

THE UNIVERSITY OF CALGARY

THE EFFECTS OF LOW TEMPERATURES ON THE  
FLAMMABILITY LIMITS OF SOME GASEOUS FUELS  
AND THEIR MIXTURES IN AIR

BY

KEVIN P. HARRIS

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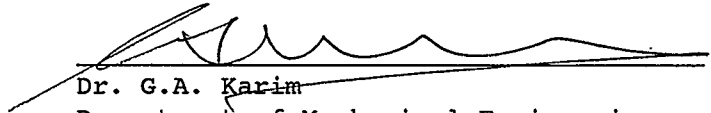
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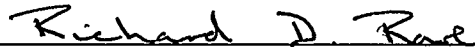
The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "The Effects of Low Temperatures on the Flammability Limits of Some Gaseous Fuels and Their Mixtures in Air" submitted by Kevin P. Harris in partial fulfilment of the requirements for the degree of Master of Science in Mechanical Engineering.



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## ABSTRACT

A study was made of the flammability limits of gaseous fuels at low initial temperatures using an apparatus that was developed for this purpose. Tests were conducted at atmospheric pressure with the flame tube open at the lower end where the mixture was ignited.

The rich and lean limits of flammability for pure gaseous fuels including methane, ethane, propane, n-butane, ethylene, propylene, carbon monoxide, and hydrogen were obtained over an initial temperature range of 23°C to -60°C. Additionally, rich and lean flammability limits were also determined for binary mixtures of a wide variety of gaseous fuels over the same initial temperature range. Tests were also performed to investigate the effects of low temperature on the flammability limits of "diluted" fuels (i.e., fuels containing carbon dioxide or nitrogen).

It was found that for the fuels and fuel mixtures tested, both the lean and rich limits of flammability changed linearly with the lowering of initial temperature. Different predictive approaches were discussed.

Calculations showed that the rich and lean limits of the mixtures studied could be adequately predicted using Le Chatelier's rule, with the exception of rich limits of mixtures containing large quantities of hydrogen combined with small amounts of other fuels. For some of these mixtures, the relative deviations were substantial. The extent of the relative deviation was found to be essentially independent of the initial mixture temperature for the conditions tested.

Results indicated that the lean limits of flammability for methane mixtures containing either nitrogen or carbon dioxide could be accurately

Results indicated that the lean limits of flammability for methane mixtures containing either nitrogen or carbon dioxide could be accurately calculated using simple methods. Furthermore, the "constant flame temperature method" provided excellent predictions for lean methane/nitrogen limits at the temperatures at which it was applied. Slightly higher errors were obtained when this method was used on methane/carbon dioxide mixtures, especially for those that were highly diluted.

Reasonable predictions were obtained for the rich limits of methane/diluent mixtures over the temperature range considered, by using appropriate correlations.

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## NOMENCLATURE

$a_f$	empirical constant to be used with fuel mixtures containing diluents
$C_p$	specific heat at constant pressure
$(F/A)$	fuel to air ratio on a volumetric basis
$(F/A)_s$	stoichiometric fuel to air ratio on a volumetric basis
$L_i$	flammability limit of the $i^{\text{th}}$ fuel in a fuel mixture
$L_m$	flammability limit of the fuel mixture
$g$	acceleration due to gravity on earth
$\Delta H_c$	net heating value
$\Delta H_f$	enthalpy of formation
$LL$	lean flammability limit of the fuel in air, % by volume
$LL_c$	calculated lean flammability limit of the fuel in air, % by volume
$LL_{CH_4}$	lean flammability limit of methane in air, % by volume
$LL_e$	experimental lean flammability limit of the fuel in air, % by volume
$LL_m$	lean flammability limit of a fuel mixture in air, % by volume
$RL$	rich flammability limit of the fuel in air, % by volume
$RL_c$	calculated rich flammability limit of the fuel in air, % by volume
$RL_{CH_4}$	rich flammability limit of methane in air, % by volume
$RL_e$	experimental rich flammability limit of the fuel in air, % by volume
$RL_m$	rich flammability limit of a fuel mixture in air, % by volume

$t_s$	spark duration
$T_f$	calculated adiabatic flame temperature
$T_{in}$	initial temperature of the fuel/air mixture before ignition
$Y_F$	volumetric fraction of the flammable component in the fuel mixture, % by volume
$Y_i$	volumetric fraction of the $i^{th}$ gaseous fuel in a gaseous fuel mixture, % by volume
$\phi$	equivalence ratio = $(F/A) / (F/A)_s$

## CHAPTER 1

### INTRODUCTION

#### 1.1 Prologue

Explosions caused by the combustion of gaseous fuels in air have resulted in heavy losses, both human and economic [15,16]. Historically, the determination of flammability limits has been important, not only to afford hazard assessment in industrial environments, but also to be used in situations where combustion is desirable. Flammability limits were originally studied on mixtures of "firedamp" (methane) and air in order to develop a safe light to be used by miners. Since this time, limit determinations have been made for a variety of fuels ranging from commonly used industrial fuels to more exotic fuels such as some of the anaesthetics used in hospital operating rooms. A large portion of this work has been conducted by researchers associated with the U.S. Bureau of Mines.

Although a great deal of work has been done on lean limits of gaseous fuels in the past, they have become an area of renewed interest of late, because of the recent efforts in reducing the emission levels in the exhaust gases produced by internal combustion engines. Increasing attention is being focused on the rich and lean limits of flammability of various fuels containing inert diluents because of the increasing use of "low-Btu" fuels.

The frequent presence of pressure liquified fuels introduces the possibility of accidental combustion occurring at the low temperatures created by escape and subsequent vaporization of these fuels [71]. This

group of fuels includes flammable gases used in cryogenic applications and also liquified natural gas (LNG). There is also an increasing need to use fuels under very low ambient temperature conditions, both in space exploration and as man continues to make increased use of earth's polar regions.

For safety considerations, limits of flammability for upward propagation are normally quoted because they are usually wider than those determined for downward or horizontal flame propagation. The actual limits of flammability are often defined in slightly different ways by various researchers. Limits quoted in this investigation are the "0% propagation" limits [7,14], in other words the borderline composition that will not propagate a flame through the fuel/air mixture. The 0% designation was applied because the determined limits were tested repeatedly and only those mixtures in which the flame did not propagate during any of the trials were recorded as flammability limits.

## 1.2 Rationale for the Present Work

Examination of the available literature indicates that there is a lack of information on the flammability limits of the majority of commonly used fuels in air at temperatures below 25°C. This information is needed to accurately assess the possible hazards involved in the handling and use of these fuels when their vapor is mixed with air at low temperatures.

### 1.3 Objectives

The objectives of the work carried out in this research are as follows:

1. Develop an apparatus designed specifically to determine the flammability limits of fuel vapors in air at temperatures below 25°C for upward flame propagation.
2. To provide consistent data for the rich and lean flammability limits of commonly used pure fuels in air at temperatures down to -60°C using the new apparatus.
3. Investigate the flammable range of a number of binary fuel mixtures in air at initial temperatures down to -60°C.
4. Determine the behavior of the flammability limits of methane/air mixtures containing varying quantities of inert diluents over the temperature range below 25°C.
5. To establish guidelines for the prediction of the rich and lean flammability limits of pure fuels, binary fuel mixtures, and fuel/diluent mixtures in air at various low temperatures.

### 1.4 Organization of the Text

Chapter 2 gives a brief review of the literature on flammability limits of gaseous fuels, concentrating on the effects of various factors on the limits, and a brief summary of the most recent developments in the field.

Chapter 3 describes the details and development of the apparatus, the experimental procedure, and some of the difficulties encountered during

the research.

Chapter 4 presents the experimental results along with detailed analysis and discussion. Comparisons are made to some results available in the literature. The behavior of the rich and lean limits are analyzed with respect to initial temperature. Correlations are provided to allow the rich and lean limits of pure fuels and binary mixtures of a variety of pure fuels to be predicted.

Chapter 5 contains some conclusions as well as recommendations for possible future studies. Finally, a list of the publications referred to in the text concludes the presentation.

## CHAPTER 2

### LITERATURE SURVEY

#### **2.1 Background**

Combustion of most fuels takes place readily at fuel/air ratios near stoichiometric, where the flame temperature, flame speed, and heat release are maximum. As the fuel/air ratio is changed to either the rich or lean side, the flame temperature and reaction rate decrease until a point is reached where a flame will not propagate through the mixture, even though it can be ignited. These points are referred to as the rich limit and lean limit of flammability. Almost all fuels will exhibit lean limits of flammability. Most fuels also have rich limits, with the exception of some that contain an oxidizer or have a positive enthalpy of formation (in which case they may decompose exothermically) [69].

In the literature, the term flammability limit is often referred to as the "limits of flammability", "inflammability limits", "limits of deflagration", and "explosive limits". Current terminology classifies deflagration processes as flames that travel at subsonic velocity with respect to the unburnt mixture, while a detonation is an exothermic reaction taking place in a wave moving at supersonic velocity relative to the reactants. Explosions are violent releases of pressure that may be caused by detonations, deflagrations, or some other source. With most fuels, the flame propagation process near the limits of flammability is by deflagration. The actual detonation limits are normally narrower than the limits of flammability and depend a great deal on temperature, pressure, and apparatus length and diameter [58].

There are also several designations in the literature for the rich and lean limits of flammability. The lean limit can be called the lower limit or the weak limit, while the rich limit is often referred to as the upper limit.

Flammability limits were originally established to improve safety conditions in mines. Since then, numerous results have been published on flammability limits for a large number of fuels. Much of this data has been compiled in reviews by Coward and Jones [15], Barnett and Hibbard [4], Zabetakis [70], and Lovachev [41,42]. Most of the past research studied the influence of initial conditions and other parameters on the limits in an effort to determine the important factors relating to flammability limits.

Examination of the published data from the first half of the century suggests that flammability limits are not repeatable because there are large variations in the results of different researchers. This is most likely due to the wide variety of experimental methods and apparatus used in different studies [15]. Data from more recent studies tend to have less variation because the tests and apparatus have become more standardized and technological advances have made more accurate measurements possible.

One of the more important factors to consider in flammability tests is the direction of flame propagation. Temperature gradients in a gas under the influence of gravity cause buoyancy effects such that flammability limits determined for upward flame propagation are usually wider than those found for the downward direction [15,70]. Limits determined with the flame propagating horizontally are normally between those quoted



for upward and downward propagation, and widen as the angle increases in the upward direction [48].

Some researchers [15,19,58,70] have suggested that the flammability limits determined in zero gravity conditions should also be between those for upward and downward propagation at one g. Other studies [9,22,25,31,34,39] have predicted that limits at zero g will be wider than those determined at one g and this view seems to be supported by recent studies that were performed in a microgravity environment [33,52,56,57]. Experiments on the effect of acceleration level on the flammability limits of methane [41], has confirmed that as the acceleration level increases, the flammable range decreases for both upward and downward flame propagation. The effect is more pronounced with downward propagation, where it was found that the rich and lean limits meet at about 97 g.

Many of the publications have described the effects of apparatus size on experimentally determined flammability limits [4,6,15,33,41,49, 55,70]. In general, the apparatus diameter must be larger than the quenching distance and the length must be sufficiently great that the flame travels outside the realm of influence of the ignition source. For most fuels in air at initial temperatures of 25°C, the limits are constant for diameters of 51 mm or greater [70]. Similarly, most limits approach a constant value for tube lengths of one metre or greater if the flame propagation is in the upward direction and the bottom of the tube is open to the atmosphere [41]. These dimensions were adopted by the U.S. Bureau of Mines for its standard flame tube, and have also been used by many other researchers [15].

A large fraction of the early flammability tests were done in closed

tubes instead of open to the atmosphere. When the tube is closed during a flammability test, the pressure increases during combustion instead of remaining at approximately atmospheric pressure as in an open tube. Although closed tubes seem to give slightly wider limits for some fuels, they have the disadvantage that the limits vary with tube length, even for tubes much longer than one metre [41]. Most recent tests have been done in open tubes to avoid this complication.

Numerous investigations [4,6,8,15,21,29,33,41,46,60,70,72] have pointed out that the method and strength of the ignition source can have a significant effect on the flammability limits. Methods that have been used for ignition in flammability limit experiments include pilot flames, hot rods or wires, fused wires, spark ignition, break-spark, chemicals, and most recently plasma jets.

The importance of the ignition system in flammability limit studies is illustrated by examination of early investigations into the cause of coal mine explosions. Incomplete understanding about ignition source energy requirements led to the belief that pure coal dust was non-explosive and that the real cause of all mine explosions was the ignition of "firedamp" (methane). During a period from about 1890 to 1910, it was common practice in the United States to pack borehole explosives with coal dust to prevent such mishaps [29]. This misbelief was finally corrected by a Royal Commission investigation which used a system with adequate ignition energy to discover the real explosion hazards of suspended coal dust [29].

Pilot flames were used in much of the early research compiled by Coward and Jones [15]. They concluded that although pilot flames could

often produce flame propagation over a wider range than some electric sparks, the results were not as consistent as with electric sparks.

Researchers for the National Advisory Committee on Aeronautics conducted some work on the hot body ignition method, including wires and rods [4]. It was concluded from this research that ignition using hot bodies was very inefficient and did not work well in non-flow situations except with very diffusive fuels such as hydrogen.

Recent studies on plasma jets [60] and chemical igniters [29] as ignition sources in flammability limit tests have indicated that the rich limits of certain fuels can be increased by very high energy sources. The investigators point out, however, that it is possible the limits are being "overdriven" because, when the igniters were activated in a closed vessel containing only air, a significant pressure rise occurred which was comparable to that produced from an actual flammability test. In general, it was concluded that although plasma jets and chemical ignition sources provide superior ignition to spark discharge systems, they alter the properties and initial conditions of the test mixture too much to be used for flammability limit determinations.

Spark ignition continues to be the preferred method of ignition for flammability limit tests, chiefly because of the tight control of ignition energy which is available with these systems. Comprehensive studies on spark ignition were conducted by Blanc et al. [6] and also researchers for the National Advisory Committee on Aeronautics [4]. These studies found that electrode spacing, ignition power level, and spark duration are all important considerations in spark ignition systems. At electrode spacings smaller than a certain value, the flame kernel initiated between

the electrode can be quenched by the electrodes themselves. Large electrode spacings require a higher voltage to ionize the gases in the gap, and also spread the ignition energy over a larger volume of gas, hence requiring larger ignition energies. For a given fuel/air mixture and ignition system, there exists an optimum electrode spacing for the strongest ignition [4]. Ignition power and spark duration are both important because they control the total ignition energy, which is also an important consideration in flammability limit determinations. For almost all fuels, there exists a range of ignition energy where the flammability limits are independent of energy level [15]. Ignition energy should be set somewhere in this domain if the resultant flammability limits are to be truly independent of energy level. Determination of this range can be difficult for some fuels with a positive enthalpy of formation, because under the right conditions, they can decompose exothermically and hence have no rich limit. Work done by Zabetakis [71] on ethylene found that the rich limit could be raised appreciably by using a more powerful ignition source, and that a decomposition reaction could be initiated in pure ethylene at pressures over 5.27 MPa.

As suggested above, the initial pressure of the fuel/air mixture can exert a considerable influence on the flammability limits. Normal variations in atmospheric pressure do not change the limits of most fuels appreciably [15]. Lowering the initial pressure below one atmosphere does not change the flammable range of most fuels as long as the ignition energy and the test vessel diameter are increased sufficiently [58]. At very low pressures, a point will eventually be reached where a flame will no longer propagate continuously, although this pressure can be as low as

70 Pa for some fuels [58]. At pressures higher than atmospheric, the flammability limits behave in different ways for different fuels. In a majority of the cases, the flammability limits widen, with the rich limit changing more than the lean. Some mixtures will, however, display the opposite tendency, while with others the flammable range first narrows and then widens as the pressure increases. Lovachev [41,42] pointed out that in the cases where the lean limit was raised along with pressure, the flame propagation direction was downward, and suggests that this is due to convective heat losses from the combustion products. Most of the tests at high pressures have been done in closed tubes.

The effect of initial temperature on the flammability limits shows that normally, an increase in temperature will widen the flammable range [15]. The majority of the research on the effects of temperature on the limits has been conducted at 15°C or higher. Work by White [62] and Mason et al. [45] found that the downward flammability limits for methane widen approximately linearly with temperature increase over the range of 15°C to 200°C. Problems were experienced at temperatures in excess of 200°C because of slow oxidation reactions prior to ignition. This was especially noticeable with the rich limits where it was found at 300°C, that if the fuel/air mixture was allowed to reside in the hot vessel for more than 2 seconds, it could not be ignited. Lovachev [41] noted that for hydrogen/air mixtures at high fixed temperatures, the rich limit decreased linearly with increasing residence time. He also suggested that the fast inlet techniques required at high temperatures to prevent slow oxidation or decomposition reactions were limited by turbulence, temperature gradients, and other effects observed in the vessel. The

general conclusion reached by Coward and Jones [15] and also by Zabetakis [70] is that generally, in the absence of slow oxidation, the rich limit increases while the lean limit decreases in an approximately linear fashion with initial temperature rise.

A few lean limit flammability tests have been performed for methane and also methane/nitrogen mixtures, in closed tubes, at temperatures as low as  $-130^{\circ}\text{C}$  [11,58]. Low temperature lean limit determinations have also been performed for several types of jet fuels [67]. All three of these studies used the same apparatus, in which the level of pressure rise was used to detect flame propagation. The first low temperature flammability tests in open tubes seem to have been performed by Boon [7], for the lean limits of methane, hydrogen, and carbon monoxide at temperatures down to  $-130^{\circ}\text{C}$ . These low temperature investigations confirm that as temperature increases, the flammable range broadens linearly.

Premixed flammability limit tests are commonly conducted on quiescent mixtures to avoid the extra complications introduced by turbulence. Initial studies compiled by Coward and Jones [15] on the effect of turbulence on the limits suggested that for moderate levels of turbulence, the limits are usually unaffected, while at high levels, the flammable range narrows. Recently, Lovachev [41] noted that the previous investigations into turbulence effects were conducted in small tubes with inadequate ignition sources. He found that if the size of the ignition source is increased to account for the increased turbulence, the flammable range actually widens as the turbulence level rises.

Flame detection methods used in judging whether the flame has propagated the length of the tube are also an important consideration in

limit determinations. When it is possible, visible confirmation remains the most reliable method, as well as providing valuable clues about possible extinction mechanisms [39]. Many flammability limit tests have used pressure rise as an indication of flame propagation, although this method is limited to closed vessel tests. Other researchers have relied upon an analysis of the products of combustion to detect flame propagation, but this method is very time-consuming and can be misleading, because combustion is usually incomplete in the vicinity of the limits [41]. Another alternative to visible detection is the use of thermocouples to judge whether the flame reaches the end of the tube. The possible problem with thermocouples is their inability to distinguish between an actual flame and the hot gas bubble from a flame that has just extinguished. Levy [39] discovered that the hot gas bubble from an extinguished flame can continue to rise at the same velocity as the flame for as much as 150 mm before breaking up. This suggests that if the tube used in limit determinations is sufficiently long, the thermocouple method will yield an accurate result. This is confirmed by close agreement between the flammability limit results measured by visible detection and thermocouples.

