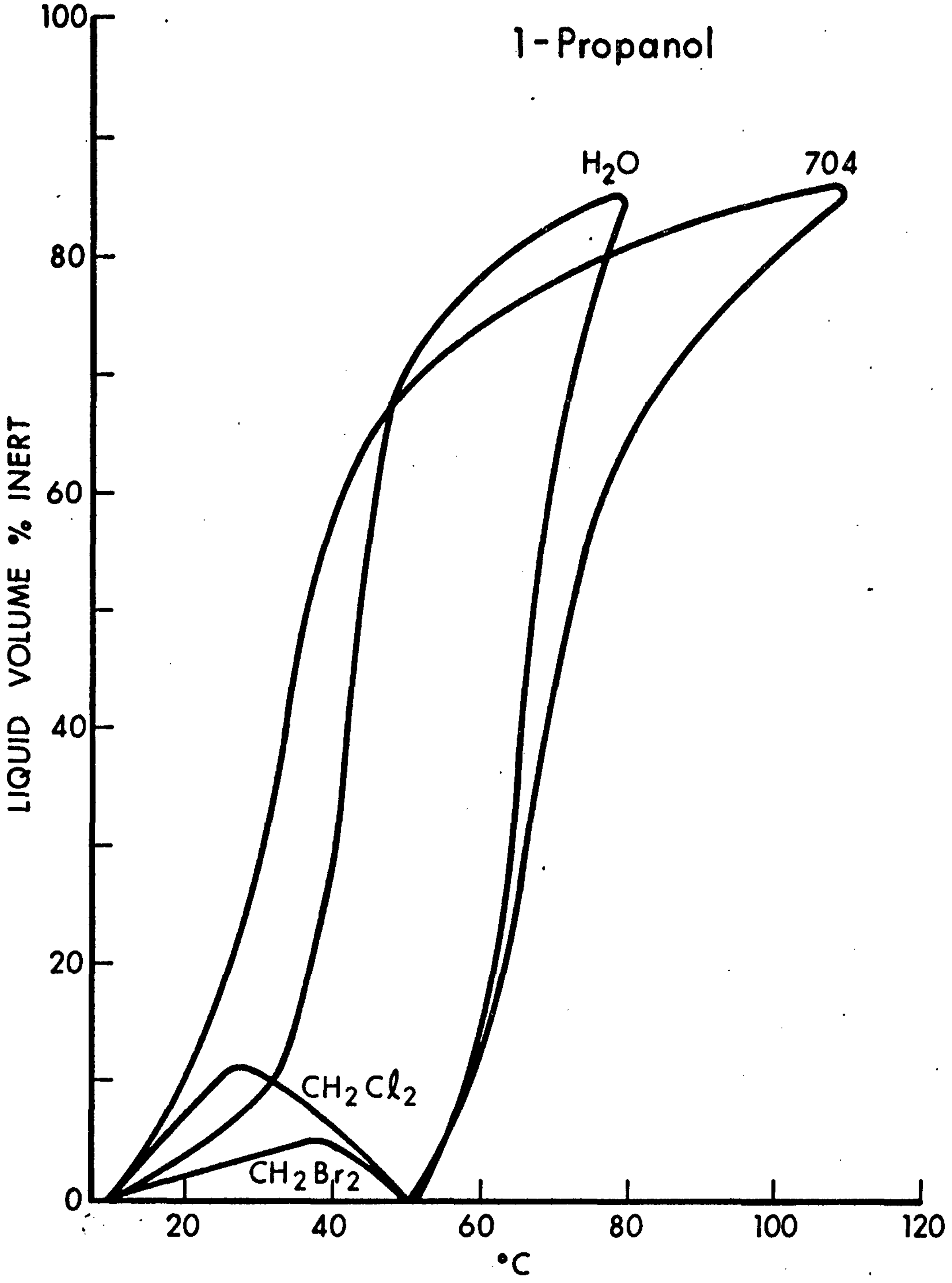

Figure 7. Liquid Flammability Curves for 1-Propanol and Four Inerts.

it is clear that in the range 0-10 liquid volume per cent water, the lower limit of methanol is not increased as much as the lower limit of propanol. This of course is expected since the temperatures in the methanol case are lower and water is much less volatile than methanol although water closely matches propanol in volatility. In Figure 8 we see that 10 volume per cent water in methanol gives only 6% in the vapor at the mixture boiling point. However 10% water in propanol gives about 44% water in the vapor when the mixture is boiling in the 95-100°C range. In the 5-30°C range as in Figures 4 and 7 the differences will not be as great but should be in the same direction. This is also suggested by the vapor pressure versus temperature curves for water, for propanol and for the azeotrope of the two given on page 319 of reference 14.

If we refer again to Figure 7 we see that at about 20 volume per cent liquid water a kink occurs in the curve (a change in the slopes of both limits) and further addition of water is not as effective as it was at lower percentages. This corresponds to the flattening out of the water + propanol curve in Figure 8. By contrast the more constant effect of additional water on the methanol limits evident in Figure 4 corresponds to the steadily rising curve in Figure 8. Similar behavior can be noted for the 704 silicone in propanol. The peak percentages for the water + methanol and water + propanol curves in Figures 4 and 7 correspond approximately to the merging of the two curves in Figure 8. Water + ethanol mixtures exhibit an intermediate behavior as shown in Figure 6. Other factors such as the greater heat of combustion of propanol and the preferential loss of methanol as we approach the mixture boiling point are, of course, at work. However, the vaporization properties of these binary mixtures seem to play a dominant role in the shape of these limit curves.

Figure 9 shows the limits for 2-ethoxy-ethanol (boiling point 135°C) and water (a nearly ideal pair) with a peak percentage less than half that for the alcohols given above. This is apparently due mostly to the relative volatilities of this fuel and water. Unfortunately butanol and other less volatile alcohols in the same series are not sufficiently water soluble for comparison. The onset of non-ideal behavior seems to precede insolubility in a series of related mixtures.

The limit curves for bromochloromethane (boiling point 67.8°C) and the alcohols methanol, ethanol and propanol are shown in Figure 10. The effects of relative volatility seem to be quite clear as with the other halons, since departures from ideal behavior are expected to be negligible in the composition ranges considered. Table II summarizes most of the data presented so far for various inerts in simple alcohols.

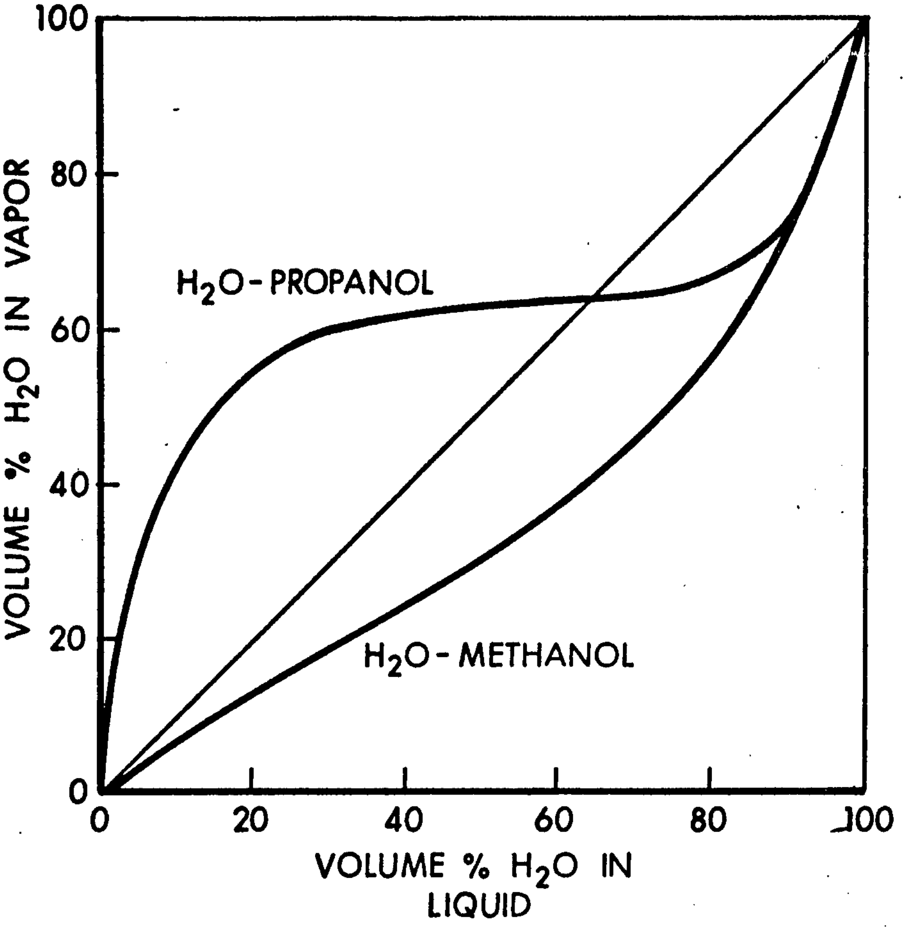

Figure 8. Boiling Liquid-Vapor Equilibrium Curves for Water in Two Alcohols.

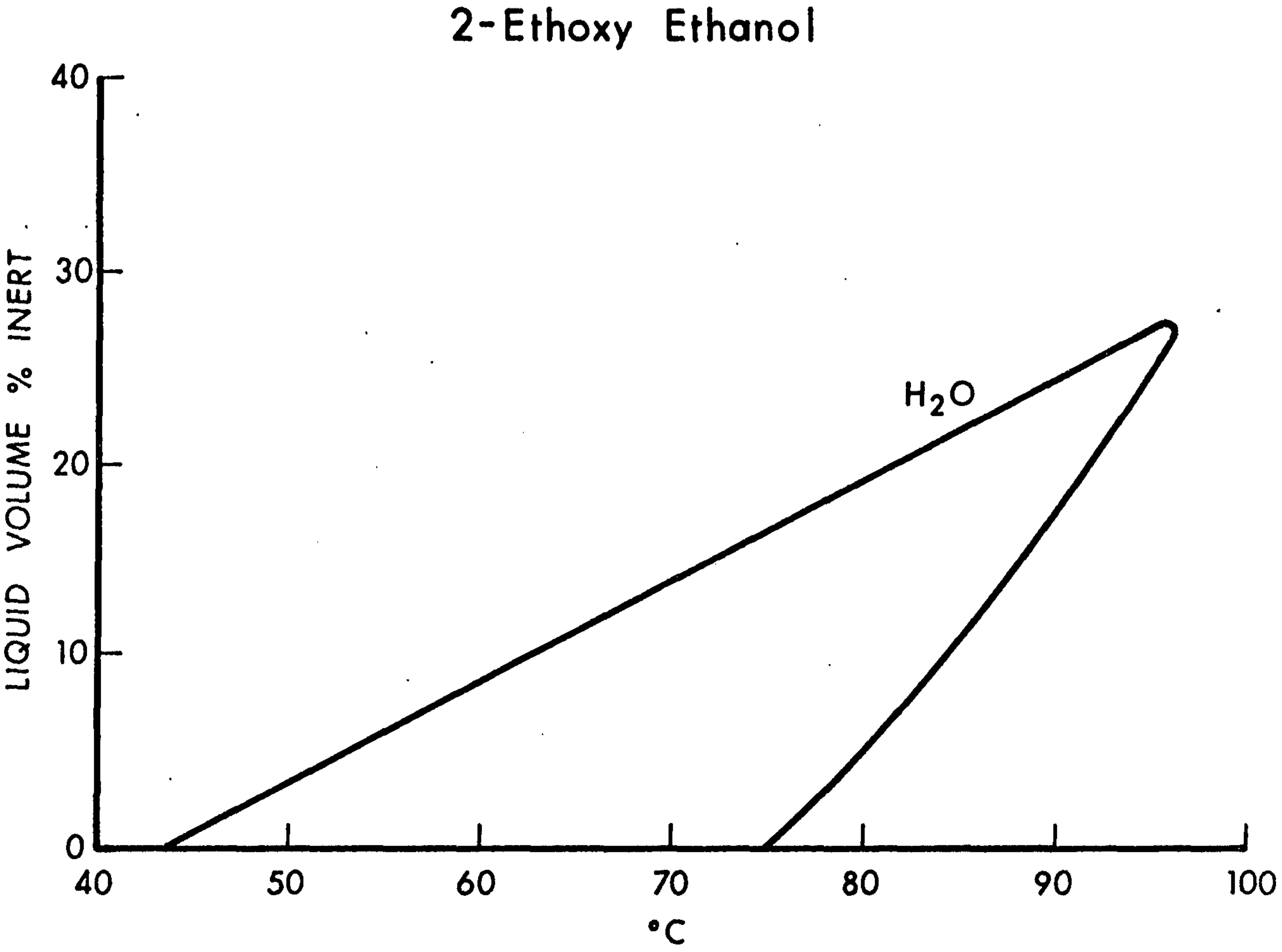

Figure 9. Liquid Flammability Curve for 2-Ethoxy Ethanol + Water.

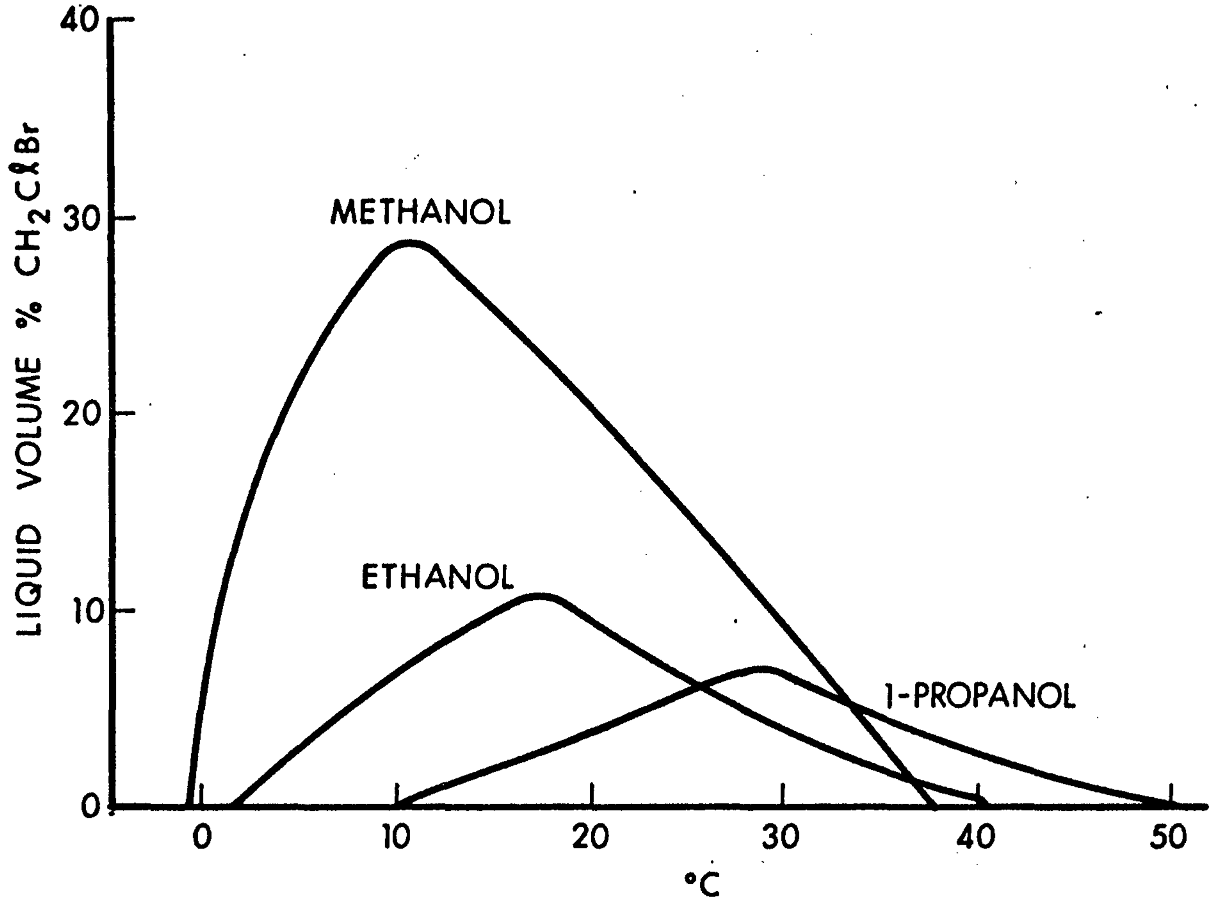

Figure 10. Liquid Flammability Curves for Three Alcohols Containing CH_2ClBr.

TABLE II

Liquid Volume Peak Percentages for Binary Alcohol+Inert Mixtures in the Layered Cup Experiment. Boiling Points (°C) are Given in Parentheses.

		CH_2Cl_2(40.1)	CH_2ClBr(67.8)	CH_2Br_2(98.2)	H_2O(100)
CH_3OH	(64.6)	24	28	35	75
CH_3CH_2OH	(78.5)	22	11	13	85
$CH_3(CH_2)_2OH$	(97.4)	11	6	4	85

VI. HYDROCARBONS

Another class of common flammable liquids is found among the hydrocarbons. Here we will give examples of some normal and branched alkanes selected with a view to illustrating the role of volatility in liquid inhibition. A few simple aromatics are also included in order to bring out a limitation of this technique. With hydrocarbons it is possible to distinguish a flash-only region as well as a fire region, so the data for different inerts in one hydrocarbon will not be superimposed in the same figure in order to avoid confusion.

Figures 11 through 15 give limit curves for n-heptane (boiling point 98.4°C) with four halons and a silicone. Three of these halons have also been studied in n-heptane (at 400-500 mm pressure and room temperature) by the tube flame-propagation technique[11]. The results from the tube experiment are (in vapor volume peak percentages): CH_2Br_2(5.2%), CH_2ClBr(7.6%) and CH_2Cl_2(>11%). Figures 11 through 13 give an order of effectiveness $CH_2ClBr > CH_2Br_2 > CH_2Cl_2$ based on liquid volume peak percentages in the cup. The reversal in order of the two brominated compounds compared to the tube order of effectiveness is due to the greater volatility of CH_2ClBr compared to CH_2Br_2, while the expected poorer performance of CH_2Cl_2 in the vapor phase is only partially compensated for by its volatility which exceeds that of the brominated compounds. If we convert this cup data from liquid volume percentage versus temperature to vapor volume percentages of inhibitor and fuel we obtain agreement with reference 11 in the order of effectiveness. The cup experiment vapor volume peak percentages are: CH_2Br_2 (0.2%), CH_2ClBr(0.3%) and CH_2Cl_2(1.8%). Again the cup peaks are much lower than the tube peaks for halons as we saw in section IV of this report for methyl ethyl ketone. For this reason they are not suitable values for safety purposes in gas phase work. With water in methanol on the other hand (as we saw in Figure 5) the vapor volume peak percentages of the two experiments are roughly comparable. For ethanol somewhat less water (about 38%) is required in the tube experiment[3] than in the vapor phase of our cup experiment (64%) for reasons already partially explained, but the vapor volume peak percentages of the two experiments still do not differ by as much as a factor of two. The sharp order of magnitude difference in the vapor phase peak percentages of the tube and cup experiments in the case of the halons in hydrocarbons and their similarity in the case of water is probably not due entirely to temperature and pressure differences and suggests that a blanketing effect by combustion products at the liquid surface in the cup is occurring for halons and not for water. This opinion is strengthened by observation of a white layer of flash products which hang in the cup in the case of halons and its absence in the case of water. The behavior of the silicone in heptane (Figure 15) is similar to its behavior in propanol (Figure 7 except for the formation of a peak percentage. This will be discussed

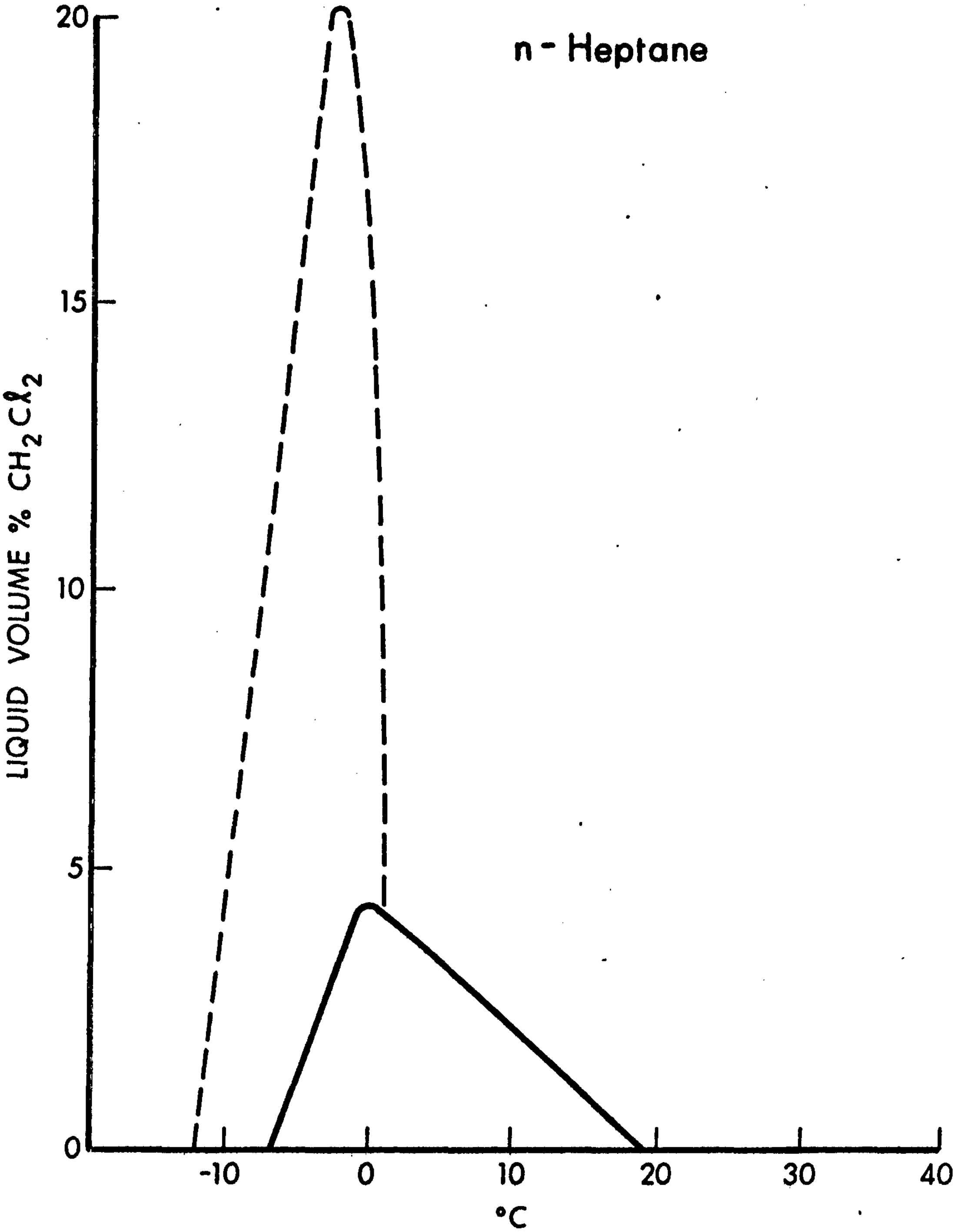

Figure 11. Liquid Flammability Curve for n-Heptane + CH_2Cl_2.

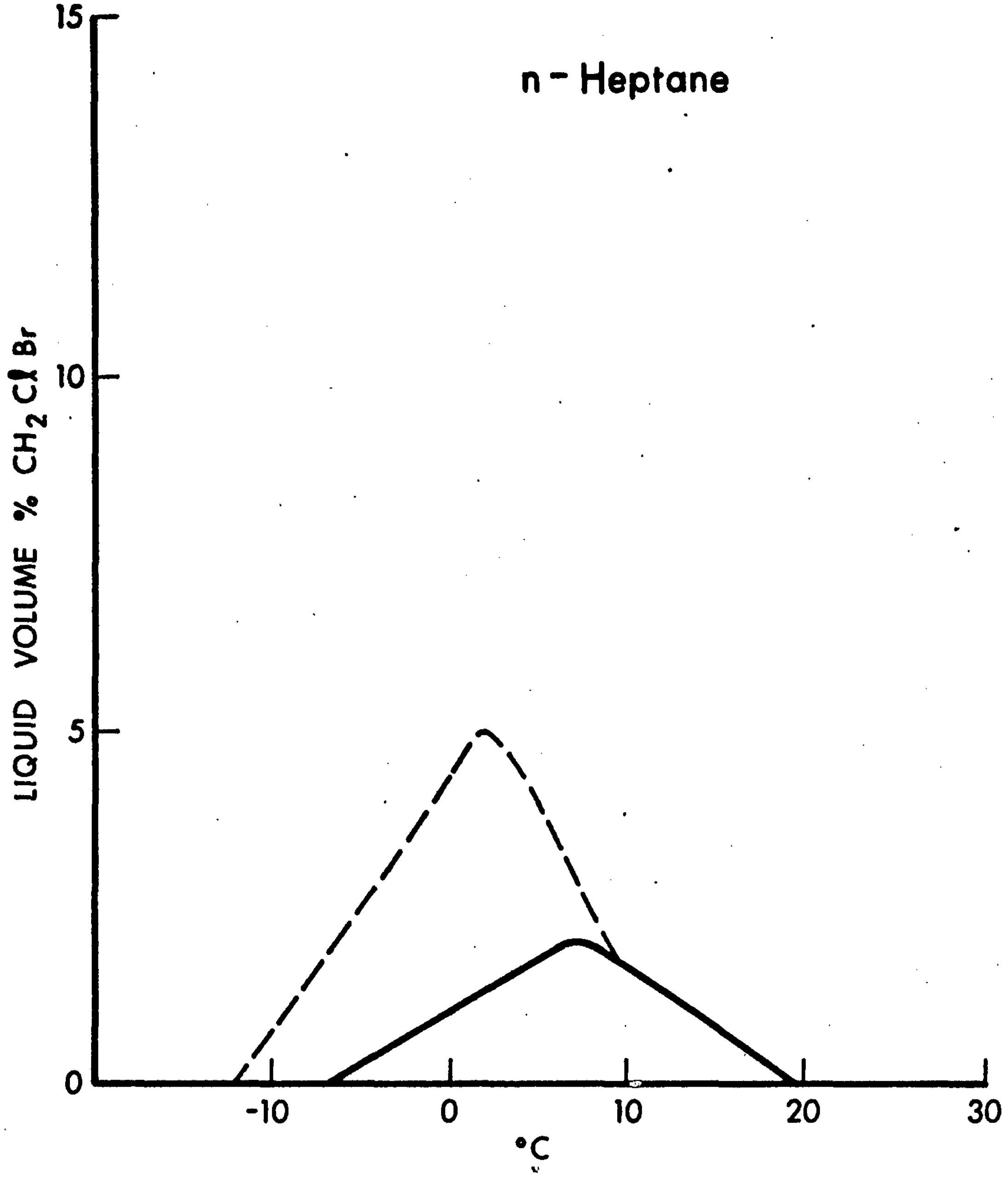

Figure 12. Liquid Flammability Curve for n-Heptane + CH_2ClBr.