Results tabulated in Coward and Jones [15] indicated that usually, the limits may be narrowed slightly by the normal levels of humidity present in the air at low to moderate temperatures. At higher temperatures, where large amounts of water vapor may be present in the air, this effect may be considerable [15]. The main exception to this rule is carbon monoxide, which exhibits the opposite tendency. Even small to moderate quantities of water vapor widen the flammable range of carbon

monoxide considerably. Water vapor is a catalyst in the oxidation reaction of carbon monoxide and as a result, it is much easier to ignite when some water vapor is present [15].

Various studies [4,7,10,14,15,36,41,49,50,65,70] have investigated the effects of adding different inert diluent gases to the fuel/air mixtures. Addition of inerts change the thermodynamic and mass transport properties of the mixture and hence affects the energy and mass flow to and from the flame. As the amount of diluents in the mixture increases, the limits of a given fuel approach each other and eventually meet at a point, beyond which the mixture is no longer flammable. The effectiveness of a diluent in reducing the flammable range of a fuel depends on such properties as heat capacity, and the thermal and mass diffusivity of the diluent in question.

The topic of diluent additions has been an area of increasing interest in recent years. This has been prompted by the rapid rise in the availability and use of "low-Btu" gases from such sources as coal gasification, landfill gases, and in situ combustion of fossil fuels. Prediction of flammability limits for fuel mixtures containing diluents is very important for safe industrial use of these gas mixtures. Occasionally, it is desirable to add enough inert diluents to a combustible gas to make it non-flammable in air in any proportion. Sometimes the opposite effect is required and a fuel such as methane will be added to a non-flammable gas mixture containing some proportion of flammable gases to allow the gas to be safely utilized [24]. Empirical methods of predicting the limits of fuel mixtures containing diluents have been discussed in several publications [7,14,24,49,65].



Le Chatelier's rule [38] is a simple and commonly used method of predicting the flammability limits of fuel mixtures from knowledge of the mixture composition and the flammability limits of the component gases. The rule assumes that a mixture of limit fuel/air mixtures is also a limit mixture (i.e., the fuels in the mixture do not interact during combustion and so they combust separately). The formula is as follows:

$$L_m = 100 / \sum_{i=1}^n (Y_i / L_i) \quad (2.1)$$

where ,

$L_m$  is the calculated flammability limit of the mixture, % by volume.

$L_i$  is the flammability limit of the  $i^{\text{th}}$  fuel component, % by volume.

$Y_i$  is the volumetric fraction of the  $i^{\text{th}}$  fuel component in the fuel mixture, % by volume.

Numerous tests by various investigators [7,14,15,24,38,63,64,70] have established that this rule is fairly accurate in predicting the rich and lean limits of a wide variety of fuel mixtures. Recent investigations [14,24,63,64] have indicated that in some instances, particularly with rich mixtures, the formula is not as accurate as previously described.

Another method for prediction of lean limits suggested by White [62], makes use of the fact that the lean limit mixtures of many hydrocarbons have similar values of calculated adiabatic flame temperatures. If a value of calculated adiabatic flame temperature is assumed, it can be used to calculate the limits of various hydrocarbons. The resulting calculated

limits has been discussed in the literature [15,44,70], and the accuracy seems to depend a great deal on the data used.

## 2.2 Recent Developments

Recently, researchers have conducted flammability tests in large scale apparatus to determine if they corroborate the results from smaller scale tests [10,29]. The results from these tests for methane and hydrogen agree quite well with those obtained by researchers using the standard U.S. Bureau of Mines flammability tube.

Optical studies using Laser Doppler Anemometry and Schlieren photography have provided insight into the mechanisms of flame extinction during upward and downward flame propagation [31,37,39,52,57]. Utilization of these methods under micro-gravity conditions has led to confirmation of the importance of radiative heat loss in the extinguishment process.

Although it has not been possible to predict flammability limits from a completely theoretical basis, a multitude of models on flammability limits have been developed. These models are usually based on one of the following: chemical kinetics, heat loss by radiation, conduction or convection, and flame stretch, [3,5,9,25,26,27,28,31,34,37,43,52,55,57]. The approach used in the bulk of these models is to choose what is considered to be the most important factor and then develop a system of equations, which is later solved to calculate the limiting flame speed. This is usually a difficult and time-consuming exercise and seldom yields calculated flame speeds that agree closely with those determined experimentally. The diversity of the models and their corresponding

predictions has led researchers to conclude that if an accurate model is ever developed, it will have to include most of the factors used in the various models.

Because of the failure in prediction of flammability limits theoretically, several empirical methods have been developed by various researchers [18,30,35]. These calculations employ physical and chemical data in correlations to predict the lean flammability limits of various fuels. The resulting limits usually have fair accuracy within the specified range of fuels, but it decreases for fuels not included in the original correlation, or when the initial conditions of the fuel/air mixture are changed.

### 2.3 Summary

As suggested in Chapter 1, a review of the available literature indicates that there is a lack of information on the flammability limits of the majority of commonly used fuels in air at temperatures below 25°C. There is also a considerable need for consistent data on the flammability limits of various fuels at high pressures, obtained at constant pressure. The theoretical models should continue to be developed, but attention should also be directed towards evolving improved methods of flammability limit prediction, using available empirical results.

## CHAPTER 3

### APPARATUS AND EXPERIMENTAL PROCEDURE

#### 3.1 Introduction

A very large number of flammability limit experiments have been performed to date by many researchers using a wide variety of apparatus designs. This vast field of equipment designs has evolved over the years into a few distinct styles that have become standards used to measure flammability limits under different conditions.

For this study, it was important that the apparatus, once constructed, would be easy to use, flexible, efficient, and could furnish precise temperature control down to moderately low temperatures of  $-60^{\circ}\text{C}$  or even lower. After consideration of these specifications, the original concept of housing the entire apparatus in an available refrigerated room was abandoned in favor of a tube with a self-contained cooling system.

Because this apparatus was to be used specifically to study flammability limits at low temperatures, the design was based on the flame tube developed by U.S. Bureau of Mines researchers such as Burgess et al. [11]. Their tube has been used as a design standard in much of the experiments on flammability limits at higher temperatures.

The new flame tube and associated ignition and cooling systems were mounted on a control panel alongside the existing flame tube that was used in previous studies [7,14]. This was done in order that some parts of the old system such as the ignition transformer, valves, manometers, and readouts could be used with the new apparatus.

The schematic diagram of the experimental set-up is shown in Figure

3.1.1, and a photograph of the actual apparatus in Figure 3.1.2. These show the general layout of the equipment.

### 3.2 Flame Tube

The flame tube used was similar in design to that used by the U.S. Bureau of Mines to test flammability limits. Previous work has shown that for many fuels, tube diameter has little or no effect on the limits of flammability at an initial temperature of 25°C, determined in tubes of 51 mm diameter or greater [4,15,33,42,48,58,70].

It was decided that dimensions of 51 mm x 1 m would also be used for the new flame tube, so that results could be compared directly with those from other studies. The flame tube was constructed from a one metre length of smooth, 304 stainless steel tubing with an inside diameter of 50.8 mm (2 in.). Flanges were silver soldered to the top and bottom to allow the ends to be sealed with threaded caps. The bottom cap contained feedthroughs for the ignition system as well as a large vent tube with a valve to allow the test to take place at atmospheric pressure. Both caps also had a fitting for the tubes that connected to the mixing chamber and vacuum pump, so that the tube could be filled or evacuated from the top and bottom simultaneously.

Ignition electrodes were located at the bottom of the tube, and a concentric copper tube was slipped around the flame tube and silver soldered in place to facilitate the mounting of the cooling system.

Considerable sealing problems were encountered when the tube was cooled to low temperatures. These leaks had to be located at only moderately low temperatures because the available leak detecting fluid

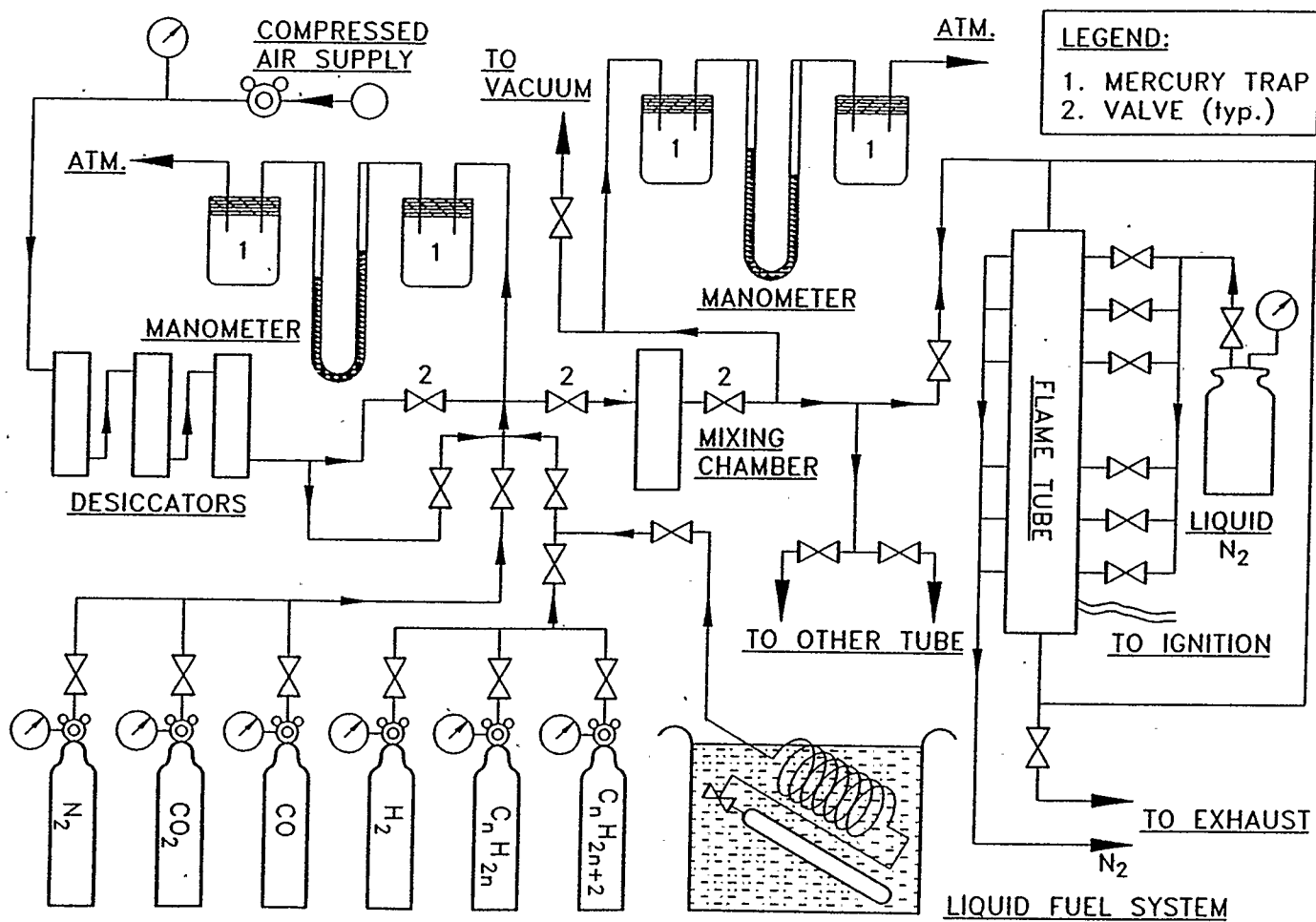


Figure 3.1.1 - Schematic Diagram of the Apparatus



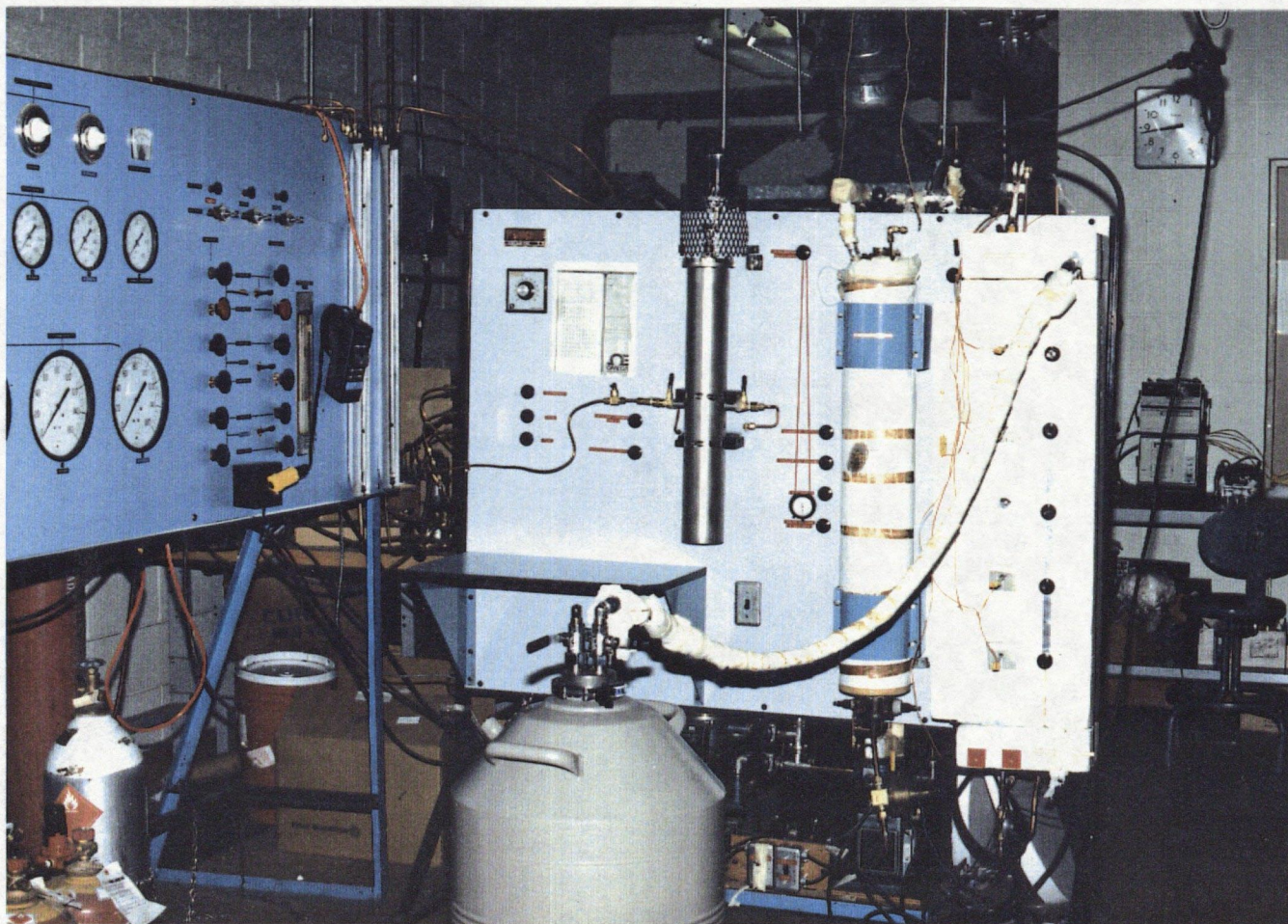


Figure 3.1.2 - Photograph of the Experimental Apparatus.



with the lowest freezing point, would freeze at  $-54^{\circ}\text{C}$ . Leaks were found at the gaskets that sealed the top and bottom caps and also the ignition feedthroughs in the bottom cap. Various gasket materials were tried, with limited success, until it was found that the application of vacuum grease to the cap threads and ignition feedthroughs stopped the leaks. This also made it easier to service the ignition system, because previously it had been necessary either to make a new gasket, or to anneal the old one, every time the bottom cap was removed.

### 3.3 Ignition System

Ignition of the test mixture was obtained by an electric arc passed between two horizontal, conical, tungsten electrodes that were centred in the tube, 35 mm from the lower end. The electrode gap size was adjusted using set screws in the ceramic (lava) blocks supporting the electrodes. A cutaway of this system is shown in Figure 3.3.1 along with the flame tube and liquid nitrogen cooling system.

High voltage power to the electrodes was supplied by a 10 kV, 23 mA, current limited, centre-tapped transformer. Power for the primary was obtained from the 60 Hz AC mains supply, with a measured voltage of 123.7 V. The spark duration was controlled by the use of an interval timer. A schematic diagram of the ignition circuit is given in Figure 3.3.2.

A different electrode arrangement was used in the previously existing flame tube [7,14], in which glass coated, stainless steel electrodes passed through nylon insulators placed in the tube wall. This had the advantage that the electrode gap could be adjusted without removing the bottom of the tube. One problem experienced with this design was vacuum