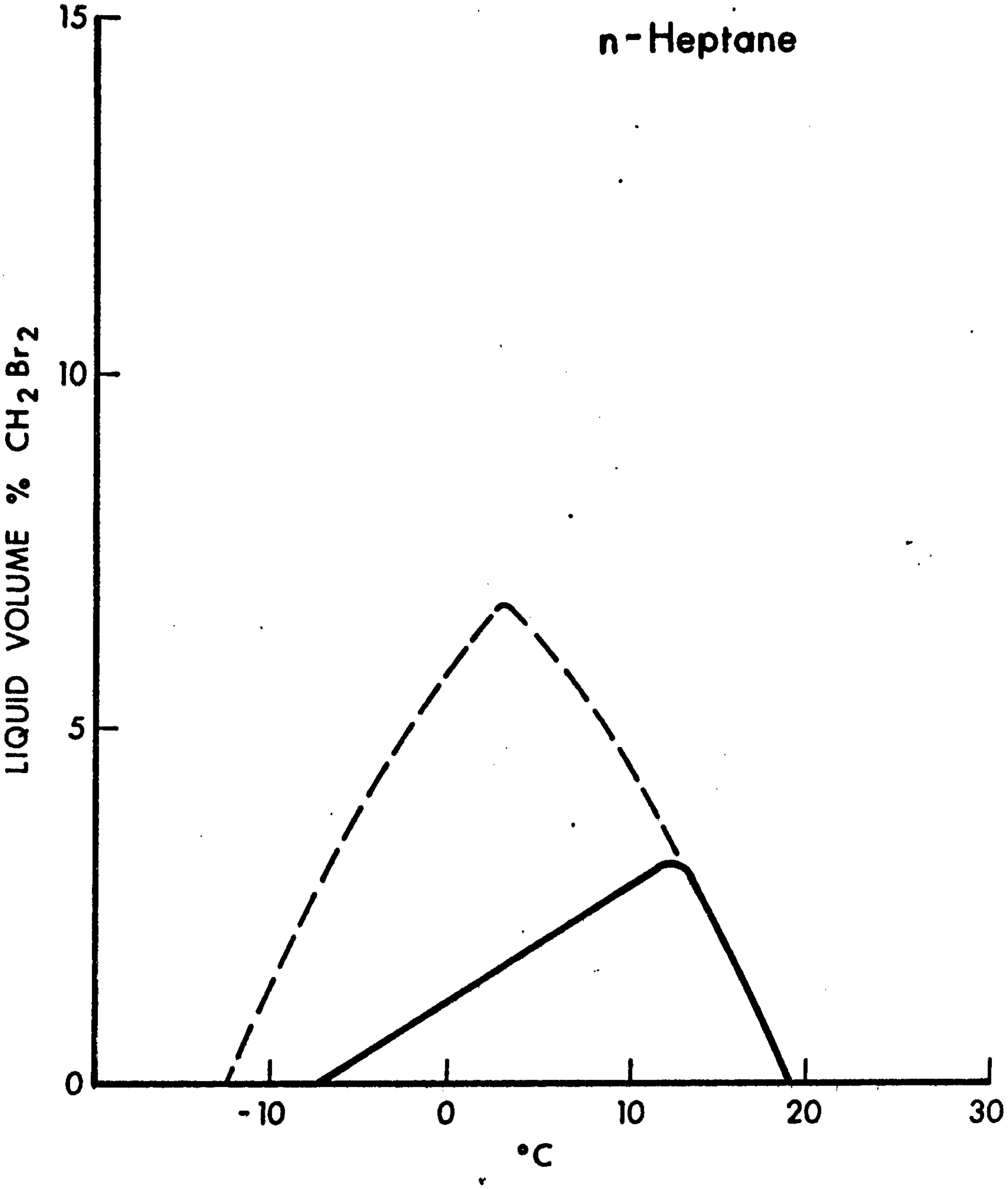

Figure 13. Liquid Flammability Curve for n-Heptane + CH_2Br_2.

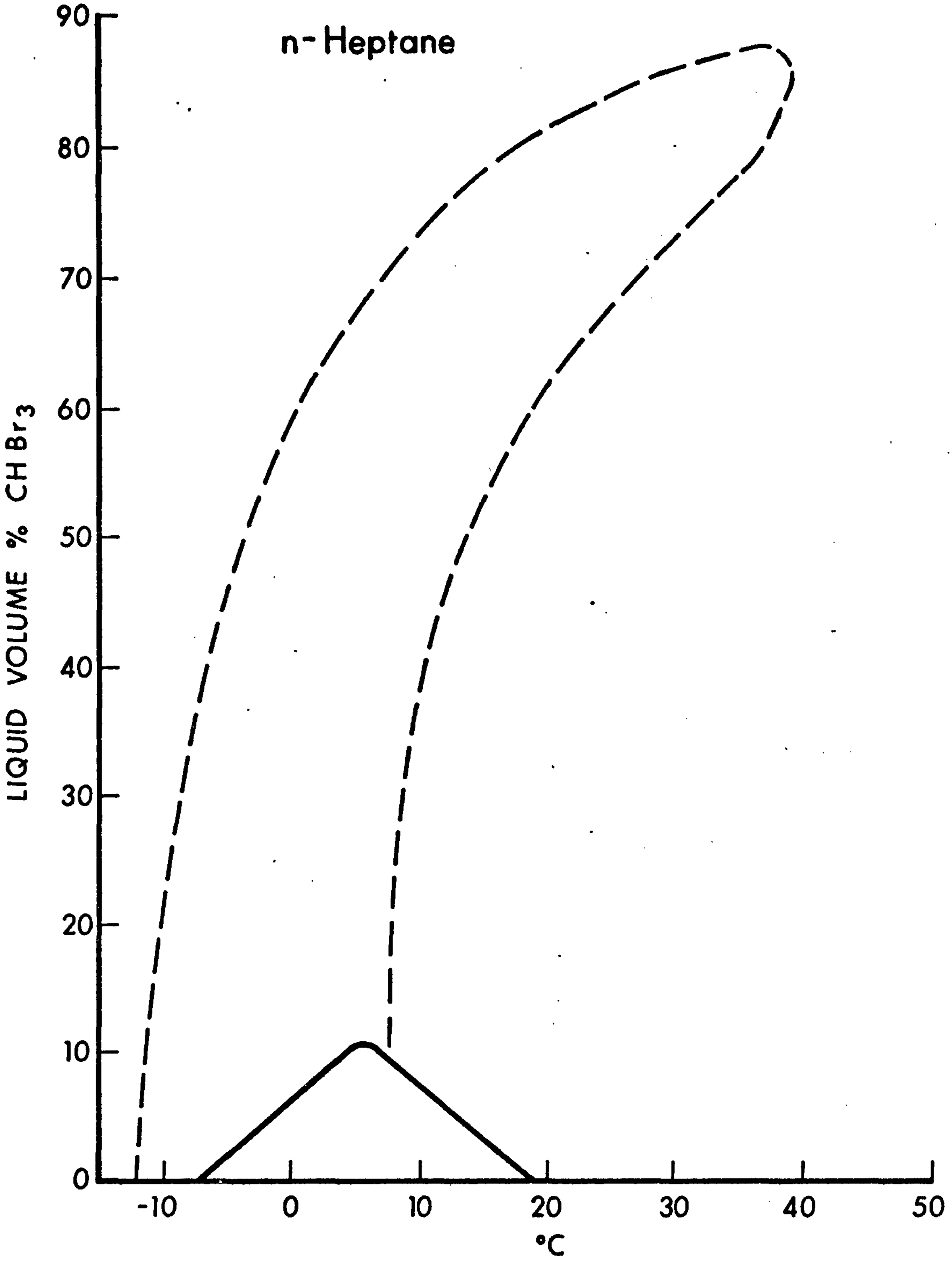

Figure 14. Liquid Flammability Curve for n-Heptane + $CHBr_3$.

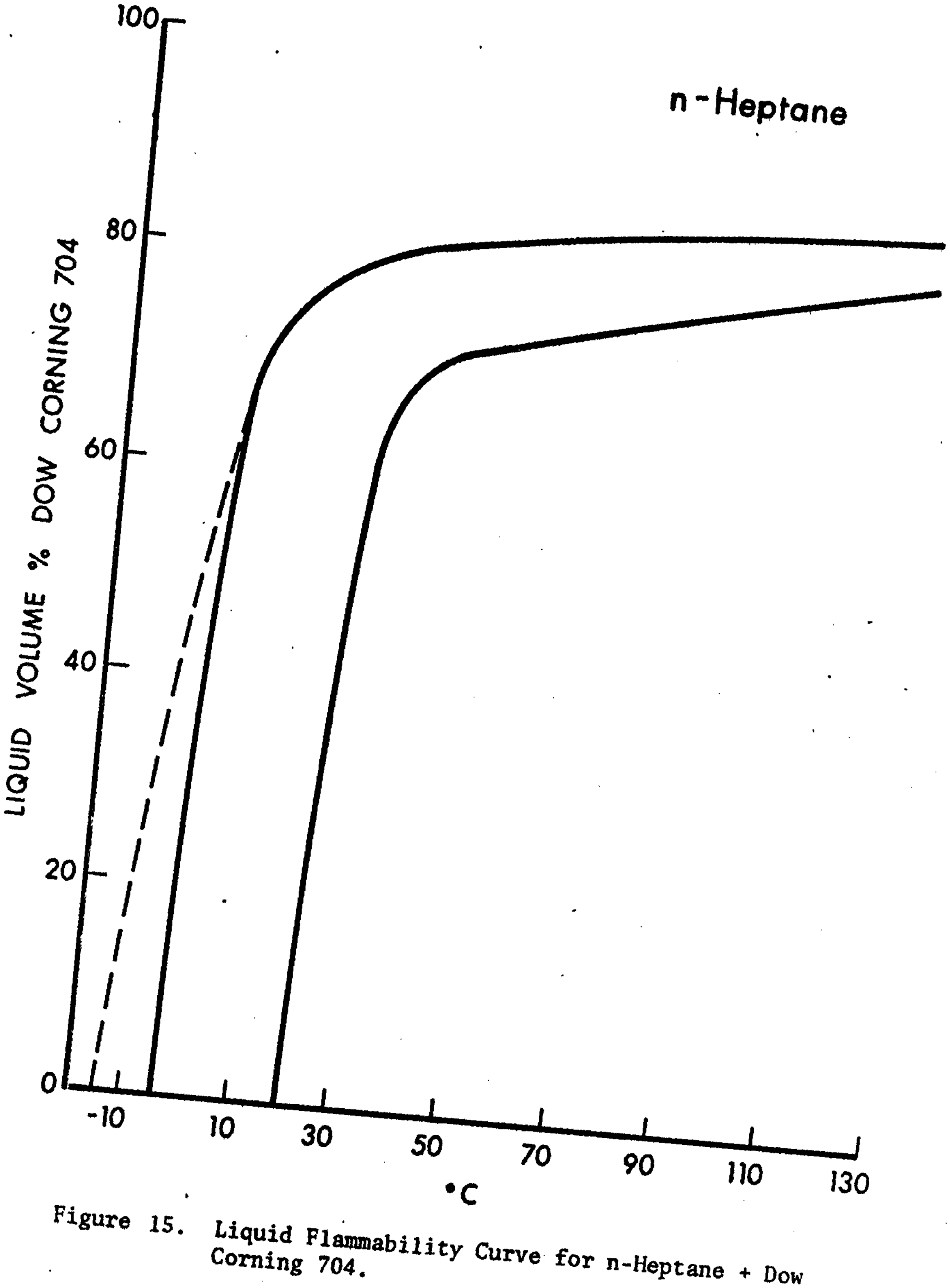

Figure 15. Liquid Flammability Curve for n-Heptane + Dow Corning 704.

further in section VIII of this report.

Figure 16 gives the limit curves for n-octane and bromoform and should be compared with Figure 2a for methylene bromide in n-octane. The fire peak percentages differ by a factor of two as we might expect from a comparison of relative volatilities, but the flash-only peak percentages differ by more than a factor of ten (about 70% for bromoform versus 4% for methylene bromide). If we anticipate a little it is interesting to compare the flash-only peak percentages and fire peak percentages of bromoform (boiling point 149.5°C) in n-decane (boiling point 174°C), n-nonane (boiling point 150.8°C) and n-octane (boiling point (125°C). As we hold the inhibitor constant and vary the fuel, the flash-only peaks progress from 4% to 8% to 70% as the volatility of the fuel becomes approximately equal to and then surpasses the volatility of the inhibitor, while the fire peaks progress from 2% to 3% to 4.5%. Similar behavior is observed if we keep the fuel constant and vary the inhibitor. For n-nonane we have data with carbon tetrabromide (boiling point 189.5°C), bromoform and methylene bromide (boiling point 98.2°C). The flash-only peaks decrease from about 78% to 8% to 3% as the volatility of the inhibitor becomes equal to and then surpasses that of the fuel, while the fire peaks decrease from 10% to 3% to 1.5%. Again these observations are suggestive of fire suppression due partially to a surface blanketing effect by combustion products resulting from a flash in the vapor containing halons. These products do not suppress the flash since they follow it, but they seem to play a role in preventing the transition from flash in the vapor phase to fire anchored over the liquid surface. The importance of having an inhibitor at least as volatile as the fuel is also obvious.

In the case of brominated halons in alcohols a white layer of products is visible after a fire (as has been mentioned) although it is not known whether they are the same as the products formed after halon + hydrocarbon flashes. The lack of an observable flash-only region might be connected with a shorter ignition delay which does not allow time for the formation of a blanket of products to aid in fire prevention. This is not unreasonable in view of the fact that alcohols already contain some oxygen. However, the lower luminosity of alcohol flames might also be a contributing factor, although darkened rooms reveal no flash.

Limit curves for n-nonane are shown in Figures 17 through 19. We note in connection with Figure 19 that carbon tetrabromide is a solid under normal conditions. Small volume percentages in the liquid were measured by weighing the solid and using its known density to calculate the volume. At the higher inert percentages the same procedure was used, but it was necessary to heat the mixture in order to form a solution. Fortunately the temperatures required were lower than the

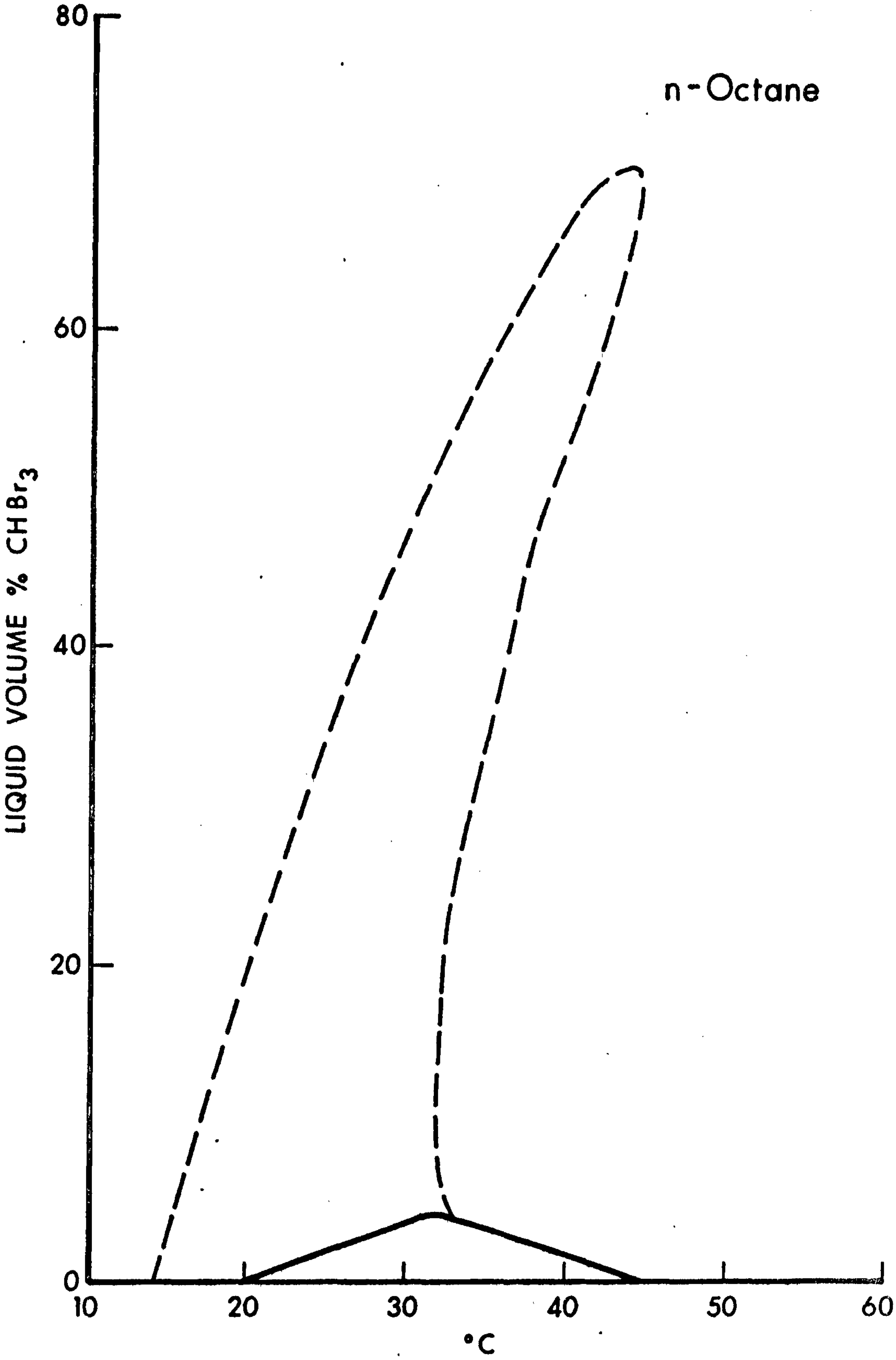

Figure 16. Liquid Flammability Curve for n-Octane + $CHBr_3$.

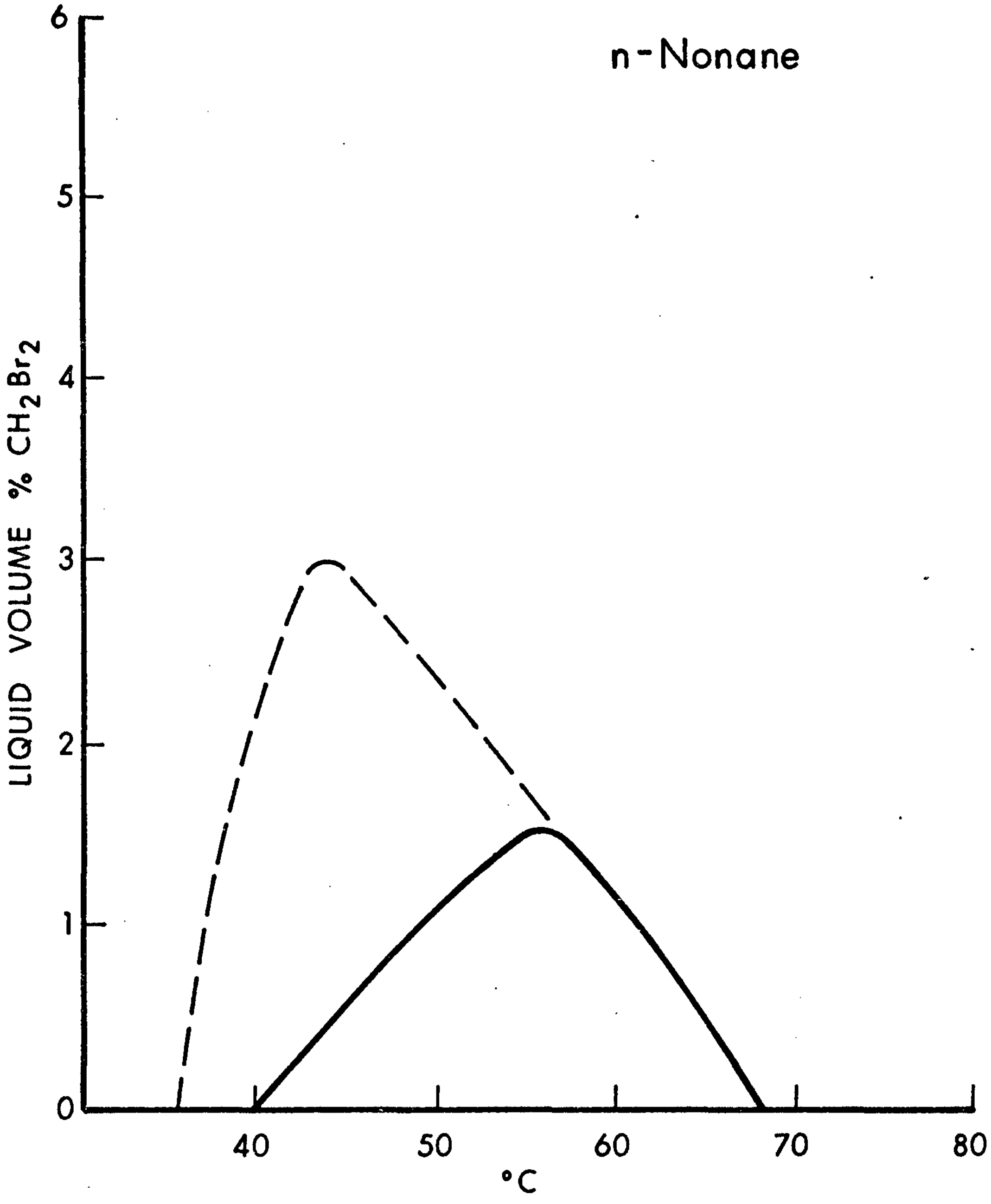

Figure 17. Liquid Flammability Curve for n-Nonane + CH_2Br_2.