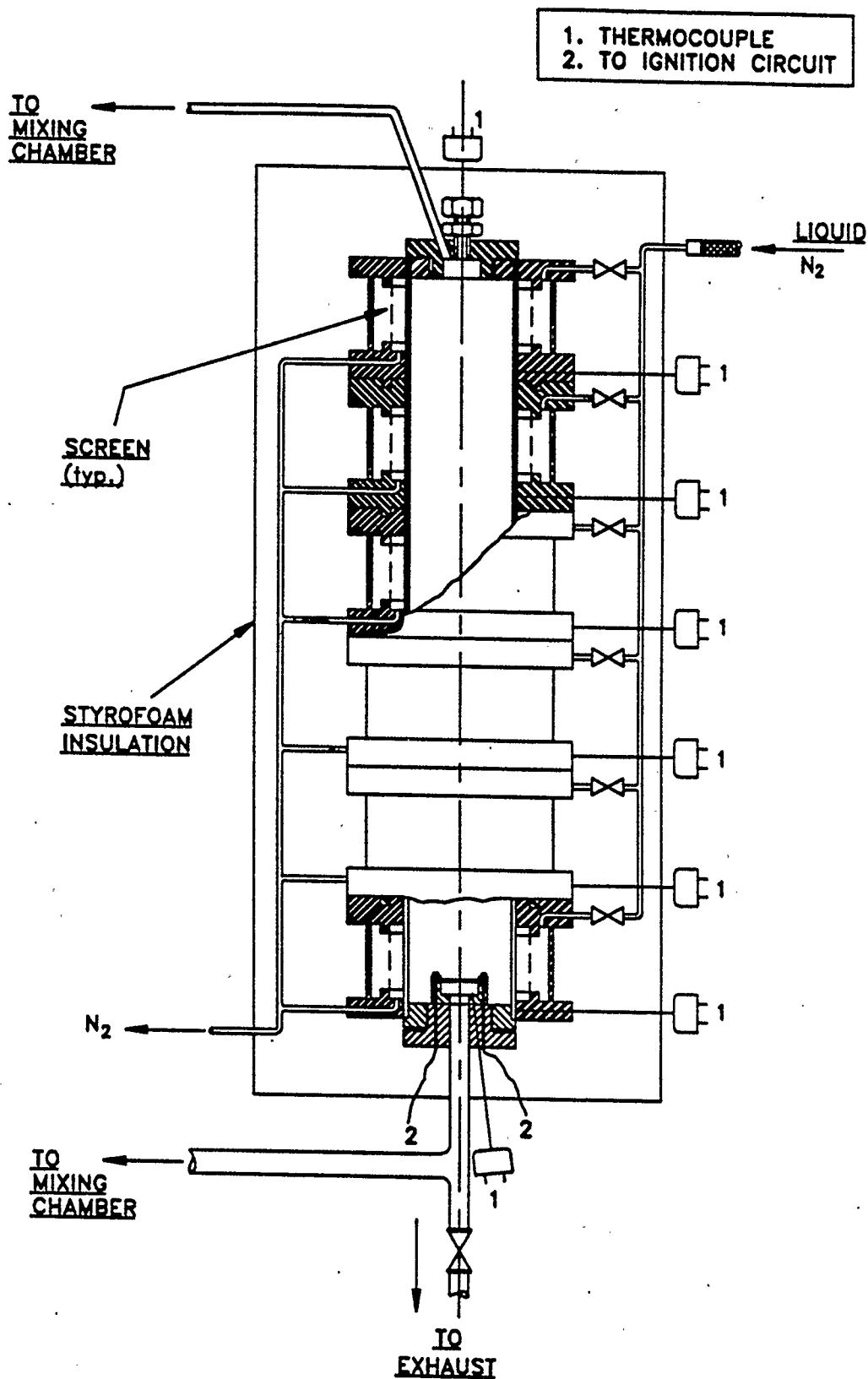


Figure 3.3.1 - Cross-Section of Flame Tube and Associated Cooling System

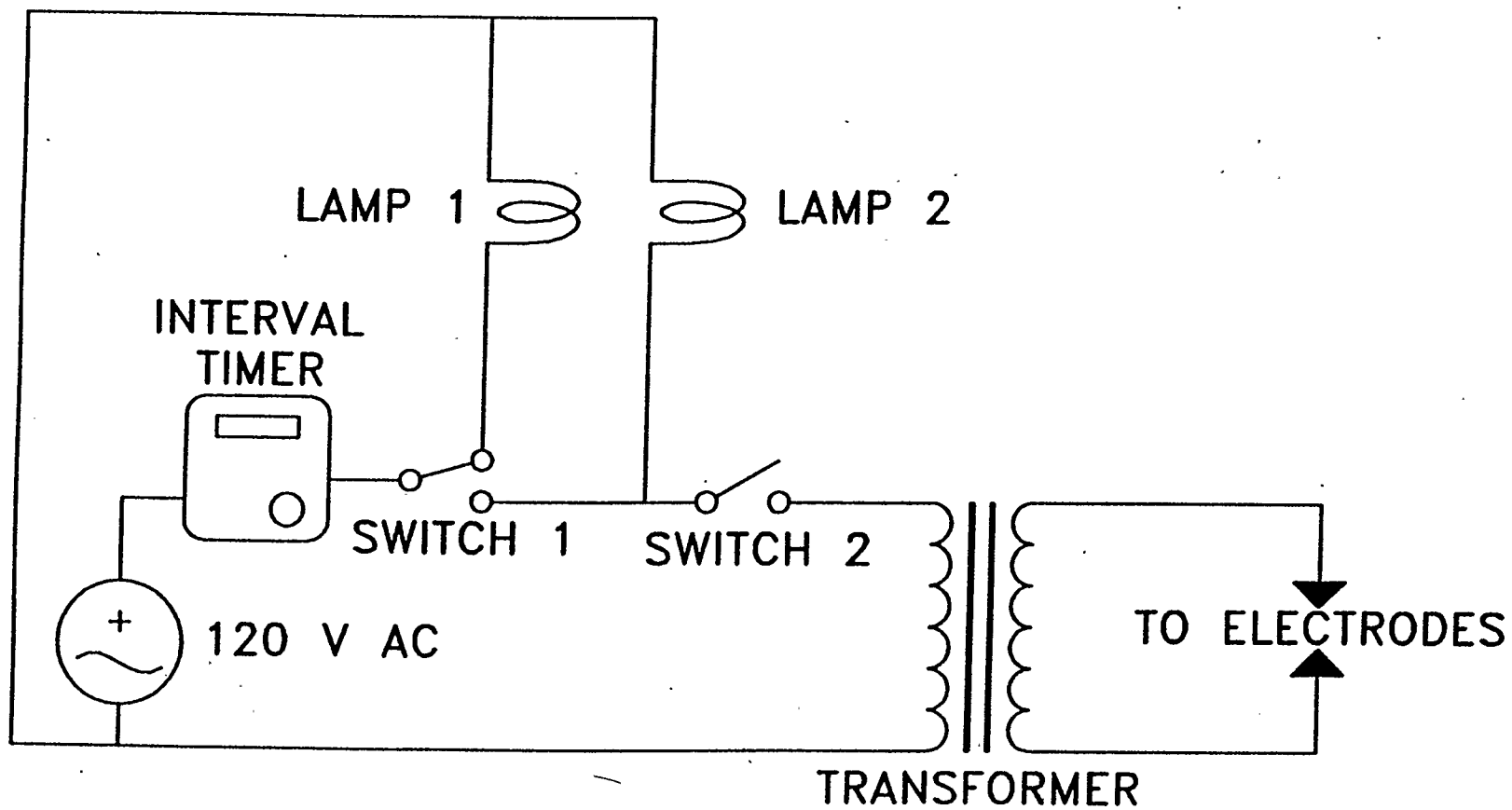


Figure 3.3.2 - Schematic Diagram of the Ignition System

leakage at low temperatures because of the uneven contraction of the different materials. Accordingly, a new electrode arrangement with both electrodes located inside the flame tube was chosen for the new tube because it was thought that it would solve this problem, as well as reduce heat transfer from the room to the cold flame tube. The transformer in this system was the same as that used in the previous tube [7,14].

Since research on ignition systems [4,6,8,15,21,46,70] has suggested that there is an optimum electrode gap, it was decided that the gap should be optimized for this system at 23°C. Because of the difficulty in adjusting the electrode gap in the new apparatus, the tube from previous studies was used for these tests. The gap size was varied from 2.5 to 20 mm, and the results for the rich limits are shown in Figures 3.3.3 and 3.3.4. Tests were also performed for the lean limits, but they showed that the lean limits are independent of the gap size in this apparatus over the range tested. Tests on the rich limits indicated that the limits decrease at gap sizes less than 6 mm. It is likely that this is caused by quenching of the flame kernel by the electrodes, because the gap size is approaching the quenching distance [4]. At the 20 mm gap size setting, the results in the first series of tests were not repeatable. Operation of the ignition system at this gap size without the bottom cover-plate on the tube demonstrated that the electrodes would periodically arc to ground (the tube wall) instead of each other. It was also noted that the rich flammability limits of some fuels began to drop at gap sizes greater than about 7 to 10 mm. From these tests, it was concluded that a 6.5 mm gap would be large enough to avoid quenching effects, while avoiding arcing problems, so it was used in the new ignition system. Although it may be

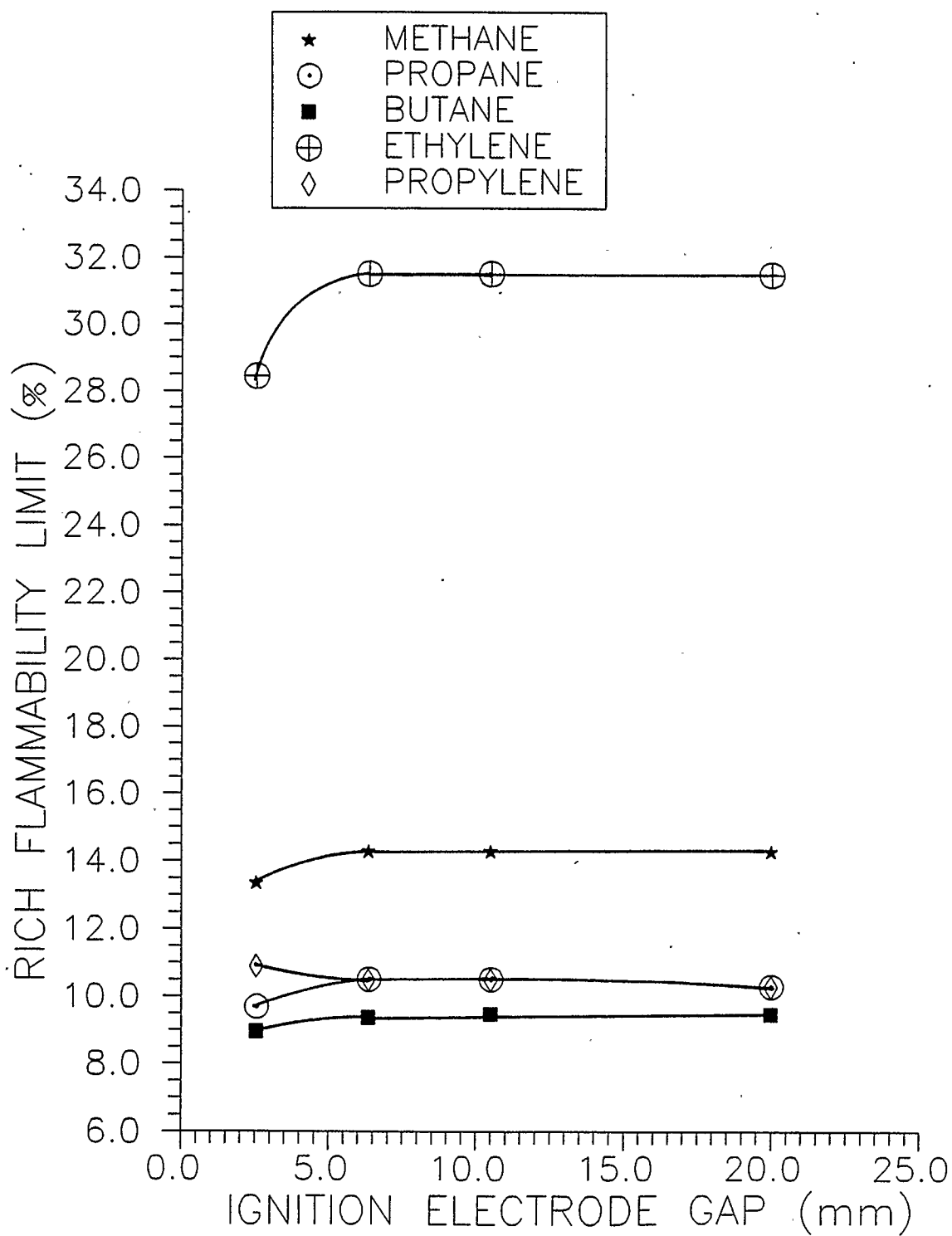


Figure 3.3.3 - The Effect of Ignition Gap Size on Rich Flammability Limits of Various Hydrocarbons in Air at 23°C

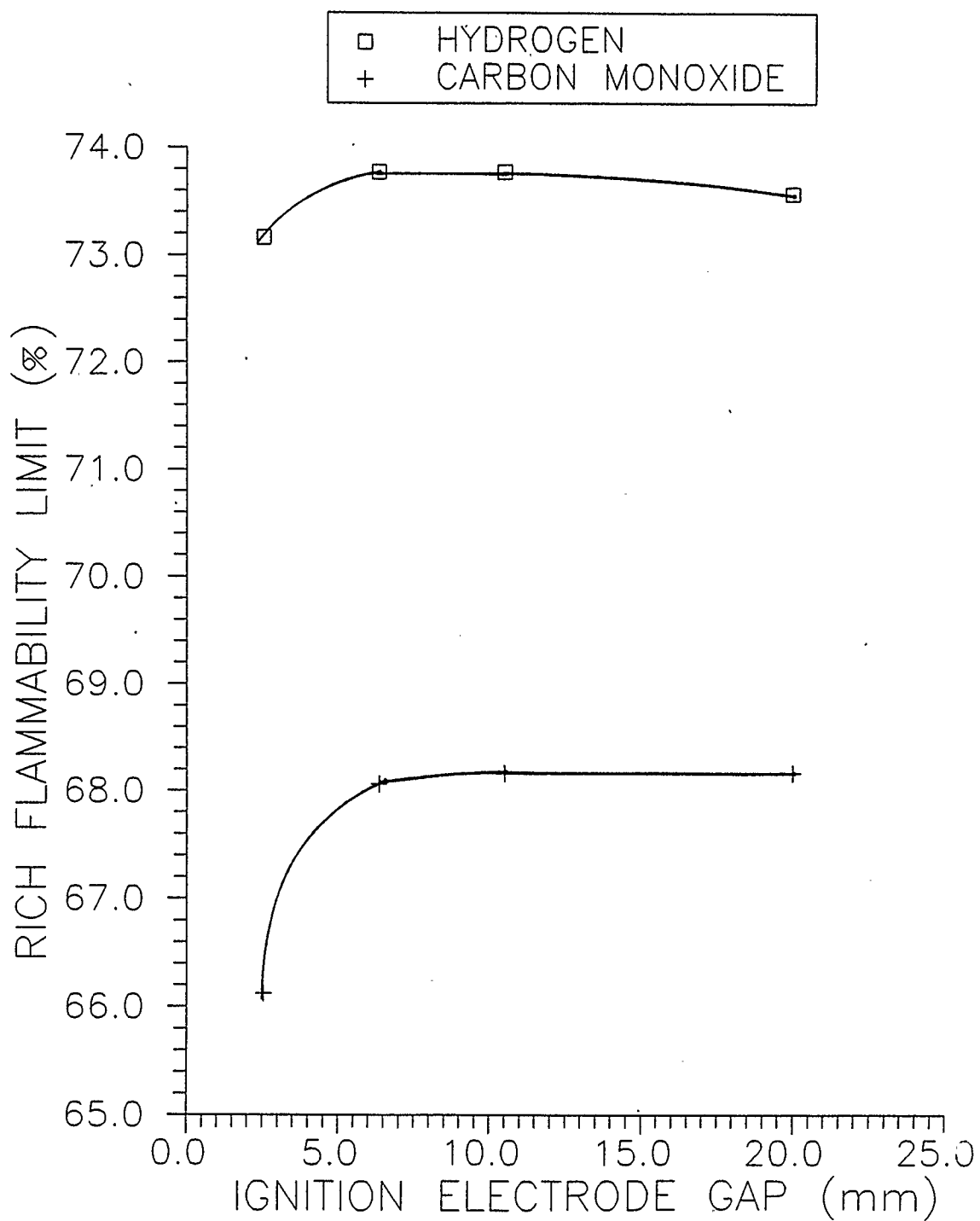


Figure 3.3.4 - The Effect of Ignition Gap Size on Rich Flammability Limits of Hydrogen and Carbon Monoxide in Air at 23°C

that a slightly larger optimum gap size is needed at lower temperatures, it was decided that the gap size should be kept constant regardless of initial temperature, in order to reduce the number of variables being changed.

### 3.4 Cooling System

Cooling systems used in past low temperature experiments [7,11,58, 67], consisted of a perforated tube wrapped around the flame tube. Insulation was placed around this system and liquid nitrogen was circulated through the tubing. This method suffered from poor temperature control along the length of the tube and also restricted flow of liquid nitrogen because evaporated nitrogen was vented through the insulation. Since the new tube was to be used exclusively for low temperature studies, an improved system was needed.

The new system consisted of two annuli constructed from copper tubing, and spaced concentrically around the flame tube with brass rings. Each annulus was divided into six chambers of equal length. The liquid nitrogen flow to each outer chamber could be controlled independently. Once the liquid nitrogen was in the outer chamber, it was sprayed through fine holes in the tubing into the inner chambers. After evaporating and cooling the flame tube wall, the nitrogen gas was vented from each chamber through an exit pipe.

Liquid nitrogen was stored in a 50 l dewar flask, from which it was supplied to the cooling system through a 25 mm braided stainless steel hose. This hose was connected to the top of the cooling system because this resulted in better liquid distribution than when mounted at the

middle or bottom.

Heat transfer to the system was reduced by covering the cooling system with 50 mm of foam insulation. This necessitated the lengthening of the stems of the liquid nitrogen control valves by 50 mm. Typically, the consumption of liquid nitrogen was approximately one litre per test at  $-60^{\circ}\text{C}$ . Most of the heat transfer to the tube came from room temperature air moving from top to bottom between the insulation and the cooling system. This air movement was visible as a steady stream of mist from the bottom of the insulation, but could not be prevented because the cooling system had to be accessed for occasional maintenance. A pressure of approximately 70 kPag was needed in the dewar to supply an adequate liquid nitrogen flow rate. The cross-section of the cooling system is shown in Figure 3.3.1, along with the flame tube.

### 3.5 Mixing Chamber

The mixing chamber in the system, used by Boon [7] and Cheng [14], had to be filled twice to provide enough fuel/air mixture to fill the flame tube to a pressure slightly above atmospheric pressure at  $23^{\circ}\text{C}$ . Three or more fillings of the mixing chamber were required at lower temperatures. Because the method of determining flammability limits is by trial and error, several thousand tests were to be performed during the course of this research. Any reduction in the number of steps in the process of preparation of the fuel/air mixture would not only reduce experimental time, but also reduce the number of opportunities for errors in measurement.

Accordingly, a new mixing chamber was designed, choosing a volume such that when it was filled to the maximum working pressure of the mercury manometer (89 kPag), it would contain enough gas to fill the flame tube to atmospheric pressure at  $-70^{\circ}\text{C}$ . The resulting mixing chamber had a volume of 4.3 l and was constructed from 100 mm diameter stainless steel tubing.

Many other systems [7,14,15,38,58,62,67] have relied on diffusion or turbulence during filling to provide a homogeneous fuel/air mixture. Other experimenters [49] have noted that the degree of mixing is one of the more important factors influencing premixed flammability limit results. Variation in preliminary experimental results, especially those of tests employing gases of widely varying densities, suggested that a more vigorous, consistent, and reliable mixing method was needed.

The first mixing method considered was a spinning bar magnet driven by a magnetic stirrer outside the mixing chamber. Another possibility was fitting the chamber with a feedthrough that would allow an internal propeller to be driven from outside the mixing chamber. Driving a propeller with an electric motor inside the mixing chamber was not considered because of the possibility of accidental ignition.