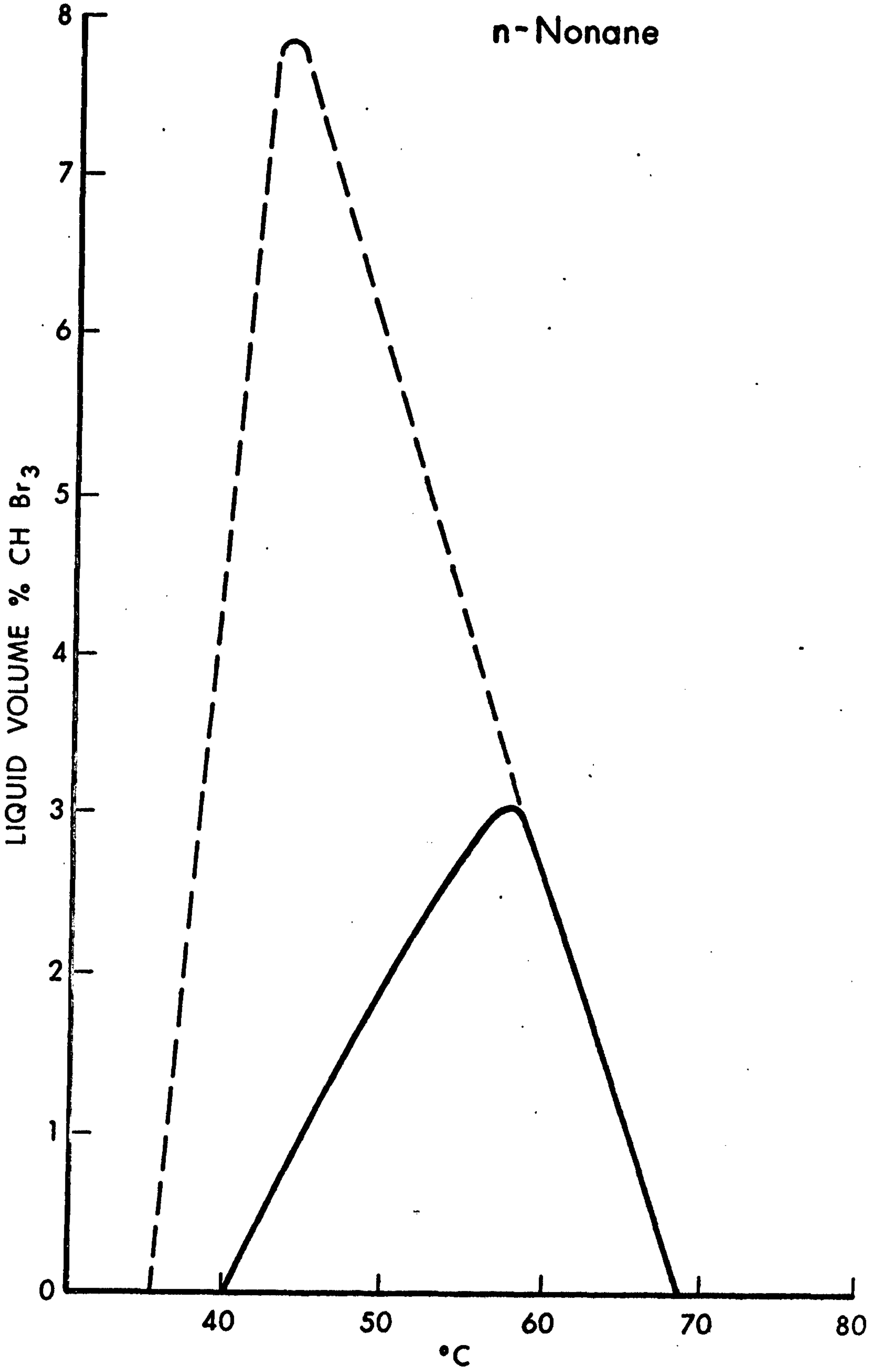

Figure 18. Liquid Flammability Curve for n-Nonane + CHBr$_3$.

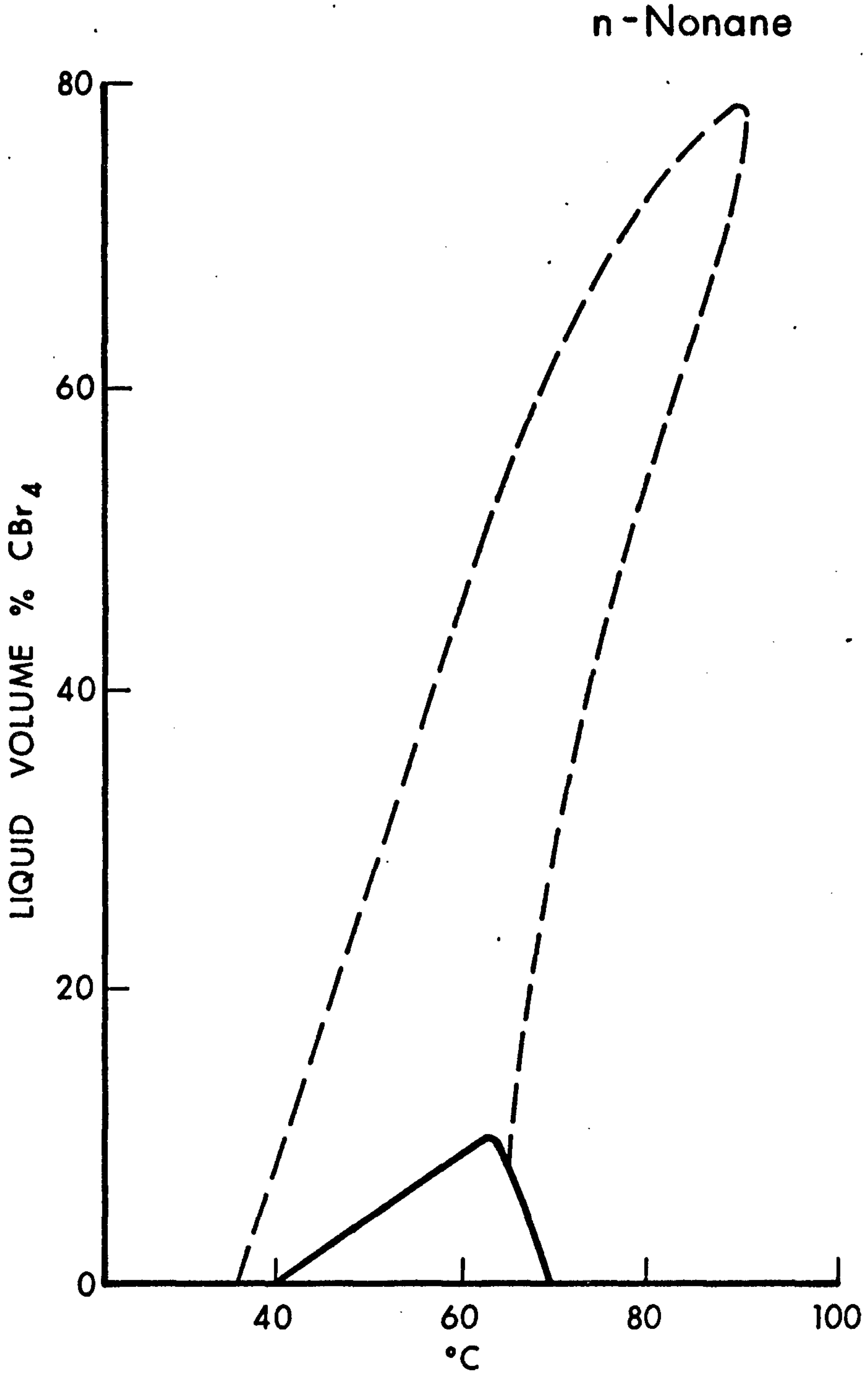

Figure 19. Liquid Flammability Curve for n-Nonane + CBr_4.

lean flash limit. However, the apparent melting point of the sample used was about 50°C in approximate agreement with handbook data[21] for the α phase prior to 1963, but in disagreement with more recent data[21] which gives a melting point closer to 90°C. The probable cause was sample impurity. Still, this did not seem to affect the boiling point of 189.5°C noticeably.

Figures 20 and 21 show limit curves for n-decane. The lean limit fire point for pure decane found here (60°C) is somewhat lower than the value (66°C) found by Roberts and Quince[16] in a similar experiment. This is to be expected however since they sparked 3.5 mm above the liquid surface in a shallow vessel rather than at the surface as we are doing here. Figure 2 shows us how the temperature of the lean fire limit can increase with sparking distance above the liquid surface. The halons in Figures 20 and 21 show the expected small peak percentages since they are both more volatile than decane.

In Figure 22 we see data for methylene bromide in iso-octane (2,2,4-trimethylpentane, boiling point 99.4°C) which suggests that volatility might not be as important as carbon number in this branched-chain example since the peak percentage required (2.2%) is closer to that for n-octane (2.5%, boiling point 125°C) than that for n-heptane (3%, boiling point 98.4°C). However, the differences are not large enough to draw definite conclusions.

Table III summarizes some of the halon-alkane data presented so far. The effects of relative volatilities are clear from a comparison of the rows and columns of Table III. When the fuel and inhibitor are closely matched in boiling point as in the cases of heptane+methylene bromide and nonane+bromoform, three per cent is approximately the peak percentage required for these compounds. This is only slightly lower than that required for the propanol+methylene bromide case (Table II) where the boiling points are also closely matched but the fuel contains some oxygen. In Table III where the percentages of halon are fairly small we do not expect departures from ideal behavior to be significant. Consequently it should not be important to evaluate this effect when transposing liquid volume per cent versus temperature data to volume percentages of fuel and inert in the vapor phase.

In Figures 23 and 24 we see curves for m-xylene (boiling point 139.1°C) and toluene (boiling point 110.6°C) mixed with methylene bromide to give fire peak percentages of 1% and 2%. These ring compounds appear to be slightly easier to inhibit with methylene bromide than straight chain alkanes of comparable volatility, although flash-only peak percentages appear to be higher. The lean limit fire point for pure m-xylene found here (42°C) can be compared to the value of 44°C found by Roberts and Quince[16] who sparked 3.5 mm above the surface instead of at the surface.

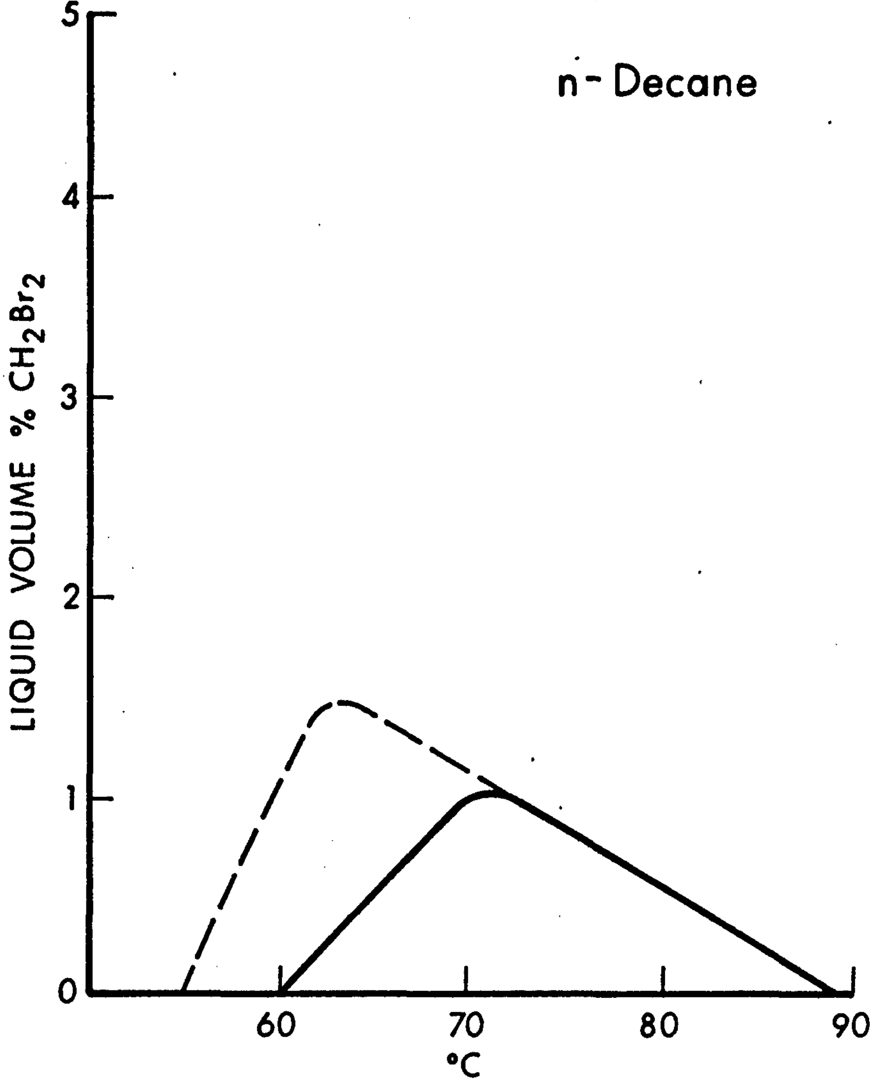

Figure 20. Liquid Flammability Curve for n-Decane + CH_2Br_2.

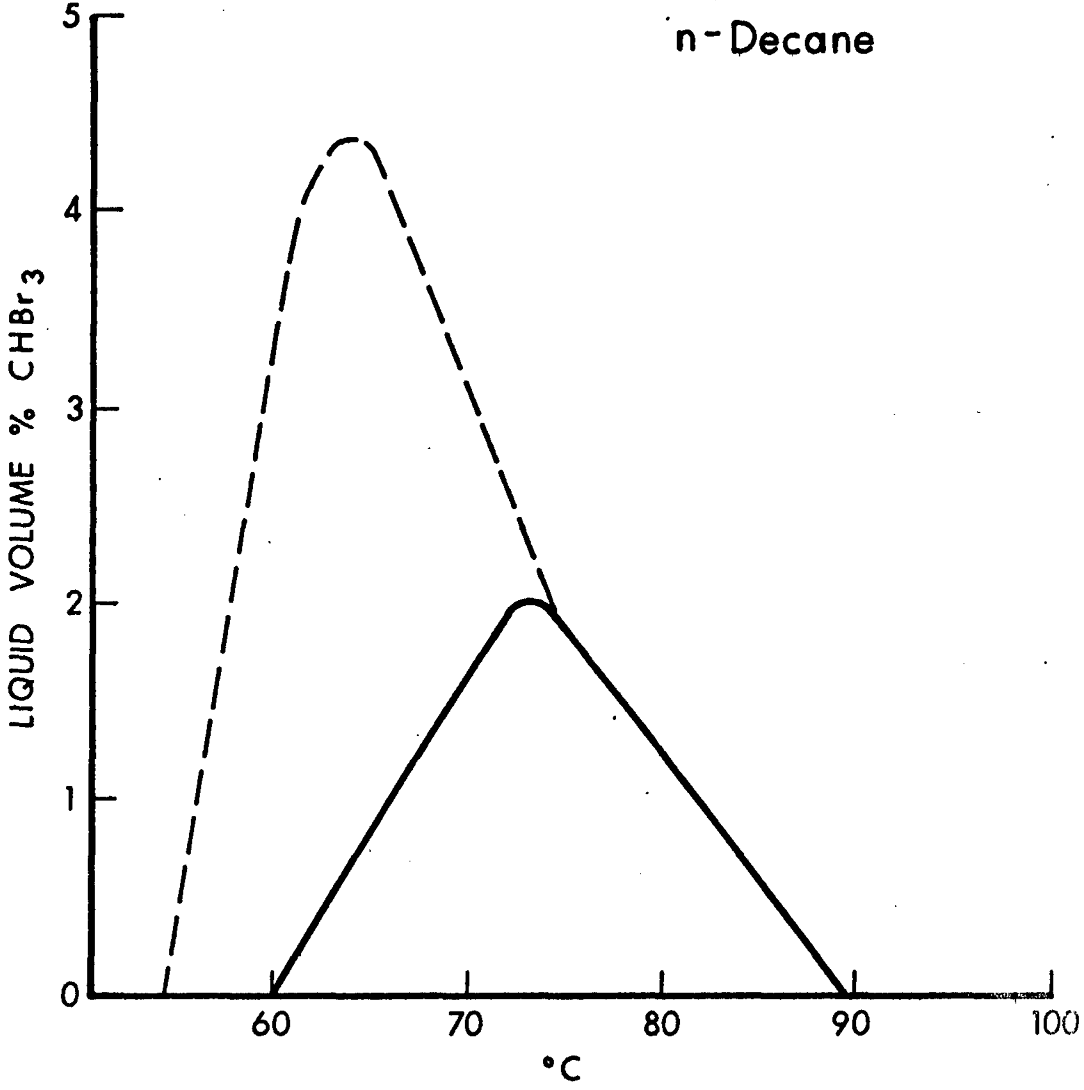

Figure 21. Liquid Flammability Curve for n-Decane + $CHBr_3$.

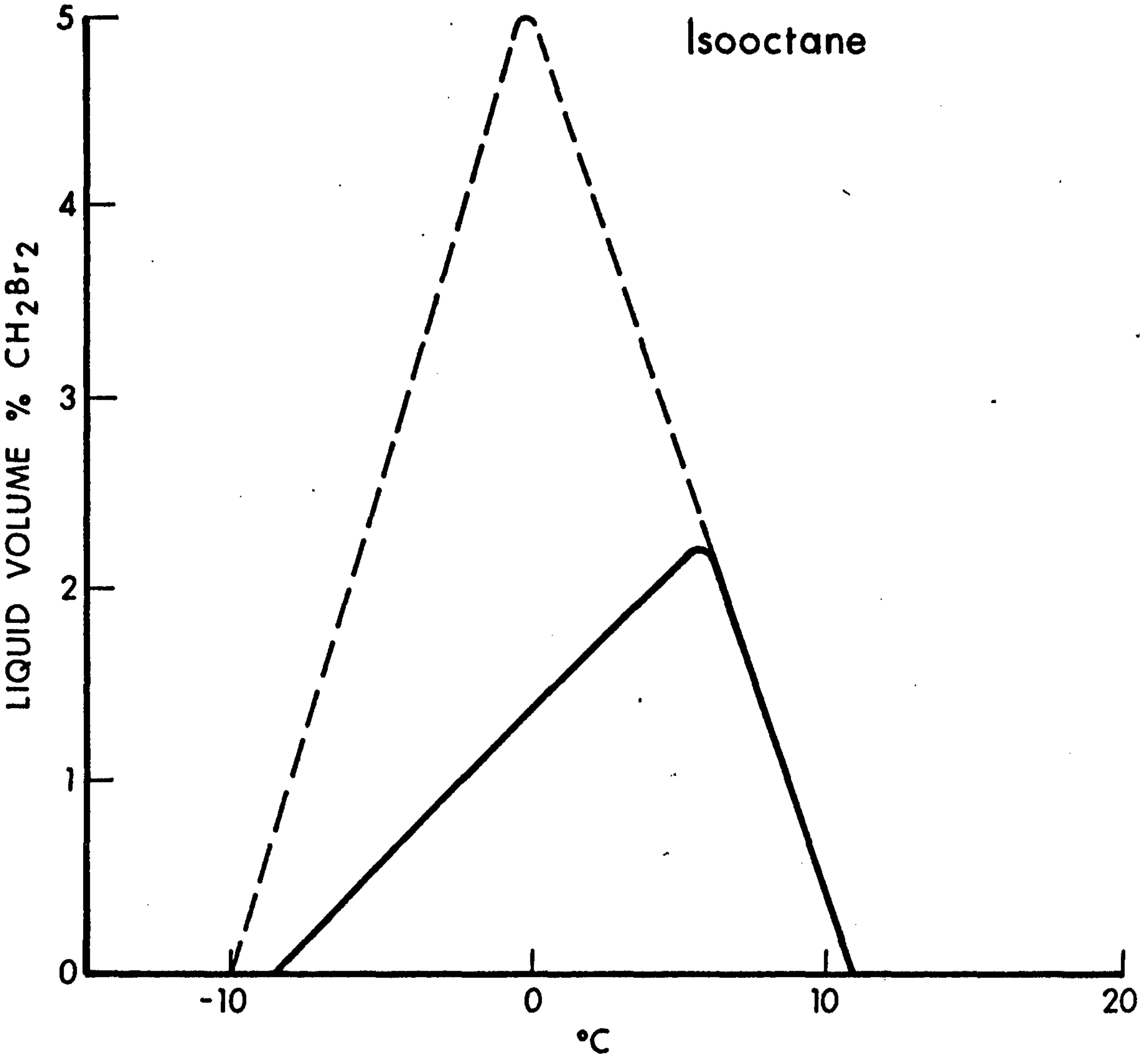

Figure 22. Liquid Flammability Curve for Isooctane + CH_2Br_2.

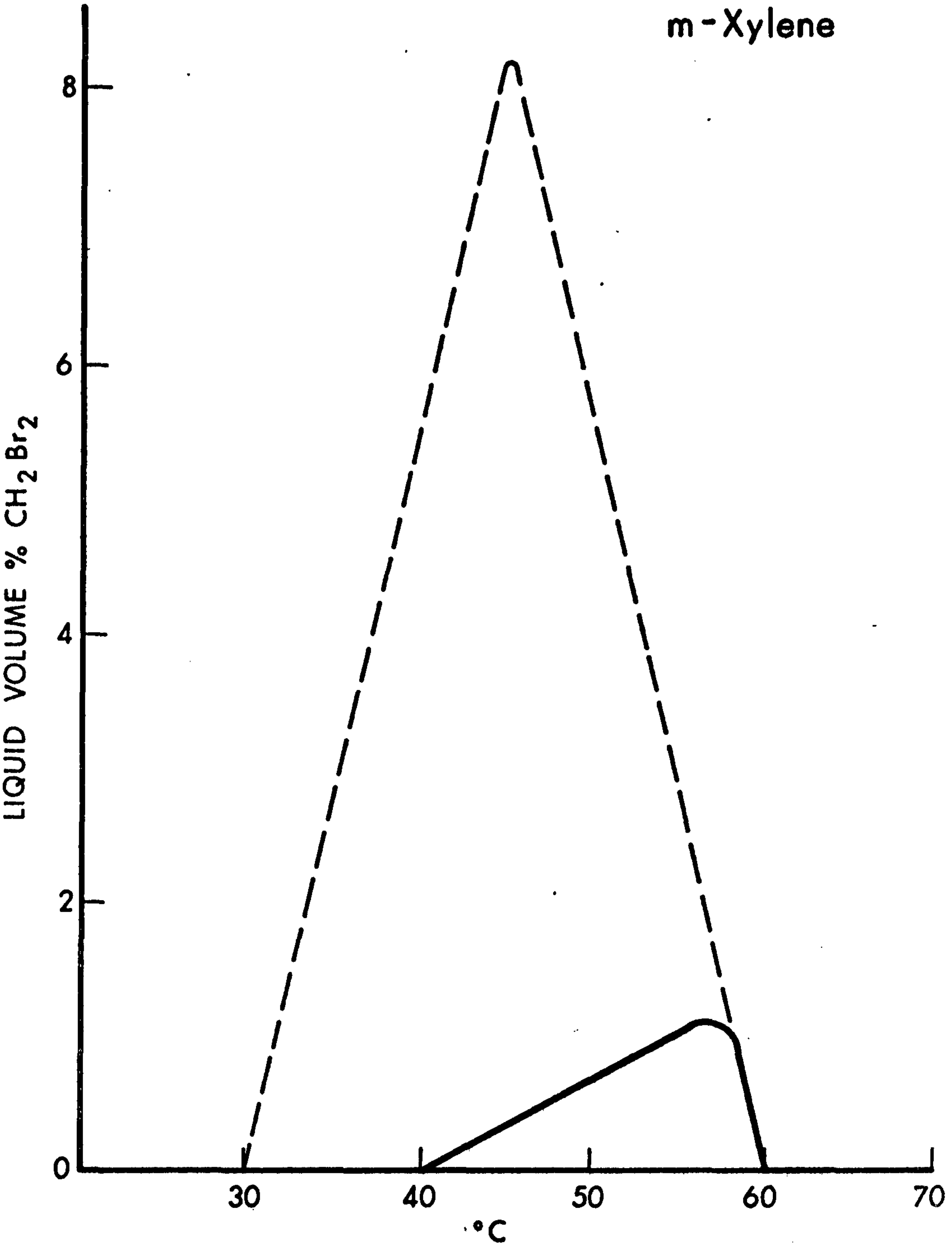

Figure 23. Liquid Flammability Curve for m-Xylene + CH_2Br_2.

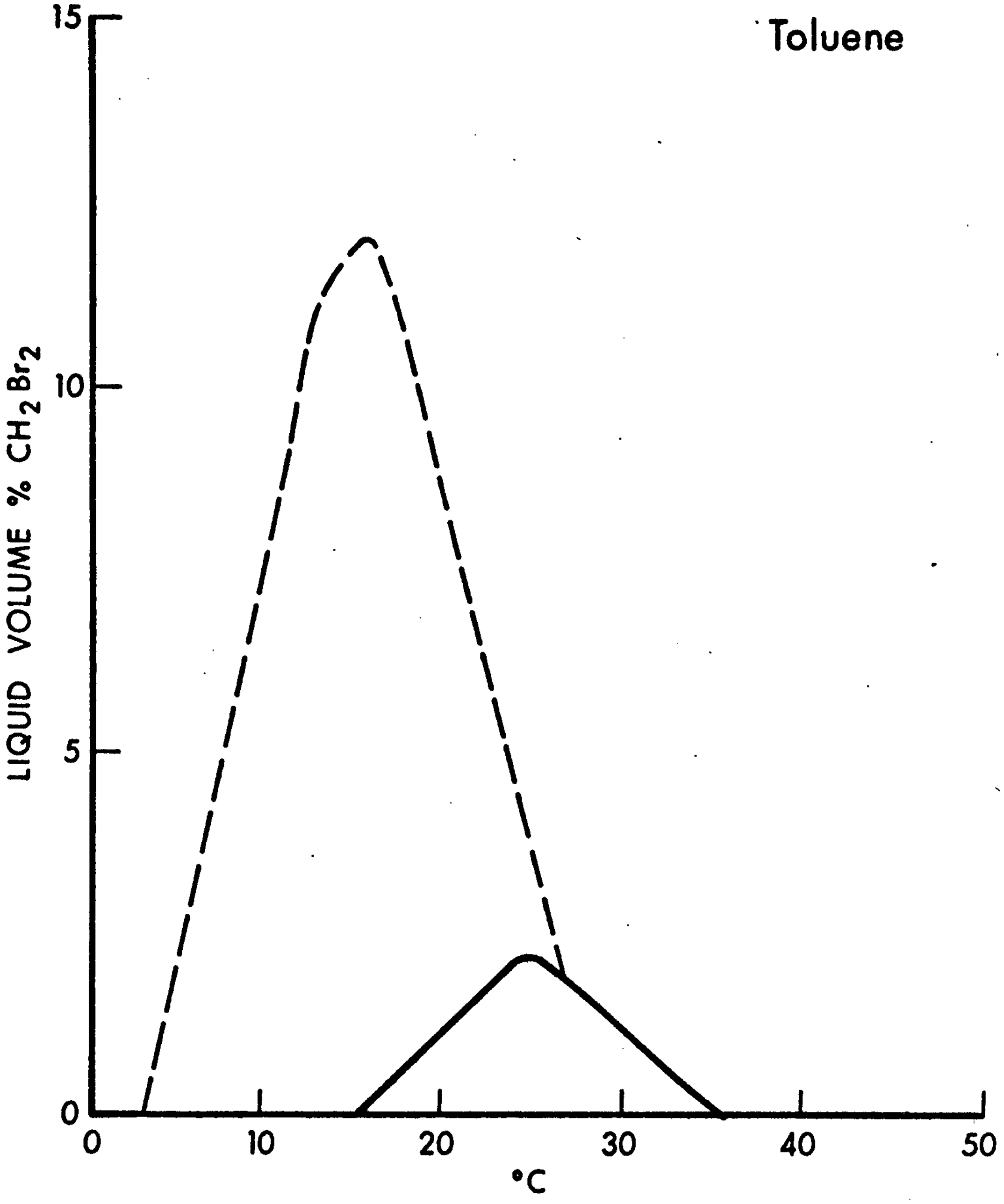

Figure 24. Liquid Flammability Curve for Toluene + CH_2Br_2.