Experiments using smoke were conducted to visually determine the effectiveness of various stirring methods. Since testing showed that the propeller was the better method, the chamber was fitted with the system shown in Figure 3.5.1. Two plastic, 90 mm, four blade propellers were mounted on the rotational motion feedthrough, which was in turn driven at 500 rpm by an electric motor/pulley system. The shaft of the feedthrough was supported by ball bearings and sealed with a small rubber O-ring that



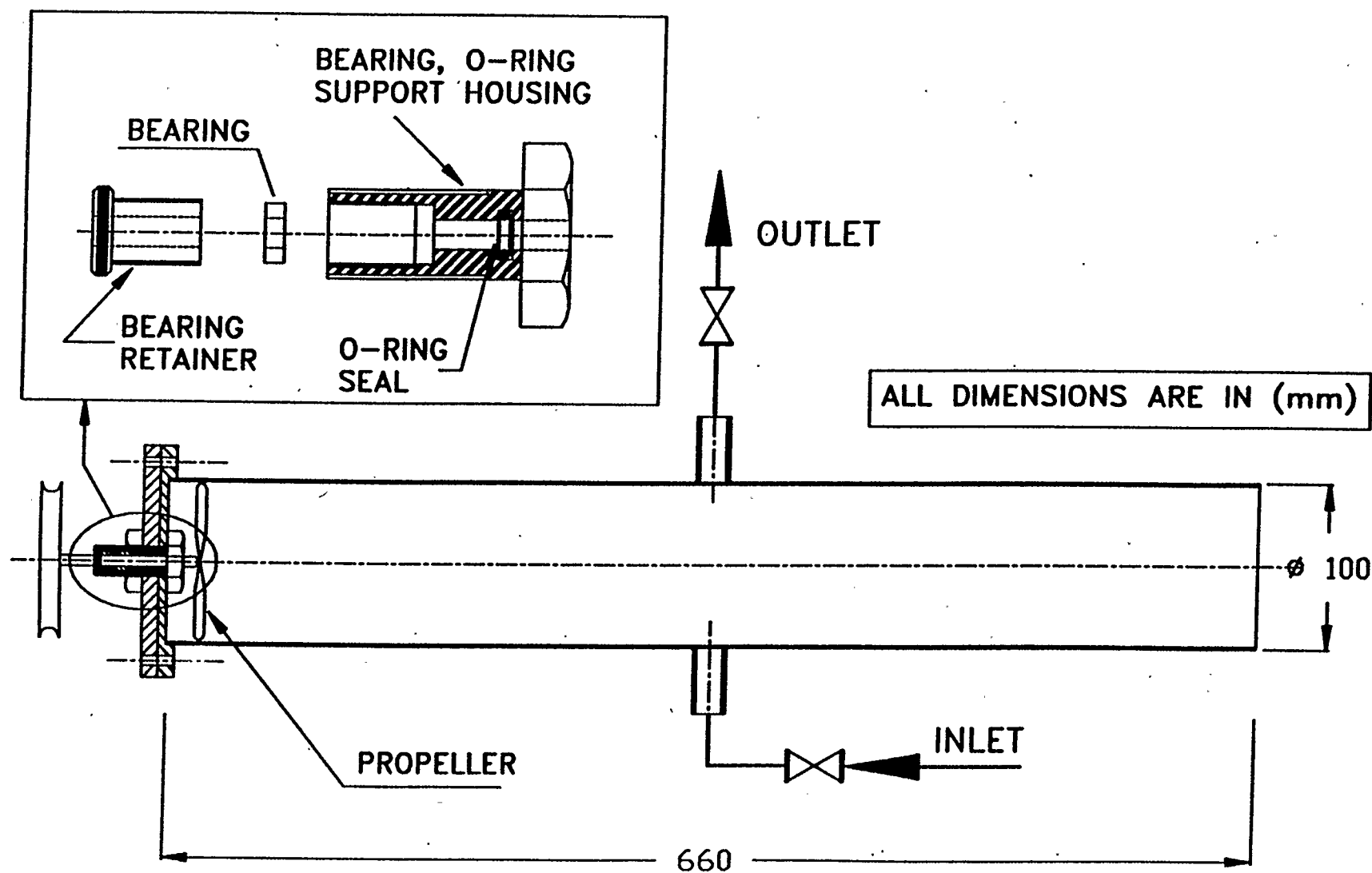


Figure 3.5.1 - Cross-Section of the Mixing Chamber

had to be changed periodically. Tests that were run after installation of the mixing system showed that five minutes of mixing provided very repeatable experimental results.

### **3.6 Fuel/Air System**

#### **3.6.1 Gaseous Fuel System**

The gaseous fuel system was used with any fuels that were gaseous at room temperature and pressure. Since only binary fuel mixtures and pure fuels were to be studied in this phase of the research, only two fuel lines were connected to the mixing chamber. At the mixing chamber inlet, there was a valve for air, as well as the two fuel valves. Air supplied from a compressor flowed through an oil/water separator and then into three 67 mm x 290 mm calcium sulfate desiccators hooked up in series. Originally, only one desiccator was used, but initial tests on the carbon monoxide lean limit yielded widely varying results. It has been shown [14], that the lean flammability limit of carbon monoxide is very sensitive to water vapor content, which suggested that the humidity of the air supply was inconsistent. Further experimentation produced the system with three desiccators and a limit on the maximum flow rate of air of 4 l/min, which was sufficient to give good repeatability.

Each fuel line was hooked up to its own manifold with valves for three gas bottle/regulator lines. This reduced the need to constantly disconnect and connect gas bottles. The gaseous fuels used in this research are listed in Table 3.6.1, along with their declared purities. Inert gases that were used in the fuel mixtures are also included.

### 3.6.2 Liquid Fuel System

Although the primary task was to investigate the flammability limits of gaseous fuels, a limited number of tests were conducted with liquid fuels. In order to test the flammability limits of fuels that were in liquid form at room temperature and pressure, one branch of the fuel line was connected to a system designed to vaporize liquid fuels. The liquid evaporator consisted of a 0.2 l aluminum cylinder, submerged in a 20 l bucket of room temperature water, to prevent the fuel in the cylinder from being cooled by evaporation to a point where it did not have adequate vapor pressure to supply the required partial pressure for preparing the fuel/air mixture. To ensure that the fuel vapor was at room temperature when the partial pressure was measured, a coiled 2 m length of 6.3 mm (0.25 in.) copper tubing connected the cylinder to the fuel line.

Table 3.6.1 - Purity of Gases Used.

Gas	Purity(%)
Methane	99.99
Ethane	99.9
Propane	99.5
Butane	99.95
Ethylene	99.9
Propylene	99.9
Hydrogen	99.95
Carbon Monoxide	99.9
Carbon Dioxide	99.8
Nitrogen	99.9

### 3.6.3 Vacuum System

System evacuation was achieved with a vacuum pump capable of providing a vacuum down to 1% of atmospheric pressure. Valves were installed in each part of the system, so that specific sections of the apparatus could be evacuated independently.

## 3.7 Instrumentation

### 3.7.1 Thermocouples

A set of stainless steel sheathed, grounded, chromel-alumel (ISO type-K), 1.6 mm thermocouples was used to monitor the temperature of the flame tube wall in each cooling chamber. In addition, two similar, but unsheathed thermocouples were used to observe the gas temperature at the centre of the top and bottom of the tube. Shielded thermocouples had been tried, but they were not sensitive enough to detect the lean limit hydrogen flame, and did not accurately measure the gas temperature when the gas was not in thermal equilibrium with the tube wall. Heat transfer from the unshielded thermocouples to the tube was further reduced by changing the connectors from brass to nylon. An extra unshielded thermocouple was used to check the gas temperature at the centre of the tube during initial tests to assure that the gas temperature was uniform along the entire tube length. It was removed after these initial tests, because it projected into the path of the flame.

### 3.7.2 Pressure Measurement

Gas pressure was monitored in the mixing chamber with a mercury differential manometer. Pressure in the flame tube was found using a similar manometer. Because of limitations in the accuracy of pressure

measurements from the manometer, actual accuracy in fuel composition was estimated to be  $\pm 0.1\%$  with respect to the total mixture. Accordingly, limits for all fuels were only determined to one decimal place. The maximum pressure that could be used with these manometers was 89.0 kPag.

### 3.8 Safety Equipment and Precautions

Safety was the most important consideration during all phases of the research. The outlet of the vacuum pump fed into an exhaust duct that removed the waste gases from the building. Flexible tubing led from the cooling system to the exhaust fan to remove the possibility of asphyxiation from the evaporated liquid nitrogen. Another length of tubing ran from the vent on the bottom of the flame tube to the fan to prevent flammable or toxic fumes from being released in the room.

Any time that a gas bottle was connected, all the fittings were checked carefully with a leak detecting liquid. If the apparatus was not in use, all the bottle valves were closed and the gas lines bled down to atmospheric pressure.

Mercury traps were installed on both sides of each manometer to prevent an accidental pressure fluctuation from contaminating either the apparatus or the room with mercury.

A micro-switch was fitted to the vent-valve at the bottom of the tube to prevent the ignition from being activated when the valve was closed.

### 3.9 Experimental Procedure

#### 3.9.1 Initial Conditions

All tests were carried out at atmospheric pressure, which had an average value of  $88.8 \pm 1.6$  kPa. All room temperature tests were performed at 23°C. Manipulation of the cooling system prevented any fluctuations in actual room temperature from affecting the tests at 23°C.

#### 3.9.2 Gaseous Fuel Procedure

The atmospheric pressure was recorded and used to calculate the partial pressures of each fuel component in the desired mixture composition. When a bottle was first hooked up, the gas was allowed to flow through the system to purge impurities from the flow line. Before each run, the entire system was evacuated and filled with air three times to ensure that the residual gas in the evacuated system consisted only of air.

The valves connecting the mixing chamber to the flame tube and vacuum supply were closed. Gases were added to the mixing chamber in the following order: combustible fuels, inerts, and finally air. Air was introduced to the mixing chamber slowly (at a flow rate of four l/min) to keep the air humidity consistently low. Proportions of each component were measured by reading the partial pressure on the mercury manometer. After each component was added to the mixing chamber, fuel lines were evacuated and flushed out with the next gas to be used. This purging procedure was done three times to ensure that successive gases were as pure as possible. After the correct quantities of each gas had been added to the mixing chamber, the gases were mixed for five minutes.

Flame tube temperature was controlled by adjusting the flow of liquid nitrogen to each of the six chambers around the tube. The tube temperature was lowered to a few degrees less than the desired test temperature just before filling with gas from the mixing chamber. The gas mixture was permitted to flow from the mixing chamber to the flame tube until the pressure in the tube was slightly above atmospheric. The valve between the mixing chamber and flame tube was then closed. Flame tube temperature was controlled to within  $\pm 1^\circ\text{C}$  of the nominal test temperature along its entire length. This temperature was maintained for ten minutes to allow the gas turbulence to recede, and for the gas to reach thermal equilibrium with the tube wall.

When both the flame tube and gas temperature were within  $\pm 1^\circ\text{C}$  of the test temperature, and the tube pressure was slightly above atmospheric, the valve at the bottom of the tube was opened slowly and carefully to allow the test to take place at atmospheric pressure. Ignition was initiated by activating the interval timer, while the top and bottom thermocouple readings were monitored. A sudden increase in the bottom thermocouple reading indicated the initiation of a flame kernel around the igniter, while a sudden rise in the top thermocouple reading marked arrival of the flame at the top of the tube.

The entire procedure was repeated for various mixture compositions until a point was found where the flame would not propagate the length of the tube, but propagation had been achieved in a mixture with 0.1% by volume more fuel for lean limits or 0.1% by volume less fuel for rich limits. Once this point was determined, two more tests were performed. A mixture was only considered to be non-flammable if the flame would not

propagate the entire length of the tube in any of the three tests. No attempt was made to determine the flammability limits to a greater accuracy than 0.1% by volume. For each fuel, the minimum spark duration was used that would still provide a detectable ignition in a mixture that was at the flammability limit. Vapor pressure data was used to verify that at each flammability limit composition, the entire fuel/air mixture was in the gaseous phase. This was done by ensuring that the partial pressure of the fuel in the fuel/air mixture was less than the vapor pressure at the temperature and pressure in the flame tube.

The criterion of three non-propagating tests was chosen to keep experimental time and liquid nitrogen requirements to a minimum while accounting for the probabilistic nature [7,14] of flammability limits. Even with this criterion, an average of eight hours of experimental time was needed to determine each flammability limit. A number of experiments were also repeated to verify their repeatability.

### 3.9.3 Liquid Fuel Procedure

The procedure for liquid fuels was similar to that for gaseous fuels except that the liquid system fuel line was used. Before the test, the fuel bottle was filled with liquid fuel and placed in a bucket of room temperature water. Because this system was at less than atmospheric pressure, any leaks would allow air to contaminate the fuel. Before the initial test of each fuel, the fuel system pressure was monitored for two hours to check for leaks. When transferring fuel to the mixing chamber, the partial pressure was increased very slowly to allow the pressure measurement to be taken at atmospheric temperature. Except for the above steps, the procedure was identical to that for gaseous fuel.



## CHAPTER 4

### RESULTS AND DISCUSSION

#### **4.1 General**

All flammability limit tests were performed for upward flame propagation, with dry air and fuels, and at atmospheric pressure. A minimum value of ignition spark duration was used that would provide a detectable ignition at the measured limit and was normally 0.2 seconds unless otherwise specified. Both rich and lean limits of flammability were determined over the temperature range from 23°C to -60°C.

Lean limits were found for a variety of pure fuels and these results are discussed in Section 4.2. The rich limits of these same pure fuels are included in Section 4.3. Sections 4.4 and 4.5 contain lean and rich limits determined for mixtures of some binary combinations of the pure fuels. Finally, the last two sections in this chapter, Sections 4.6 and 4.7 examine the lean and rich limits of some methane/diluent mixtures.

#### **4.2 Lean Flammability Limits of Pure Fuels**

Lean flammability limits of pure fuel/air mixtures were determined for the following fuels: methane, ethane, propane, butane, ethylene, propylene, hydrogen, and carbon monoxide. The range of low temperature was extended to -100°C for tests with hydrogen as a fuel. The results are presented in Table 4.2.1 and also in Figures 4.2.1 and 4.2.2. The lean flammability limits of the fuels in Figure 4.2.1 changed very little as the temperature dropped. This was also true for the hydrogen lean limits plotted in Figure 4.2.2, particularly when compared to the carbon monoxide

lean limits which changed substantially. The percentage changes in the lean limits with the reduction of the initial mixture temperature from 23°C to -60°C for the fuels in Table 4.2.1 are given in Table 4.2.2. Although there does not appear to be a great difference in the rate of change of the lean limits for the various gases in Figure 4.2.1, the differences are apparent when the rate of change is expressed as a percentage as in Table 4.2.2.

A lean flammability limit determination was also made for carbon monoxide at 23°C in air saturated with water vapor for comparison with the results obtained in dry air. The resulting lean limit was 12.4% versus 14.1% for carbon monoxide in dry air.

Table 4.2.1 - Lean Flammability Limits of fuels.

Fuel	Experimental Lean Flammability Limit % by Volume			
	Initial Mixture Temperature °C			
	23	0	-30	-60
Methane	5.0	5.1	5.3	5.4
Ethane	2.8	2.9	3.0	3.1
Propane	2.1	2.2	2.3	2.4
Butane	1.7	1.8	1.9	2.0
Ethylene	2.8	2.9	3.0	3.1
Propylene	2.3	2.4	2.6	2.7
Hydrogen	3.9	-	4.0	4.1
CO	<sup>1</sup> 14.0	<sup>1</sup> 14.9	<sup>1</sup> 16.2	<sup>1</sup> 17.8

<sup>1</sup> An ignition spark duration of two seconds was used.

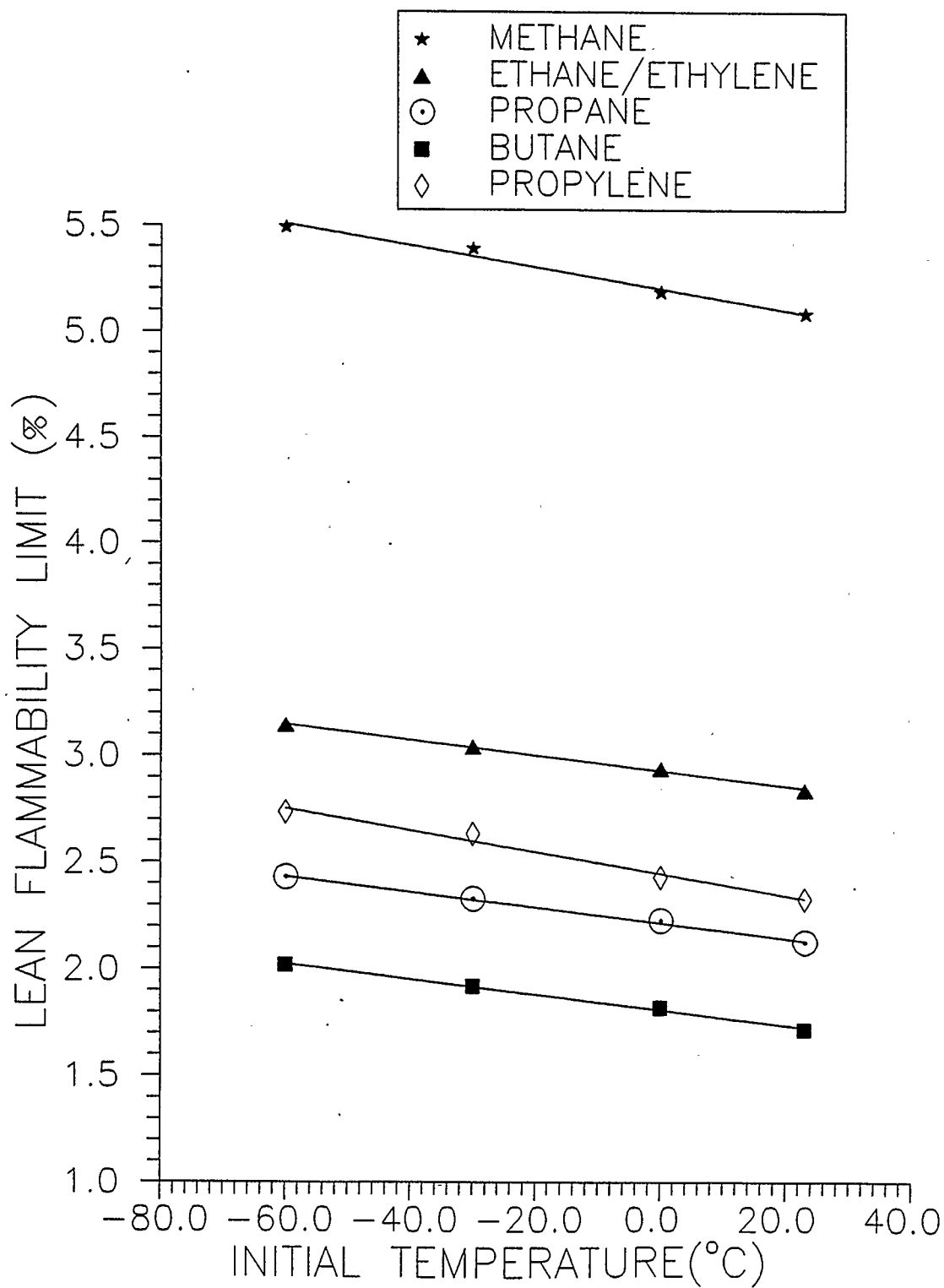


Figure 4.2.1 - Lean Flammability Limits of Hydrocarbon Fuels as a Function of Initial Temperature

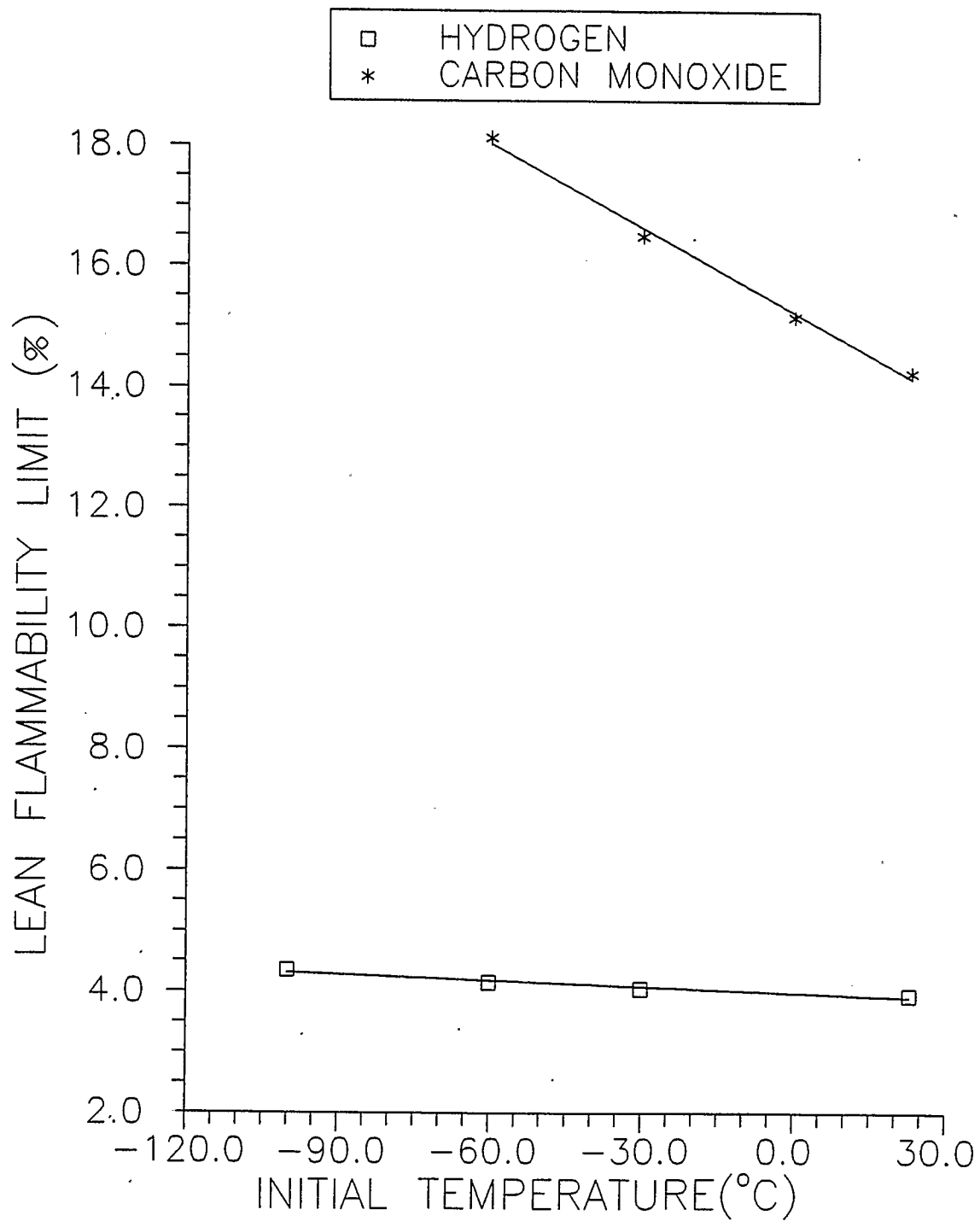


Figure 4.2.2 - Lean Flammability Limits of Hydrogen and Carbon Monoxide as a Function of Initial Temperature

Table 4.2.2 - Percentage Change of the Lean Limits of Pure Fuels With Initial Temperature Change From 23°C to -60°C.

Fuel	Change in Lean Flammability Limit With Initial Temperature Change (%)
Methane	8.0%
Ethane	10.7%
Propane	14.3%
Butane	17.6%
Ethylene	10.7%
Propylene	17.4%
Hydrogen	5.1%
Carbon Monoxide	27.1%

Ignition spark duration requirements changed from 2.0 seconds for carbon monoxide in dry air to 0.2 seconds when air with 100% relative humidity was used. This confirmed the fact that the humidity of the air is a very important factor to take into consideration if values of the lean limit for carbon monoxide quoted in the literature are to be used in practical situations.

Tests were performed on pentane, hexane, and heptane using the liquid fuel system, and the resulting flammability limits are given in Table 4.2.3.

The theoretical adiabatic flame temperatures of the lean limit mixtures were calculated using thermodynamic properties quoted in the literature [32,51,53,59]. Details of these calculations are given in

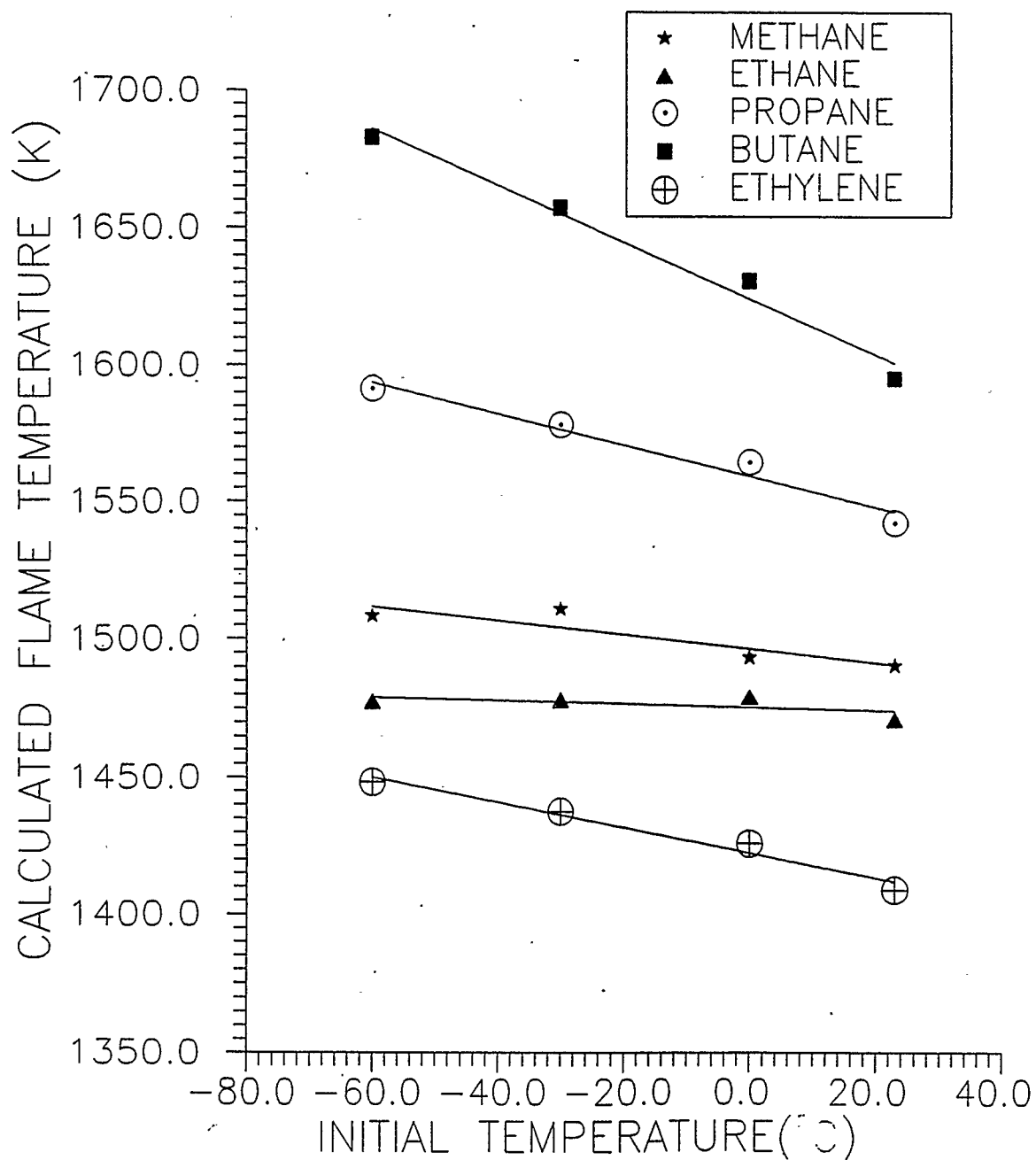


Figure 4.2.3 - Calculated Adiabatic Flame Temperatures of Lean Limit Mixtures of Hydrocarbon Fuels as a Function of Initial Temperature

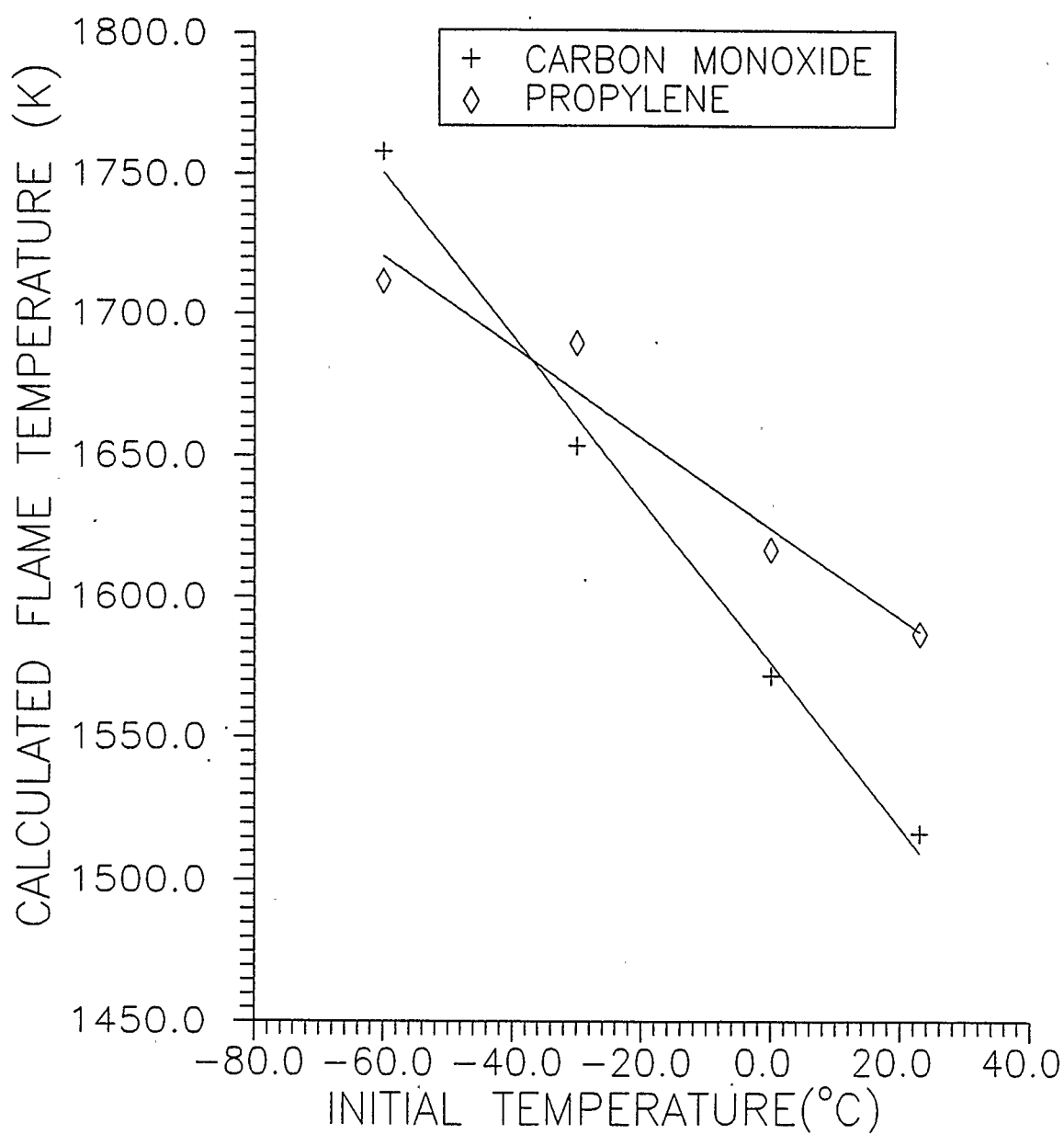


Figure 4.2.4 - Calculated Adiabatic Flame Temperatures of Lean Limit Mixtures of Carbon Monoxide and Propylene as a Function of Initial Temperature

Appendix A. These calculated flame temperatures are plotted in Figures 4.2.3, 4.2.4, and 4.2.5 as a function of initial temperature for the fuels that were tested. The flame temperatures were displayed in units of Kelvin (K) rather than degrees Celsius ( $^{\circ}\text{C}$ ) because this is the practice followed in most of the literature. Generally, the calculated flame temperature of the lean limit mixtures increased linearly as the initial mixture temperature was reduced, rather than being constant. This is probably a reflection of the increasing heat losses from the flame as the initial fuel/air mixture temperature was reduced, which raised the lean limits slightly, giving higher calculated flame temperatures. The sole exception to this trend was in the case of hydrogen as shown in Figure 4.1.5, which exhibited the opposite tendency. Confirmation of this phenomenon can be found in [62] from experiments on hydrogen at higher temperatures, although no explanation has been offered to date to rationalize the behavior of hydrogen in this respect. These results reinforce the contention of other investigators [27,44] who have suggested that flame temperature calculations for hydrogen are unrealistic and too low because of the hydrogen diffusion that occurs near the lean limit.

Table 4.2.3 - Flammability Limits Obtained at  $23^{\circ}\text{C}$  Using the Liquid Fuel System.

Fuel	Rich Limit %	Lean Limit %
Pentane	8.5	1.3
Hexane	8.2	1.1
Heptane	-	1.0



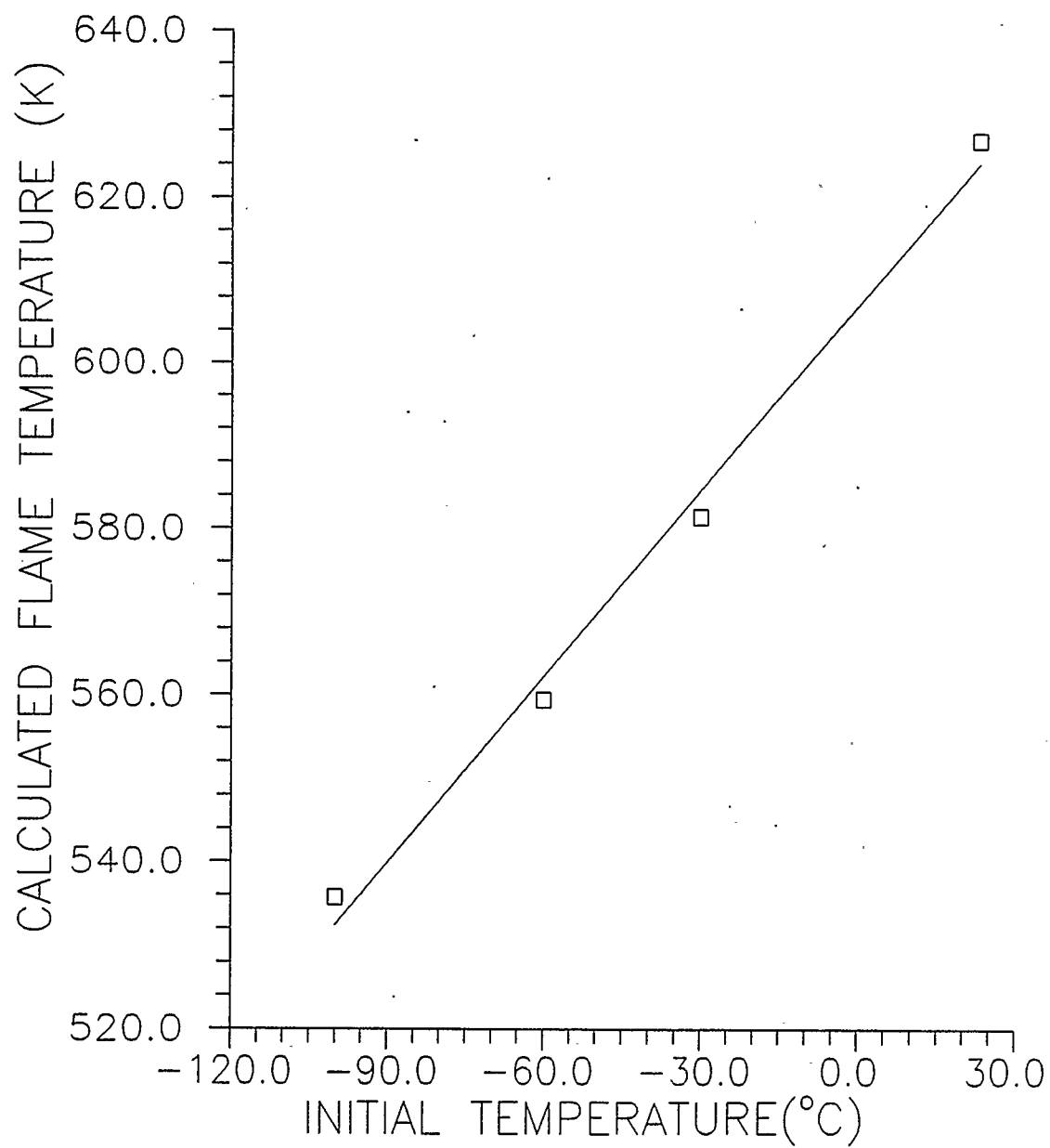


Figure 4.2.5 - Calculated Adiabatic Flame Temperatures of Lean Limit Mixtures of Hydrogen as a Function of Initial Temperature

It has been proposed by White [62], that the calculated flame temperature of one hydrocarbon lean limit mixture may be used to calculate the lean flammability limit of another hydrocarbon by assuming that it has the same limit flame temperature. The method was originally suggested because it was observed that the calculated flame temperatures of many hydrocarbon fuel/air lean limit mixtures fell in the 1400K to 1600K range. Inspection of Figure 4.2.3 confirms this observation. To evaluate this prediction method, the lean limit adiabatic flame temperature of methane at 23°C was used to calculate the lean limits of other fuels in the paraffin series up to and including heptane. Calculated lean limits of flammability are shown in Figure 4.2.6 along with lean limits determined experimentally. The accuracy of this method seems quite satisfactory as the difference between experimental and calculated limits was in the order of the experimental error. It is important to note, however, that this method should only be applied to mixtures having similar lean limit adiabatic flame temperatures and under the same conditions. Stoichiometric fuel/air mixtures are also plotted in Figure 4.2.6, and comparison shows that for most of the paraffin series, the lean limit was approximately half of stoichiometric.

Adiabatic flame temperature can also be used to predict the effect of initial temperature on lean flammability limits. If the adiabatic flame temperature is assumed to be constant regardless of the initial fuel/air mixture temperature, then the flame temperature at the lean limit for one temperature can be used to calculate the lean limits over a wide temperature range.