TABLE III

Liquid Volume Peak Percentages for Binary n-alkane+inert Mixtures in the Layered Cup Experiment. Boiling Points (^oC) are Given in Parentheses.

	CH_2ClBr (67.8)	CH_2Br_2 (98.2)	$CHBr_3$ (149.5)	CBr_4 (189.5)
n-heptane (98.4)	2	3.0	10.5	--
n-octane (125)	--	2.5	4.5	--
n-nonane (150.8)	--	1.5	3.0	10.0
n-decane (174)	--	1.0	2.0	--

Flashes were obtained by sparking at the surface of solid benzene (boiling point 80.1°C) even below its freezing point of 5.5°C. The flash-only limit was -14°C and fire anchored in the cup even while the bulk of the benzene was below -7°C. The rich limit was reached at 11°C. With an obviously non-uniform phase distribution in the fuel indicated by a liquid pocket in the solid produced by flashes above, it was difficult to determine a lower fire limit by sparking at the surface. This in turn made it hard to follow limit changes as required in determining an inhibitor peak percentage. If this technique is to be used with materials such as benzene which have a melting point in the flammable temperature region, sparking can be done higher above the liquid surface in order to locate the flammable region in the liquid temperature range. Compare the results of Figure 2 for n-octane with sparking at various heights above the liquid surface. Figure 25 gives limit curves for bromochloromethane and methylene bromide obtained by sparking 2 cm above the benzene liquid surface. Again the effects of relative volatility are evident although it is more difficult to transpose the data to a plot of vapor volume percentages than it would be if sparking were at the surface.

VII. FURTHER COMPARISONS WITH OTHER TEST METHODS

Table IV compares the results of standard flash point tests with the values we have obtained in the layered cup experiment. The standard open-cup and closed-cup values were taken from reference 17 or determined in this laboratory. Values for the alkanes are also given as T_L values in reference 3. The layered cup values determined in the present work refer to flash-only lower limit values for the seven hydrocarbons, while for the three alcohols the lower limit flash points are the fire points as they are in standard tests too. In general it can be said that there is no close agreement between the layered cup values and either of the standard values, nor do the layered cup values lie between the open-cup and closed-cup values (with some exceptions). However, the trends in a series of related compounds are the same in the layered cup as in the open-cup or the closed-cup.

In Table V we see a comparison between lower and upper flammability limits determined by the tube flame-propagation technique[3] and the values determined by the layered cup method in our present work. The layered cup values are calculated vapor volume percentages in air using the fire temperature limits we have already presented for the pure fuels and the known vapor pressure versus temperature curves, assuming equilibrium at the surface. The various temperatures involved can be obtained from the appropriate figures and are given in parentheses. For comparison the temperatures involved in the tube experiments[3] are also given in parentheses. Generally speaking, raising the temperature in the tube

TABLE IV

Comparison of Flash Points Determined by the Layered Cup Technique and By Standard Methods (°C).

	Open cup[a]	Closed cup[a]	Layered cup
n-heptane	-1	-4	-12
n-octane	22	13.5	14
n-nonane	30	31	36
n-decane	44	44	56
benzene	>5.5[b]	-11	-14
toluene	7	4.5	3
m-xylene	32[b]	25	30
methanol	13[b]	10[c]	-1
ethanol	16[b]	13[c]	2
1-propanol	29[b]	24[c]	10

a - Reference 17 except where otherwise noted.

b - This work, ASTM method D92 (Cleveland Open Cup).

c - This work, ASTM method D56 (Tag Closed Cup).

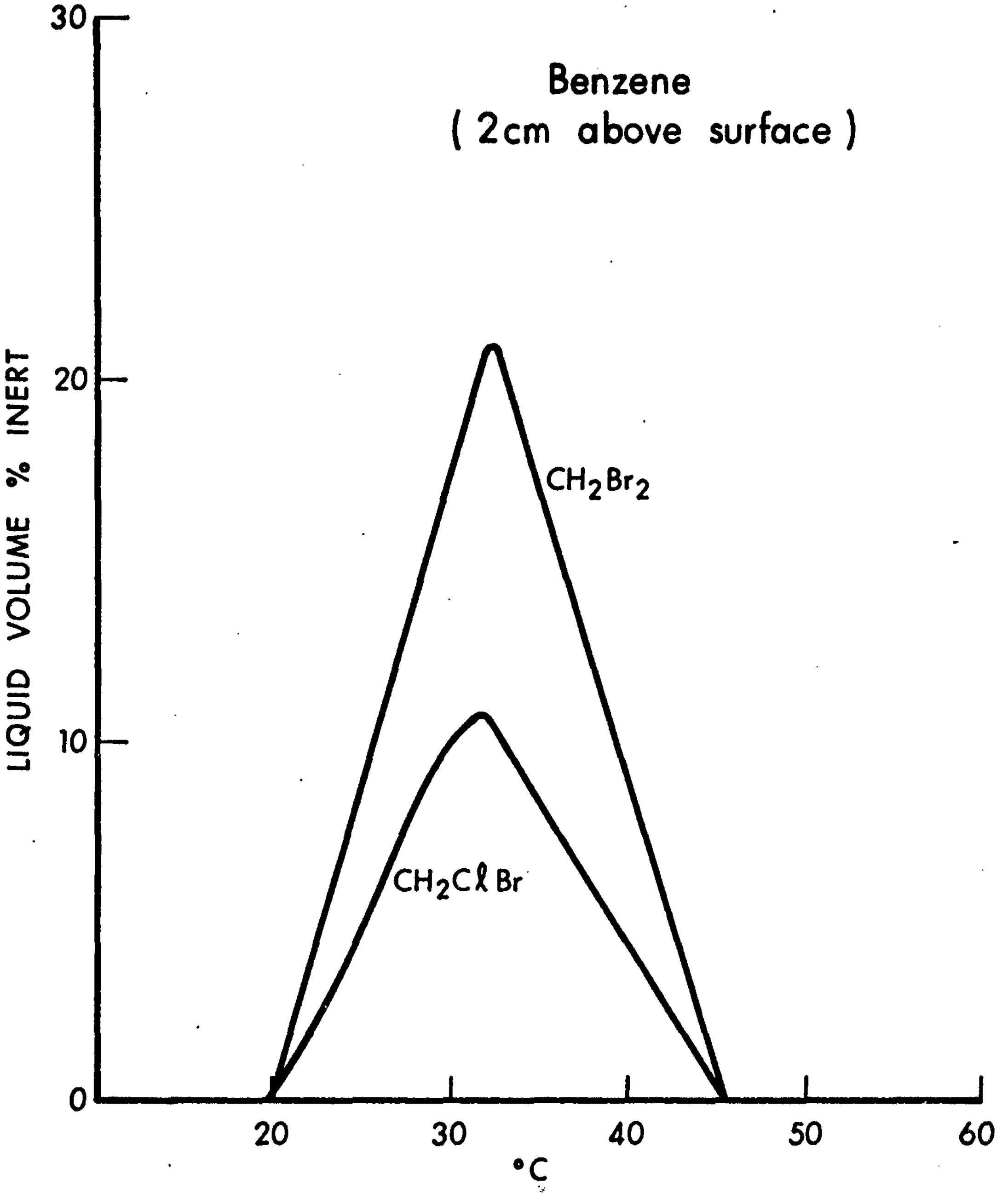

Figure 25. Liquid Flammability Curves for Benzene + Two Inerts (Two Cm Above Liquid Surface).

TABLE V

Comparison of Flammability Limits (Vapor Volume Per Cent in Air) Determined by the Layered Cup Method and by the Tube Flame-Propagation Technique[3]. Values in Parentheses are the Temperatures (°C) Involved.

	Tube		Layered Cup	
	Lower	Upper	Lower	Upper
n-heptane	1.05(25)	6.7 (25)	1.2 (-7)	4.6 (19)
n-octane	0.95(25)	--	1.3 (20)	5.0 (45)
n-nonane	0.85(43)	--	1.4 (40)	5.5 (68)
n-decane	0.75(53)	5.6 (86)	1.4 (60)	5.9 (89)
benzene	1.3(100)	7.9 (100)	--	6.8 (11)
toluene	1.2(100)	7.1 (100)	2.9 (16)	6.4 (35)
m-xylene	1.1(100)	6.4 (100)	3.0 (40)	5.7 (60)
methanol	6.7 (25)	36. (60)	3.3 (-1)	31.6 (38)
ethanol	3.3 (25)	19 (60)	2.1 (1)	19.7 (40)
propanol	2.2 (53)	14 (100)	1.3 (10)	10.5 (50)

experiment widens the composition limits but is required in certain cases to avoid condensation. If we look at the values for the cup and tube experiments we see that there is considerable agreement both in order of magnitude and in trends within series. A notable exception to trend agreement occurs for n-heptane and n-decane where the reversal cannot be blamed on simple temperature changes. Other factors are probably important when we compare a two-phase (liquid-gas) experiment and a one phase (gas) experiment. We will discuss some of these in the next section of this report.

VIII. DISCUSSION

So far in this report we have used the words inert and inhibitor interchangeably to mean fire suppressant without regard to possible mechanisms, whether active or passive, chemical or physical or some other appropriate classification. In this section we will review a few examples from tube flame-propagation experiments which tend to indicate that both physical and chemical mechanisms are at work (as we might expect) although one type may dominate in particular cases. Then we will consider some examples of the layered cup results we have been describing and draw essentially the same tentative conclusions.

At least two physical properties are important in gaseous flame propagation, specific heat, c_p, and thermal conductivity, λ. Theories of flame propagation usually lead to a velocity proportional to some power of the ratio λ/c_p. This appears to be reasonable since a flame should propagate readily when it is easy to transmit heat and raise the temperature of the unburned gas. Conversely, a good fire suppressant should decrease λ and increase c_p leading to a decrease in flame velocity and eventual extinction. In fact, one technique of fire suppression[18] deliberately chooses inerts of high heat capacity. In some cases however when wall losses become important, a high value of λ can be detrimental to flame propagation. Coward and Jones[2] noted this behavior with helium in narrow tubes and recently Gerstein and Stine[19] have quantified this explanation. Consequently, when we correlate fire suppression with a decrease in λ we presuppose a geometry where heat losses to the walls are negligible. In addition we accept the operational definition of flammability limits proposed by Coward and Jones[2] and will not consider the controversy over the theoretical existence of absolute limits which has existed in the literature for many years.

Dilution by an inert gas and its lack of a contribution to the heat of combustion in a flame are factors which border on a chemical explanation although for our present purpose we will refer to them as physical factors. We will attribute a chemical mechanism to a compound only if an estimate of physical factors fails to account for the observed facts. A chemical mechanism involves some reaction of the inhibitor and could be due to the compound itself or to its reaction products. Furthermore this action could be direct (interruption of reaction chains) or indirect (blanketing by reaction products, preventing rapid mixing of fuel and air in the case of diffusion flames). This latter mechanism could well be called physical, but we choose to call it chemical since chemical reaction is required to produce the materials which do the blanketing.

Table VI lists the heat capacities and thermal conductivities of a number of gases of interest to this discussion as well as the heats of vaporization, heat capacities and thermal conductivities of certain liquids. Increases in any of these liquid properties should make it more difficult for a flame to be self-sustaining over a liquid. The values in Table VI were taken from references 20 to 24. Values in parentheses we have estimated from values for related compounds. Although these values change with temperature their relative order and magnitudes do not so that meaningful comparisons can be made by using values at 25°C.