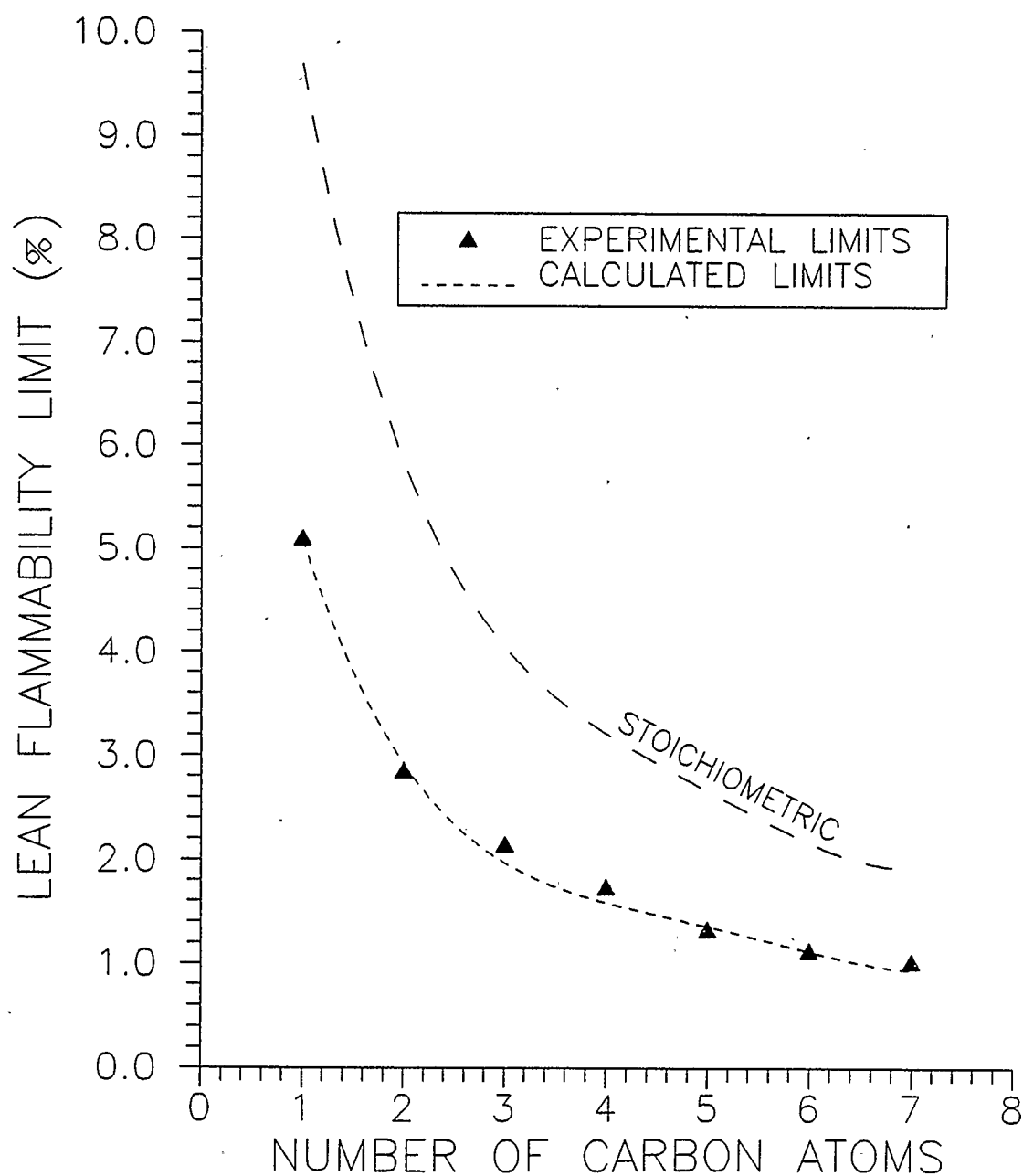


Figure 4.2.6 - A Comparison of Experimental Lean Limits for the Paraffin Series of Hydrocarbons With Those Calculated Using the Adiabatic Flame Temperature of the Methane Lean Limit at 23°C

Another method of predicting the variations in lean limits with changing initial temperature was suggested by Zabetakis [70] and is referred to as the Modified Burgess-Wheeler Law. It is based on the fact that the heating values of the lean limit fuel/air mixtures of many hydrocarbons are quite similar. This law can be expressed as follows:

$$LL_T/LL_{23C} = 1 - 0.75(T-23^{\circ}\text{C})/(LL_{23C}(\Delta H_c)) \quad (4.2.1)$$

where,

- $LL_T$  is the lean flammability limit at temperature T, % by volume.
- $LL_{23C}$  is the lean flammability limit at a reference temperature (in this case  $23^{\circ}\text{C}$ ), % by volume.
- $\Delta H_c$  is the net heat of combustion of the fuel for  $25^{\circ}\text{C}$  at constant pressure, kcal per mole.
- $T$  is the initial temperature of the fuel/air mixture,  $^{\circ}\text{C}$ .

The constant flame temperature method and Modified Burgess-Wheeler law were used to calculate the lean flammability limits of the fuels used during the course of this research, and the results of these calculations are compared with experimental values in Figures 4.2.7 through 4.2.14. Both methods gave reasonably accurate lean limit predictions for the hydrocarbon fuels studied, with the constant flame temperature system usually yielding the better results. Neither technique worked well for carbon monoxide, as is seen in Figure 4.2.14. The results may indicate that carbon monoxide was more sensitive to heat losses than the other fuels tested. It can be observed in Figure 4.2.13 that the constant flame temperature technique was inaccurate for hydrogen, which is to be expected in light of the discrepancies in hydrogen lean limit flame temperature

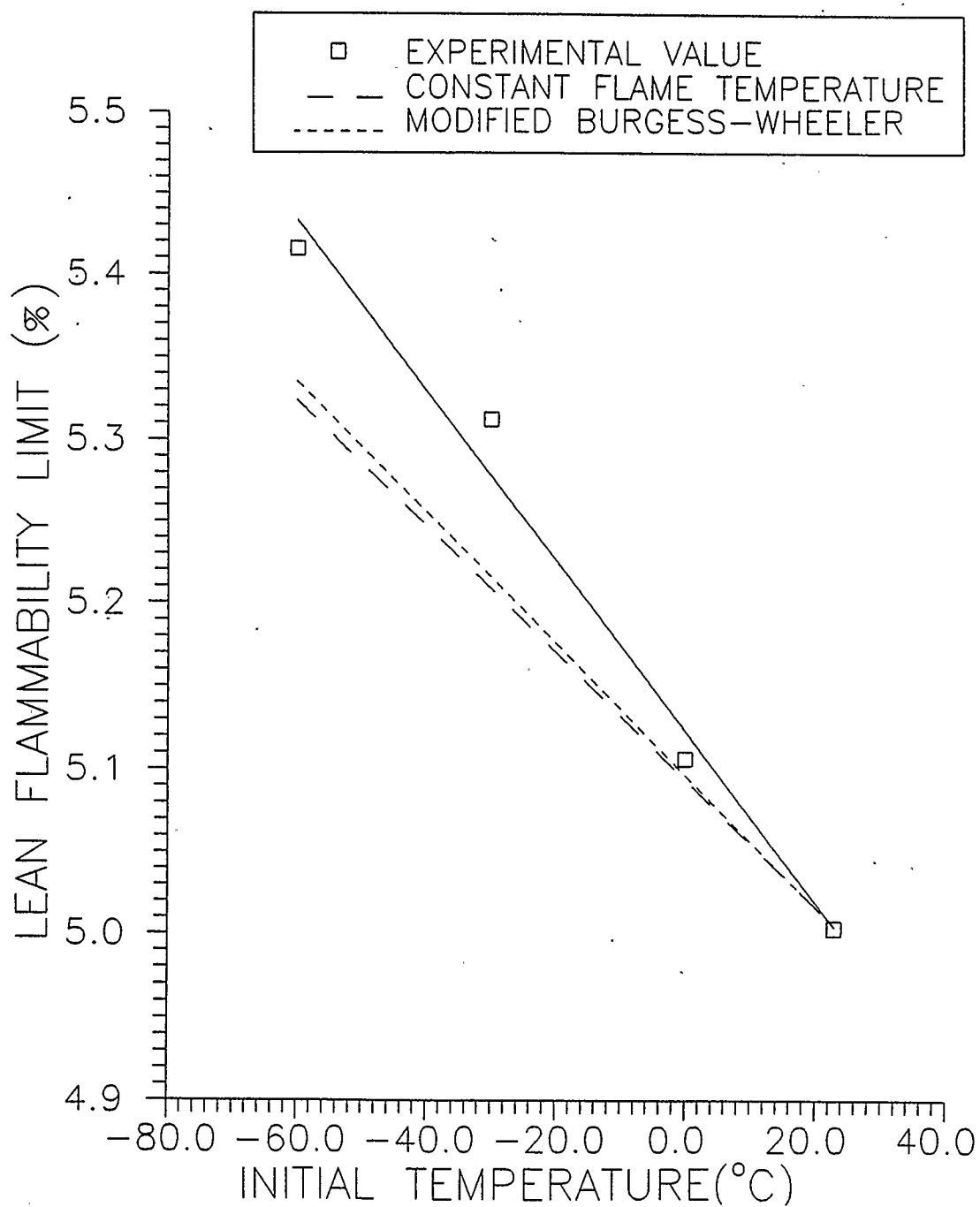


Figure 4.2.7 - A Comparison of the Lean Flammability Limits of Methane at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law and Constant Adiabatic Flame Temperature

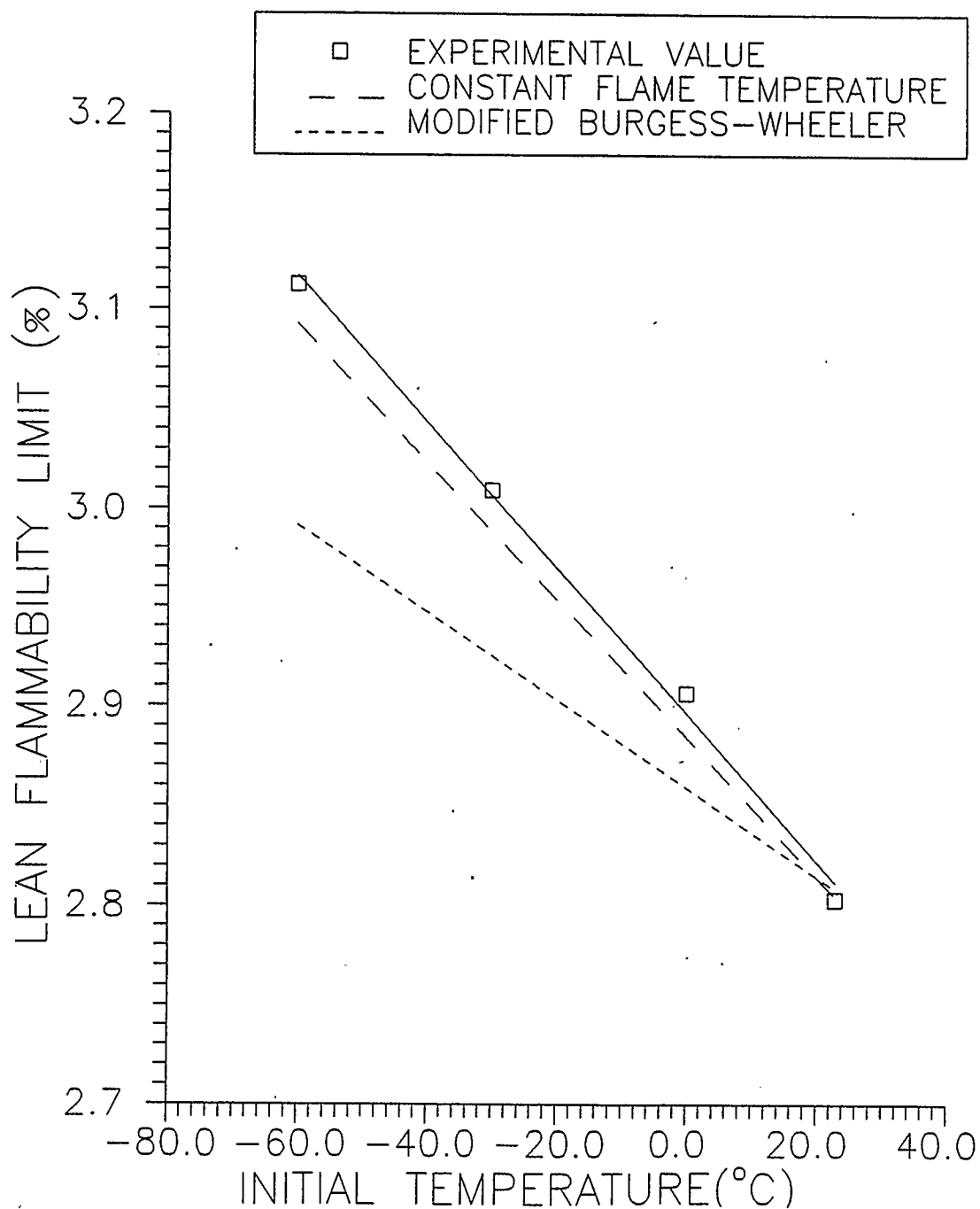


Figure 4.2.8 - A Comparison of the Lean Flammability Limits of Ethane at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law and Constant Adiabatic Flame Temperature

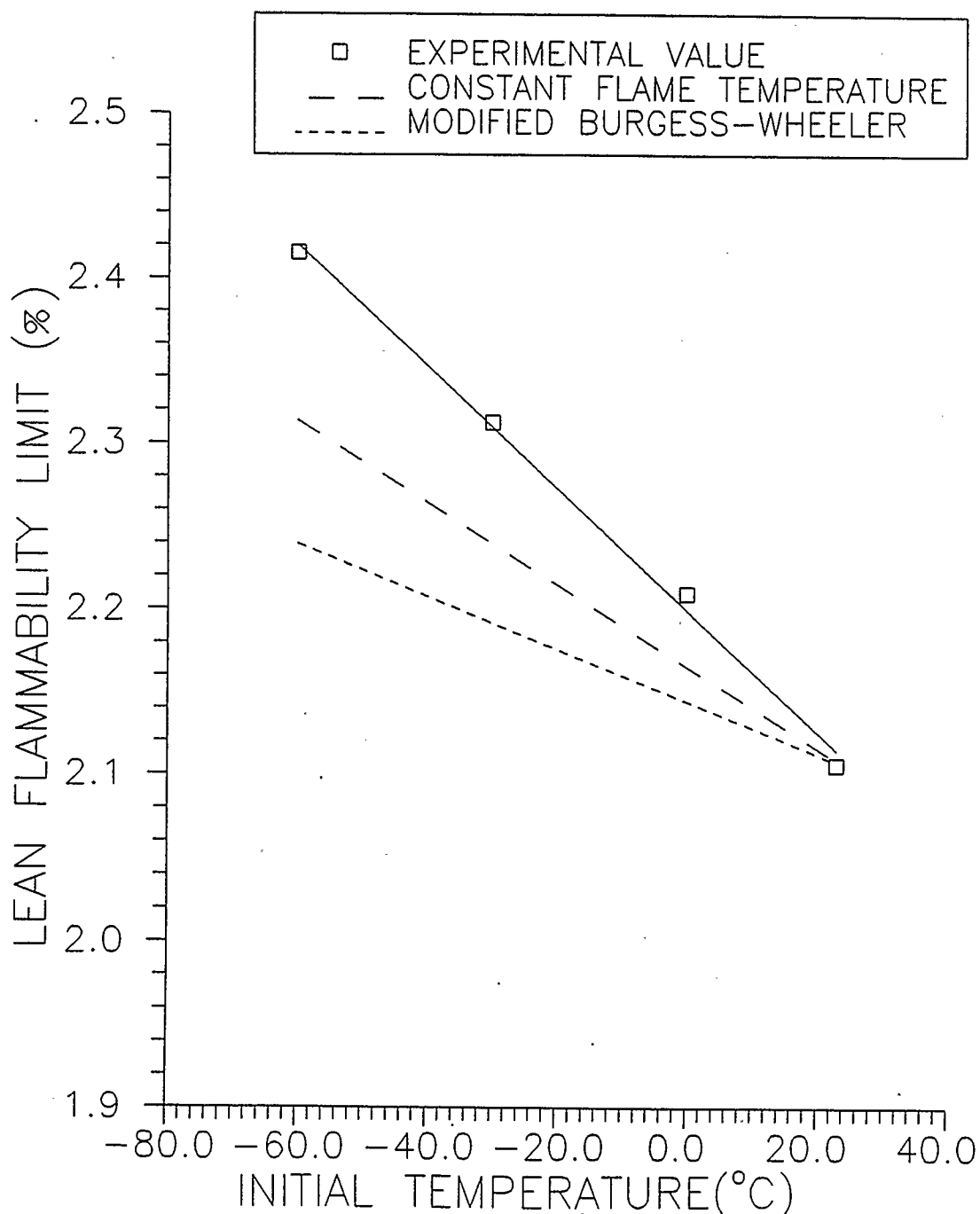


Figure 4.2.9 - A Comparison of the Lean Flammability Limits of Propane at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law and Constant Adiabatic Flame Temperature

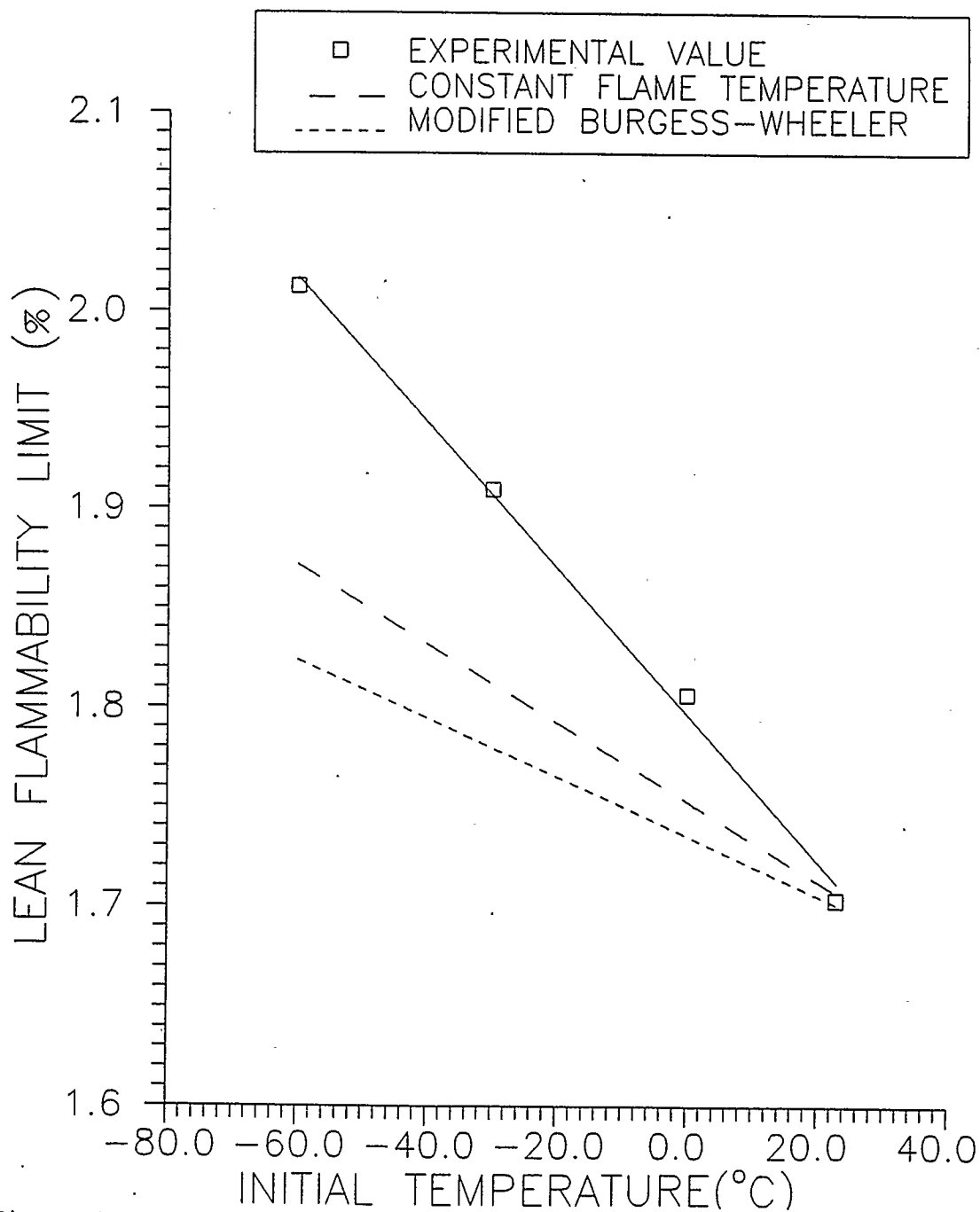


Figure 4.2.10 - A Comparison of the Lean Flammability Limits of Ethane at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law and Constant Adiabatic Flame Temperature



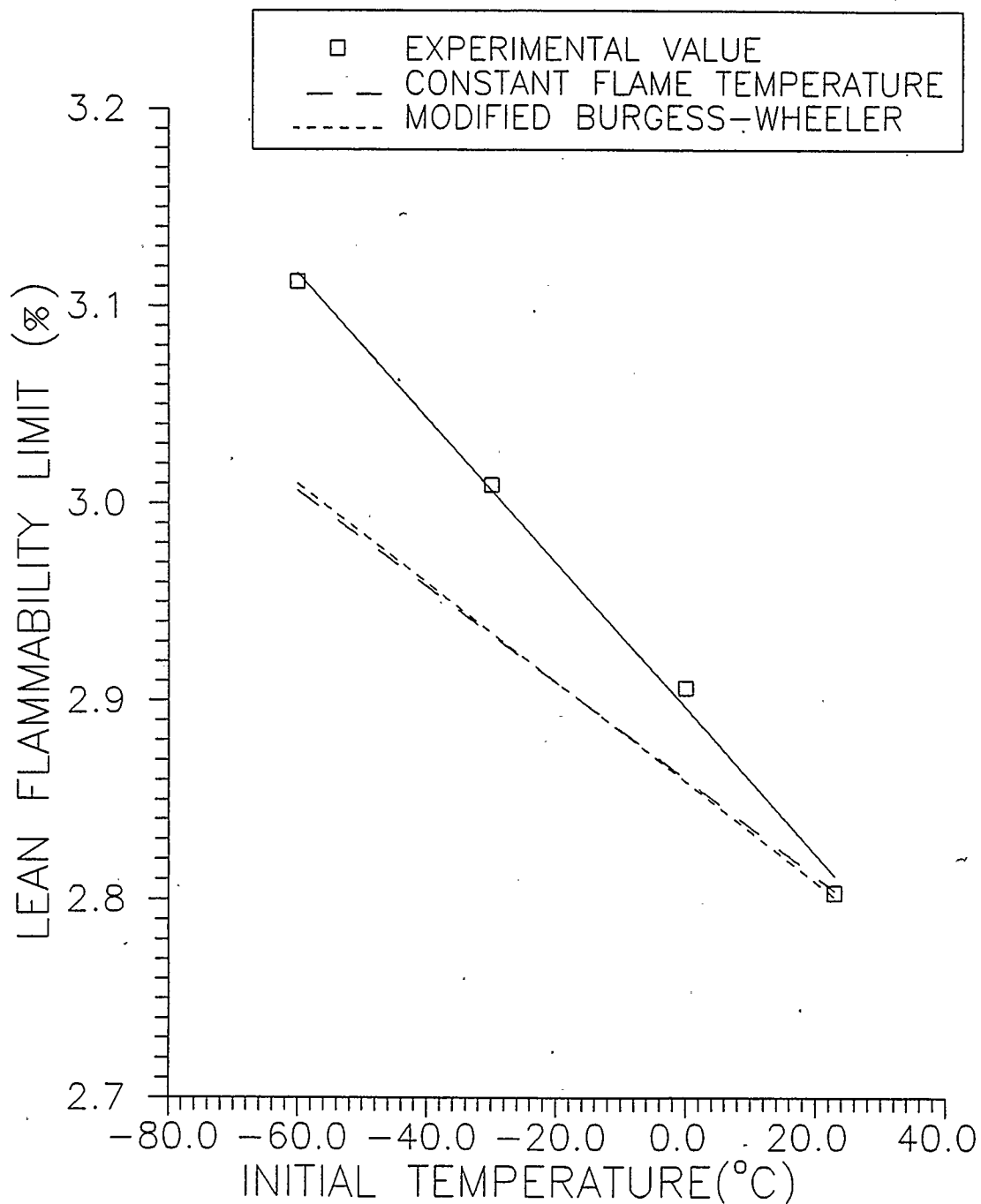


Figure 4.2.11 - A Comparison of the Lean Flammability Limits of Ethylene at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law and Constant Adiabatic Flame Temperature

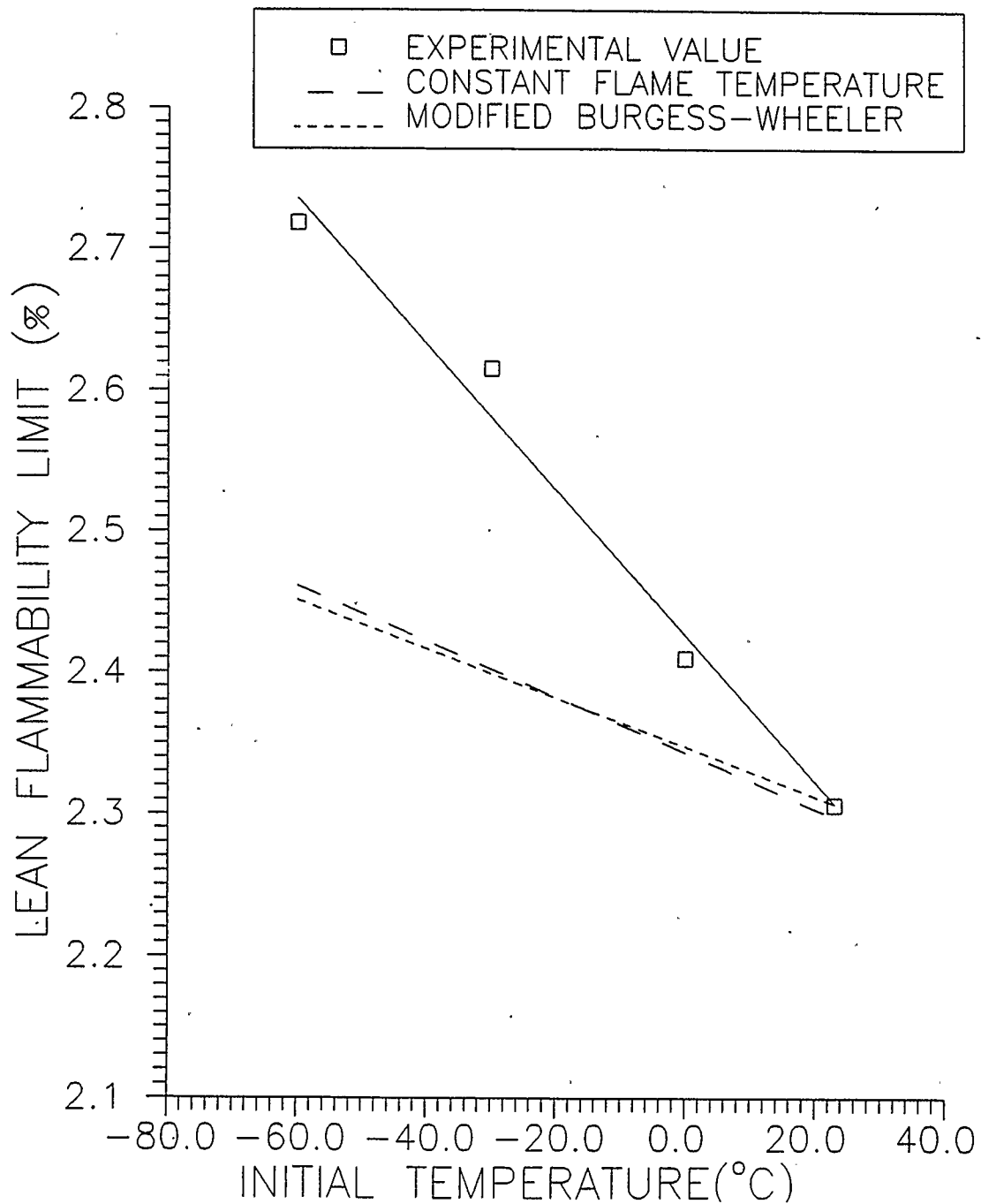


Figure 4.2.12 - A Comparison of the Lean Flammability Limits of Propylene at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law and Constant Adiabatic Flame Temperature

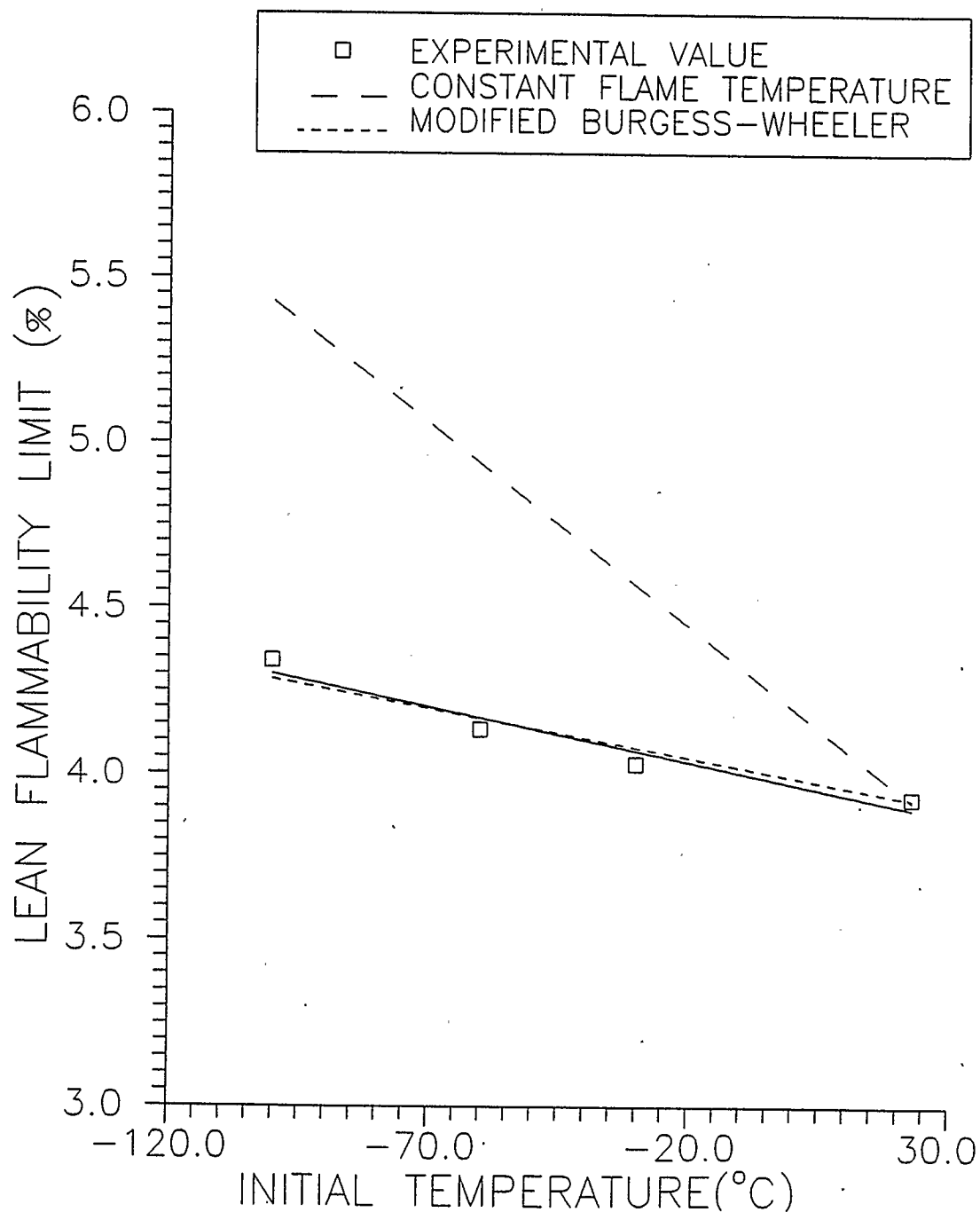


Figure 4.2.13 - A Comparison of the Lean Flammability Limits of Hydrogen at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law and Constant Adiabatic Flame Temperature

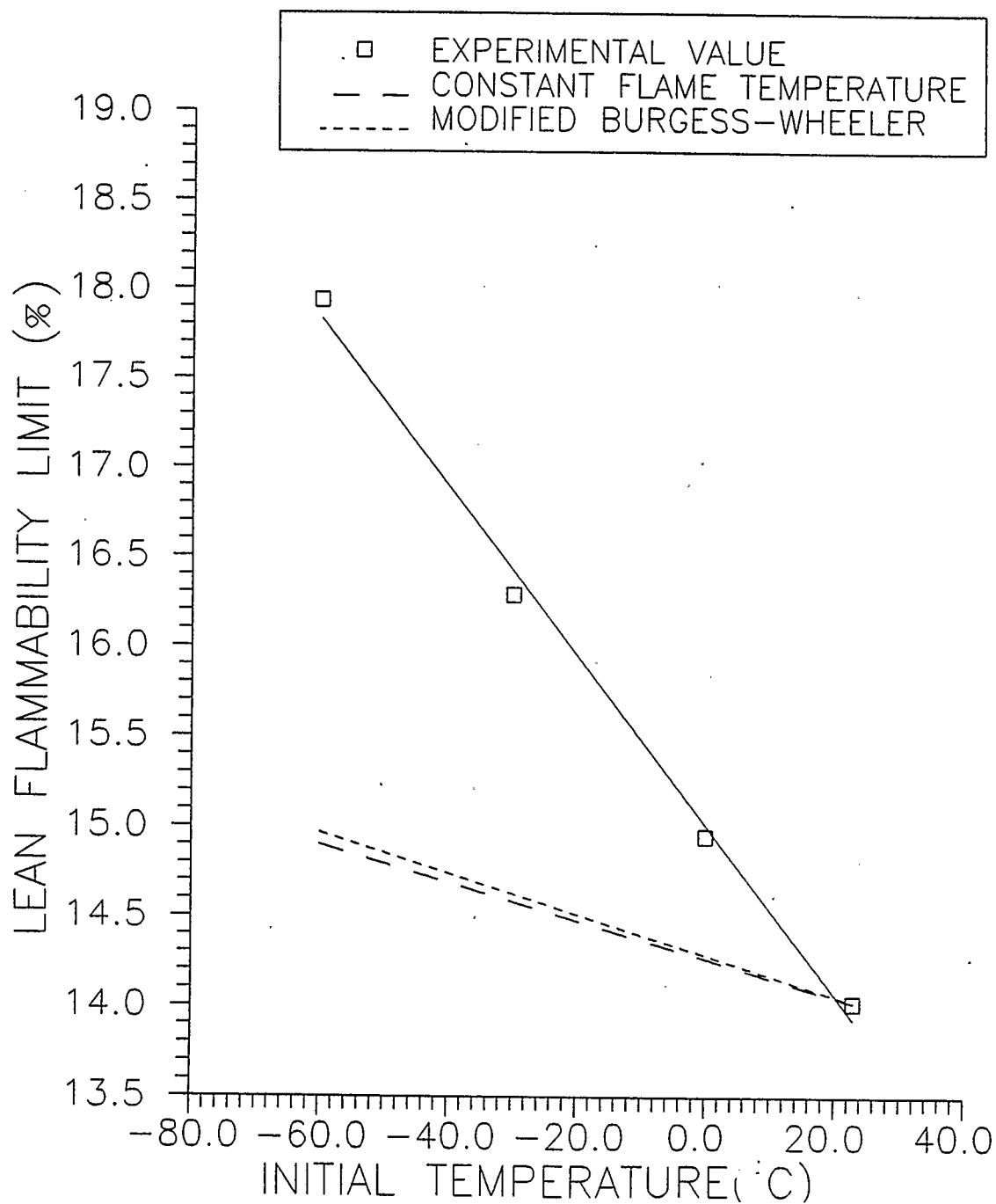


Figure 4.2.14 - A Comparison of the Lean Flammability Limits of Carbon Monoxide at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law and Constant Adiabatic Flame Temperature

behavior mentioned previously. When Equation 4.2.1 was applied to hydrogen using net heat of combustion values from [53], a curve similar to the constant flame temperature curve was obtained and so it was not included in Figure 4.2.13. When an average value of  $LL_{23}C(\Delta H_c) = 1040$  kcal/mole for paraffins suggested by Zabetakis [70] was used in Equation 4.2.1, it produced the more accurate Modified Burgess-Wheeler law prediction that is displayed in Figure 4.2.13.

#### 4.3 Rich Flammability Limits of Pure Fuels

Rich flammability limit determinations were made over the same temperature range, for the pure fuels that were used in lean limit tests with the exception of butane which was only tested down to  $-30^\circ\text{C}$  to avoid butane condensation at  $-60^\circ\text{C}$ . The resulting rich limits of flammability are presented in Table 4.3.1 and Figures 4.3.1 and 4.3.2.