In Table VII average values of c_p and λ are given for a stoichiometric methanol+air mixture as well as for mixtures containing peak percentages of nitrogen (46%) and carbon dioxide (33%) obtained in a tube[3] at 25°C. With nitrogen as the inert small changes do occur in spite of the fact that c_p and λ are almost indistinguishable for nitrogen and air because the amount of methanol at the peak is smaller than stoichiometric. As we can see, the heat capacity is slightly lowered and the conductivity slightly increased, the reverse of good fire suppressant behavior. Since nitrogen does not increase the heat of combustion we are forced to conclude that a pure dilution mechanism is at work. By contrast, 33% CO_2 raises the heat capacity and lowers the conductivity as a suppressant should so that these two physical mechanisms appear to be operative also together with dilution and absence of heat of combustion.

Average values of c_p and λ for a stoichiometric methyl ethyl ketone+air mixture appear as the first entry in Table VIII followed by values for peak percentage mixtures[3] with nitrogen, carbon dioxide and bromochloromethane (BCM). The remarks made above again hold true for N_2 and CO_2, but peak percentage for BCM is about five times smaller than for CO_2. This achieves an approximately equivalent increase in heat capacity but a smaller decrease in conductivity. In addition BCM might contribute to the heat of combustion under the right conditions. Dilution is obviously a less important factor. Something must be compensating for the smaller decrease in conductivity and any contributions to the heat of combustion, and this something we will call chemical interference in the reaction mechanism. This is hardly a new idea, but it is worth quantifying our reasoning process even in this crude way in order to make clear the nature of our tentative conclusions. We suppose then that physical

TABLE VI

Material Properties Pertinent to Flame Suppression by the Addition of Inert Compounds; Heat Capacity, c_p; Thermal Conductivity, λ; and Heat of Vaporization, l, at 25°C. Values in Parentheses Have Been Estimated.

	Vapor Phase		Liquid Phase		
	c_p (cal/mole-deg)	λ (cal/cm-sec-deg)10^{-6}	l (cal/mole)10^{3}	c_p (cal/mole-deg)	λ (cal/cm-sec-deg)10^{-3}
air	7.01	57.0	--	--	--
O_2	7.04	58.0	--	--	--
N_2	7.00	57.0	--	--	--
methanol	10.5	35.0	9.0	19.2	0.48
MEK	25.0	28.0	8.3	37.9	0.35
n-heptane	39.0	29.0	8.5	53.0	0.34
CO_2	8.8	39.0	--	--	--
H_2O	9.0	40.0	10.5	18.0	1.43
CF_2Br_2	18.5	(20.0)	--	--	--
CH_2Br_2	18.0	20.0	8.7	(30.0)	0.30
CH_2ClBr	(15.0)	(17.5)	8.6	27.3	0.29
CH_2Cl_2	12.0	15.0	7.6	24.5	0.29
$CHCl_3$	15.7	18.0	7.5	27.6	0.25
HBr	6.5	20.0	--	--	--
HCl	6.5	33.0	--	--	--
Dow Corning 704	--	--	>25	165	0.30

TABLE VII

Vapor Phase Average Values of c_p and λ for a Stoichiometric Methanol+ Air Mixture and for Tube Peak Percentage Mixtures of Methanol and Air with Two Inerts.

	c_p(cal/mole-deg)	λ(cal/cm-sec-deg)10^{-6}
methanol+air	7.4	54.4
+ 46% N_2	7.2	55.2
+ 33% CO_2	8.0	48.7

TABLE VIII.

Vapor Phase Average Values of c_p and λ for a Stoichiometric Methyl Ethyl Ketone (MEK) + Air Mixture and for Tube Peak Percentage Mixtures of MEK and Air with Three Inerts.

	c_p(cal/mole-deg)	λ(cal/cm-sec-deg)10^{-6}
MEK + air	7.7	55.9
+ 45% N_2	7.6	56.1
+ 33% CO_2	8.2	50.0
+ 7% CH_2ClBr	(8.2)	(53.3)

mechanisms are still at work but that a chemical mechanism also plays a role, although it is hard to say which type of factor dominates.

In Table IX we see similar data for n-heptane and air with various peak percentages of inerts selected from reference 11. With but two exceptions (HBr and HCl) c_p is increased while all of these inhibitors lower λ. The first thing we note is the fact that there is no critical value of c_p or λ or of the ratio λ/c_p which can be correlated with the phenomenon of a peak percentage. The first three brominated methanes give relatively small peak percentages in spite of the relatively high λ values of the mixtures and the contributions which these compounds might make to the heat of combustion. At least two of them (CH_2ClBr and CF_2Br_2) have been shown to be non-flammable in air (but not in oxygen) over wide limits[25] and none of them have flash points in air. Our conclusion is that relative to other compounds in the table for which dilution plays an important role, a chemical mechanism plays a part in the action of these halons, with bromine more effective than chlorine. Chloroform is also included because it is representative of the peak percentage mid-range in spite of the high c_p and low λ values of the mixture. There is no sharp division between the peak percentages of halons and those of other types of compounds and all values are possible depending on the heating value and other physical and chemical properties of each compound. The halogen acids (HBr and HCl) are interesting since they actually lower the average heat capacity of the mixture yet are more effective than CO_2 or H_2O as measured by their peak percentages. They also offer a sharp contrast between the relative effectiveness of bromine and chlorine in any chemical mechanism which we might invoke. This is not inconsistent with the idea that they are the agents which must be formed before other halons are effective, a process which could obscure the relative effectiveness of bromine and chlorine in halons. Finally, for CO_2 and H_2O dilution is obviously an important mechanism resulting in a reduction in reaction speed and overall heat of combustion as well as favorable c_p and λ changes. No chemical mechanism needs to be invoked. The advantage of CO_2 over H_2O is however somewhat puzzling and might be attributable to their relative effectiveness in three-body collisions or to other factors which we are not even considering.

Let us turn our attention now to the layered cup data presented in this report. Since this data involves two phases it is more difficult to interpret. The transition from a flash in the vapor phase to a fire anchored over the liquid surface is a very complex

TABLE IX.

Vapor Phase Average Values of c_p and λ for a Stoichiometric n-heptane + Air Mixture and for Tube Peak Percentage Mixtures of n-heptane and Air with Eight Inerts.

	c_p(cal/mole-deg)	λ(cal/cm-sec-deg)10^{-6}	λ/c_p
n-heptane+air	7.6	56.5	7.43
+ 4.2% CF_2Br_2	8.1	(54.9)	(6.78)
+ 5.2% CH_2Br_2	8.1	54.5	6.73
+ 7.6% CH_2ClBr	(8.1)	(53.4)	(6.59)
+17.5% $CHCl_3$	9.1	49.6	5.45
+ 9.3% HBr	7.56	52.4	6.93
+ 25.5% HCl	7.47	50.3	6.73
+ 29.5% CO_2	8.1	51.0	6.30
+ 33% H_2O	8.2	50.7	6.18

process and involves not only heat and chemical species generated and consumed in the vapor during and after the flash, but also the factors which affect heat transfer to the liquid and the properties of the liquid mixture itself. All of these factors must be taken into account if a mechanism is to be assigned. Since the relative importance of physical and chemical factors in flame suppression have not yet been clearly established even for the tube experiment, we are unlikely to do so here. Still it is worthwhile to open the discussion by considering at least those factors which seem more likely to affect flame stabilization, as we did in our discussion of tube results above. Now, however, an additional mechanism is possible near the liquid-vapor interface, namely, a blanketing of the vaporizing fuel from fresh incoming air by the combustion products of the initial flash. These products are quite visible especially in the case of brominated inhibitors, probably because of water condensation on hydrobromic acid. This mechanism we have chosen to call chemical (or chemico-physical) because reaction is needed to produce the blanketing products.

From Table X we see that all of the inerts listed raise c_p and lower λ in the vapor. Again there are no critical values characteristic of all peaks. Once more for the halons c_p is raised less and λ is lowered less than for water. This together with the small dilution factor and possible heat contributions of the halons in contrast with water leads us to postulate a chemical mechanism for halon inhibition. The very small halon percentages and the presence of a visible layer in the cup after a fire leads us to suppose that an important part of this chemical mechanism could be product blanketing, although direct interruption of reaction chains is certainly plausible. In Table XI we see liquid phase properties for methanol and binary mixtures with these same inerts. A good fire suppressant should increase the heat of vaporization, l, and increase the heat conductivity in order to increase heat losses from the flame to the liquid. Its effect on heat capacity is probably less important during the critical period when a flame is becoming established since only the surface of the liquid is heated at this time and then only a small amount. If it is important, a good flame suppressant should increase c_p. Water increases l and λ (by a factor of three) and slightly decreases c_p. By contrast the halons slightly decrease l and λ while increasing c_p a small amount. It is difficult to assign relative weights to these factors, but the advantage is probably with water over the halons, lending further credence to some need for a chemical explanation in the case of the halons.

TABLE X.

Vapor Phase Average Values of c_p and λ for a Stoichiometric Methanol + Air Mixture and for Layered Cup Peak Percentage Mixtures at the Surface Involving Methanol, Air and Four Inerts.

	c_p(cal/mole-deg)	λ(cal/cm-sec-deg)10^{-6}
methanol+air	7.5	54.4
+ 1% CH_2Br_2	7.7	54.1
+ 1.75% CH_2ClBr	(7.7)	(53.6)
+ 3% CH_2Cl_2	7.8	53.3
+ 44% H_2O	8.5	47.0

TABLE XI.

Liquid Phase Values of l, c_p and λ for Pure Methanol and Binary Mixtures of Methanol with Four Inerts at the Layered Cup Liquid Molar Peak Percentages.

	l (cal/mole)10^3	c_p (cal/mole-deg)	λ (cal/cm-sec-deg)10^{-3}
methanol	9.0	19.2	0.48
+ 24% CH_2Br_2	8.9	21.8	0.43
+ 19% CH_2ClBr	8.9	20.7	0.44
+ 17% CH_2Cl_2	8.8	20.1	0.45
+ 87% H_2O	10.3	18.2	1.30

Analogous considerations hold for Tables XII and XIII when we contrast the effects of halons and a silicone oil. The very small vapor phase peak percentages for the halons lend further credence to a blanketing mechanism by halon decomposition products although direct chemical and other physical factors are also probably at work. Although the silicone is flammable, its flash point is so high (221°C) that it acts as an inert over the temperature range we are considering. Dow Corning 704 fluid is tetramethyltetraphenyltrisiloxane which has a very low vapor pressure (boiling point 215°C at 0.5 torr) and so acts principally as a diluent in the liquid phase which results in less heptane in the vapor phase at a given temperature. In addition the average liquid heat capacity and heat of vaporization of the mixture are increased compared to pure heptane although the conductivity is hardly changed. Near the boiling point of n-heptane (98.4°C) about 84 liquid volume per cent of this silicone will prevent ignition. However, the lower and upper limits do not meet even up to 150°C although they approach rather closely. From observations of the mixture from 100°C to 150°C it seems clear that the heptane is bubbling out at a sufficient rate to maintain a fire with perhaps some contributions from the silicone carried along with the heptane. Similar observations with 1-propanol and the same silicone (Figure 7) suggest the same preferential boiling of propanol above 98°C, but in that case the limits seem to merge near 110°C, giving a peak percentage of about 86 liquid volume percent. At these temperatures preferential loss of the more volatile component makes it too difficult to determine exact percentages.

IX. CONCLUSION

In this report we have described a test method for determining the flammability limits of liquid fuels and for rating the relative effectiveness of soluble inerting agents. This method has some advantages over the tube flame-propagation technique in that it requires simple equipment and automatically includes factors which influence fires over liquid surfaces. However it is more difficult to interpret the results since they are obtained using a two-phase system. Comparisons have been made with related literature results and a discussion of possible mechanisms has been given, based on examples involving a number of fuels and inerting agents.

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TABLE XII.

Vapor Phase Average Values of c_p and λ for a Stoichiometric n-heptane+air Mixture and for Layered Cup Peak Percentage Mixtures at the Surface Involving n-heptane, Air and Four Inerts.

	c_p (cal/mole-deg)	λ (cal/cm-sec-deg) 10^{-6}
n-heptane+air	7.6	56.5
+ 0.15% CH_2Br_2	7.6	56.4
+ 0.30% CH_2ClBr	(7.6)	(56.5)
+ 1.8% CH_2Cl_2	7.7	55.5
Dow Corning 704	--	--

TABLE XIII.

Liquid Phase Values of l, c_p and λ for Pure n-heptane and Binary Mixtures of n-heptane with Four Inerts at the Layered Cup Liquid Molar Peak Percentages.

	l (cal/mole)10^3	c_p (cal/mole-deg)	λ (cal/cm-sec-deg)10^{-3}
n-heptane	8.5	53.0	0.34
+ 6% CH_2Br_2	8.5	51.6	0.34
+ 4% CH_2ClBr	8.5	52.0	0.34
+ 10% CH_2Cl_2	8.4	50.2	0.34
+ 65% Dow Corning 704	>19.	115.	0.32

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