Rich limits obtained in this flame tube agreed well with those obtained in the previous flame tube which was used during the ignition gap size study and also by previous researchers [7,14]. The only discrepancy between the results from the two flame tubes arose in the case of the ethylene rich limit, which was 28.1% in the new apparatus at  $23^\circ\text{C}$  compared to 30.7% in the old tube. Since these two limit determinations were made with the same ignition power supply, electrode gap, and spark duration and the internal dimensions of the two tubes are almost identical, the difference was presumably due to dissimilarity in the physical design of the electrodes and electrode supports. The heat transfer rates in both tubes should be about the same, since they have the same dimensions and were made from the same material. It was observed that the flame tube

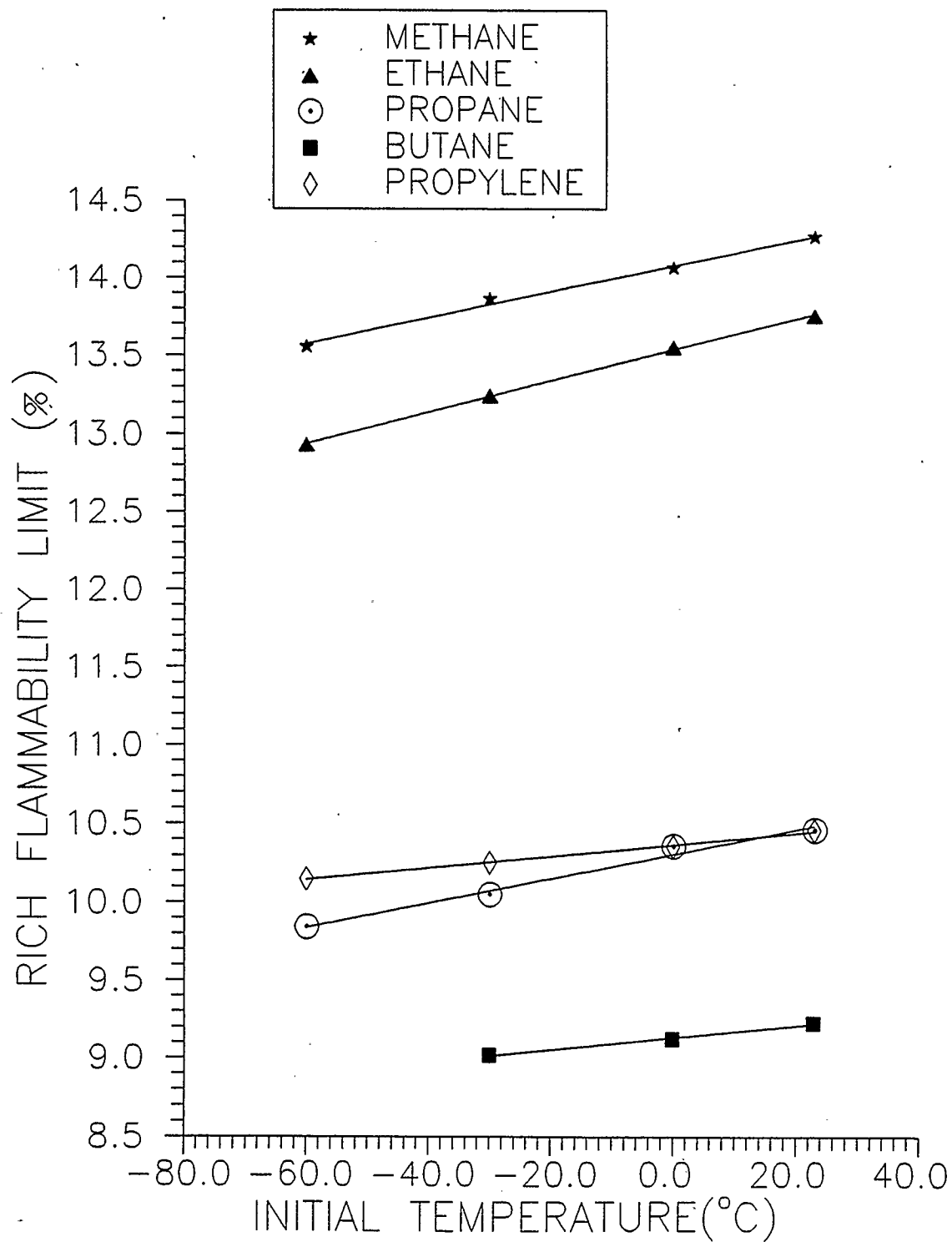


Figure 4.3.1 - Rich Flammability Limits of Hydrocarbon Fuels as a Function of Initial Temperature

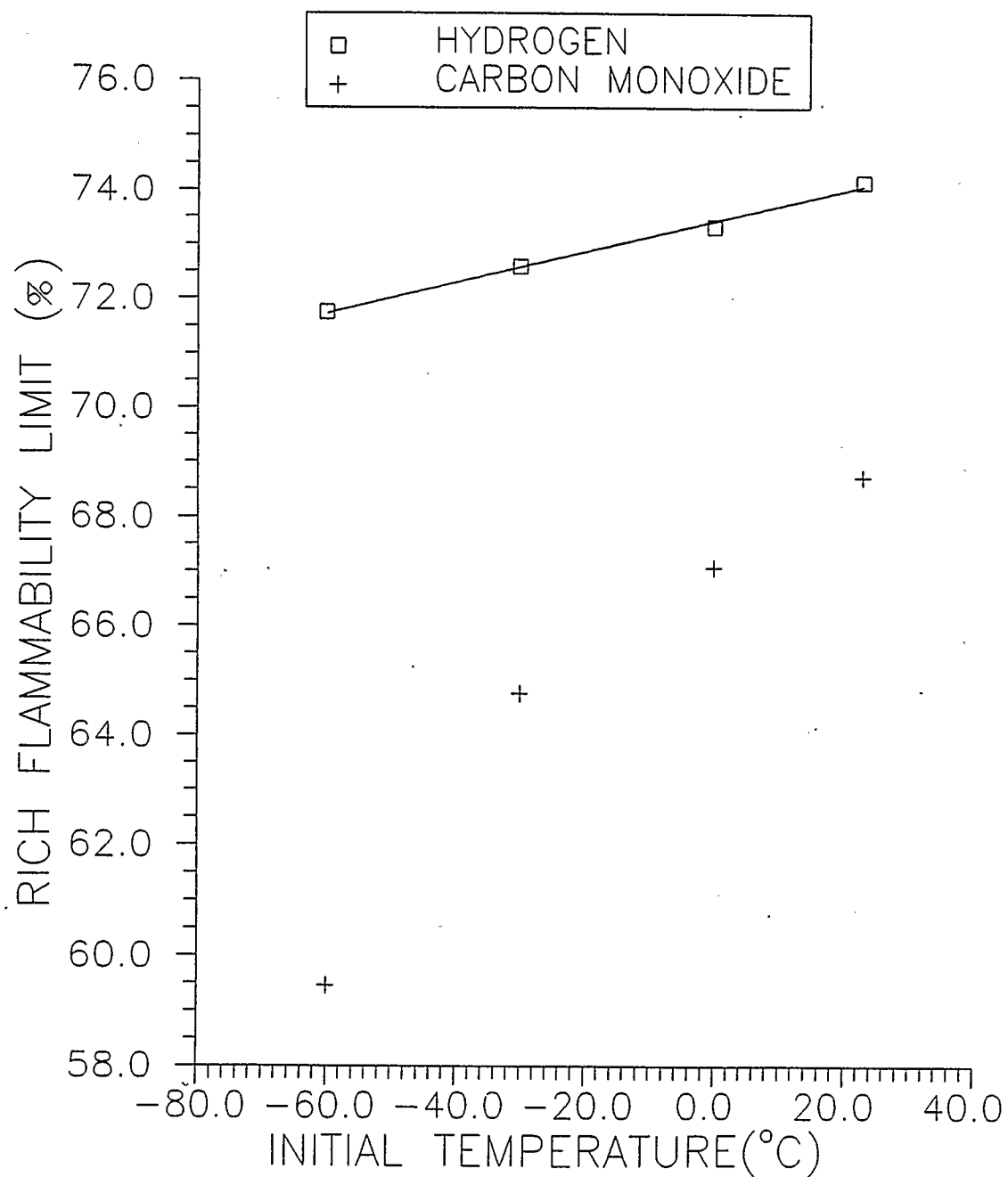


Figure 4.3.2 - Rich Flammability Limits of Hydrogen and Carbon Monoxide as a Function of Initial Temperature

temperature did not change measurably after tests near the limit when propagation was recorded. Although the heat capacity of the new tube is probably higher because it has more mass than the previous tube, the heat transfer rates are likely similar because the heat capacity of either tube is much higher than that for the fuel/air mixture. Cheng [14], measured the ignition power supplied to the electrodes from the transformer used in these tests, and found it to be approximately 12 W for a similar electrode gap. A further test was made in the new tube using a variac to increase the primary transformer supply voltage to 147.0 V from 123.7 V, in order to increase the ignition energy. The resulting ethylene rich limit was 28.6%, an increase of 0.5% by volume over the lower energy system. Further increases in ignition energy were not possible with the transformer because its secondary current was limited to about 23 mA. It is important to emphasize that the ethylene rich limits determined in this research are not independent of ignition energy and that changes in ignition energy or source geometry may elevate these limits.

For the fuels tested, the rich limits decreased essentially linearly with temperature decrease, except for carbon monoxide, which seemed to be non-linear below  $-30^{\circ}\text{C}$ , as shown in Figure 4.3.2. During the experiments on the carbon monoxide rich limit, it was noted that at  $-60^{\circ}\text{C}$ , the region where there was strong ignition but incomplete flame propagation was much larger than usual. It may have been that at  $-60^{\circ}\text{C}$ , a tube diameter of 51 mm was insufficient to test the carbon monoxide rich limit because of heat loss from the flame to the walls. There is also a possibility that the quantity of water vapor in the air was reduced at  $-60^{\circ}\text{C}$ , although previous tests indicated that the dew point of the air was below  $-75^{\circ}\text{C}$ . The



percentage change in the rich limits with temperature decrease, shown in Table 4.3.2, was generally less than that for the corresponding lean limits.

Table 4.3.1 - Rich Flammability Limits of fuels.

Fuel	Experimental Rich Flammability Limit % by Volume			
	Initial Mixture Temperature °C			
	23	0	-30	-60
Methane	14.1	13.9	13.7	13.4
Ethane	13.6	13.4	13.1	12.8
Propane	10.4	10.3	10.0	9.8
Butane	9.2	9.1	9.0	-
Ethylene	<sup>1</sup> 28.1	<sup>1</sup> 26.5	<sup>1</sup> 25.5	<sup>1</sup> 24.2
Propylene	10.4	10.3	10.2	10.1
Hydrogen	<sup>2</sup> 73.5	<sup>2</sup> 72.7	<sup>2</sup> 72.0	<sup>2</sup> 71.2
CO	<sup>2</sup> 68.3	<sup>2</sup> 66.7	<sup>2</sup> 64.5	<sup>2</sup> 59.4

<sup>1</sup> Tests where there was no detectable ignition at the measured limit and  $t_s = 4.0$  seconds.

<sup>2</sup>  $t_s = 2.0$  seconds.

Figure 4.3.3 illustrates the flammable range of the paraffin series of hydrocarbons and demonstrates that as the molecular weight of the fuel increased, both limits decreased. As noted earlier, the lean limits were about half of stoichiometric, and it can be seen here that the rich limits in this series of paraffins could be as high as four times stoichiometric. The lean limits of carbon monoxide, ethylene, and propylene were also roughly half of stoichiometric. Hydrogen exhibited an exceptionally large

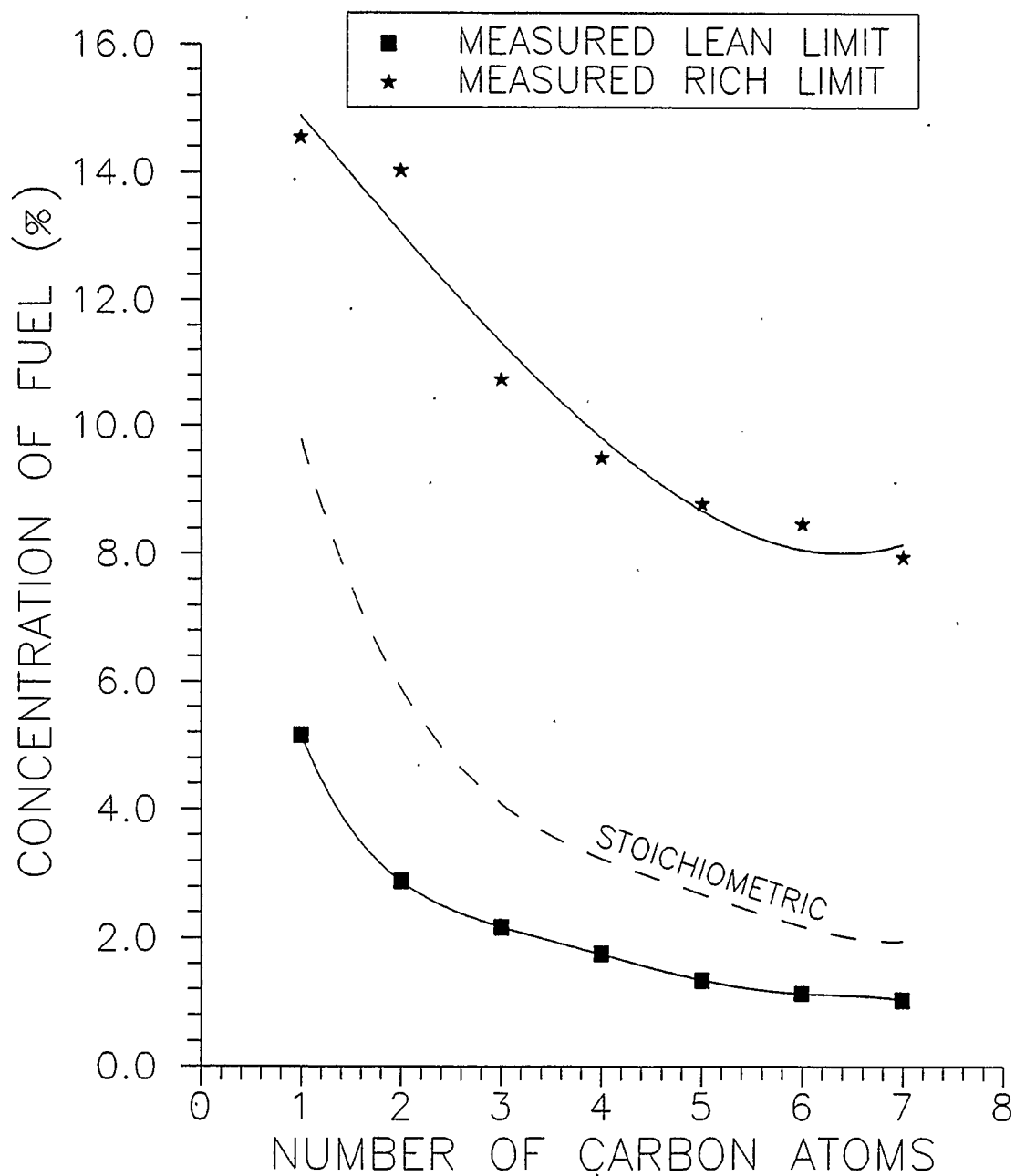


Figure 4.3.3 - Rich and Lean Flammability Limits Compared to the Stoichiometric Fuel/Air Mixtures for the Paraffin Series of Hydrocarbons at 23°C

range of flammability, having a lean limit of around one sixth of stoichiometric and a rich limit of almost two and a half times stoichiometric. The rich limit of ethylene was nearly four and a half times stoichiometric.

A rich flammability limit determination was also made for carbon monoxide at 23°C in air saturated with water vapor to investigate the reported effect of humidity. The resulting rich limit was 73.4% versus 68.3% for carbon monoxide in dry air. As mentioned earlier, air humidity must be considered whenever carbon monoxide flammability limit data are to be utilized.

Table 4.3.2 - Percentage Change of the Rich Limits of Pure Fuels With Initial Temperature Change From 23°C to -60°C.

Fuel	Change in Rich Flammability Limit With Initial Temperature Change (%)
Methane	5.0%
Ethane	5.8%
Propane	5.8%
Butane	<sup>1</sup> 2.2%
Ethylene	13.9%
Propylene	2.9%
Hydrogen	3.0%
Carbon Monoxide	13.0%

<sup>1</sup>Calculated over the temperature range from 23°C to -30°C.

It is not possible at this time to accurately calculate adiabatic flame temperature for rich limit mixtures because of the complexity of the reaction mechanisms of very rich fuel/air mixtures. As a result, when data on rich flammability limits of most pure fuels are required, experimental data is needed because of the lack of predictive methods. Equation 4.2.1 can be used to predict the relation between rich flammability limits and initial temperature, and is referred to as the Modified Burgess-Wheeler law if it is in the following form:

$$RL_T/RL_{23C} = 1 + 0.75(T-23^{\circ}\text{C})/(RL_{23C}(\Delta H_c)) \quad (4.3.1)$$

where,

- $RL_T$  is the rich flammability limit at temperature  $T$ , % by volume.
- $RL_{23C}$  is the rich flammability limit at a reference temperature (in this case  $23^{\circ}\text{C}$ ), % by volume.
- $\Delta H_c$  is the net heat of combustion of the fuel for  $25^{\circ}\text{C}$  at constant pressure, kcal per mole.
- $T$  is the initial temperature of the fuel/air mixture,  $^{\circ}\text{C}$ .

Figures 4.3.4 through 4.3.11 show that the Modified Burgess-Wheeler law provided poor estimations of the change in the rich flammability limits as initial temperature varied. A better fit was obtained when the following version of the Burgess-Wheeler law was used which is referred to as the Ratio Burgess-Wheeler law:

$$RL_T/RL_{23C} = 1 + 0.75(T-23^{\circ}\text{C})/(LL_{23C}(\Delta H_c)) \quad (4.3.2)$$

Equation 4.3.2 assumes that the total heat release at the rich limit is equal to that at the lean limit [70]. Equation 4.3.2 is plotted in Figures 4.3.4 through 4.3.11. For most of the pure fuels tested, the

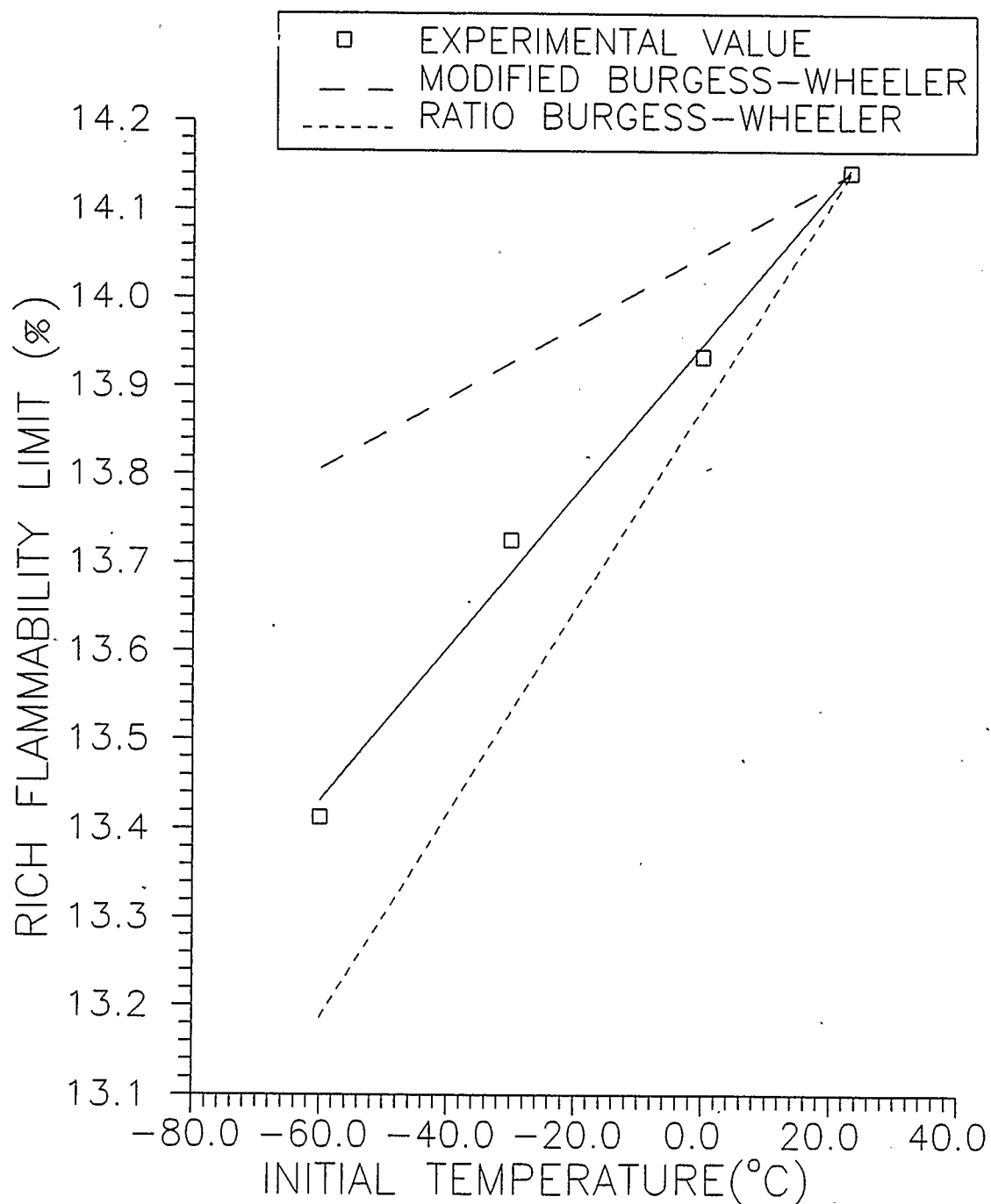


Figure 4.3.4 - A Comparison of the Rich Flammability Limits of Methane at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law

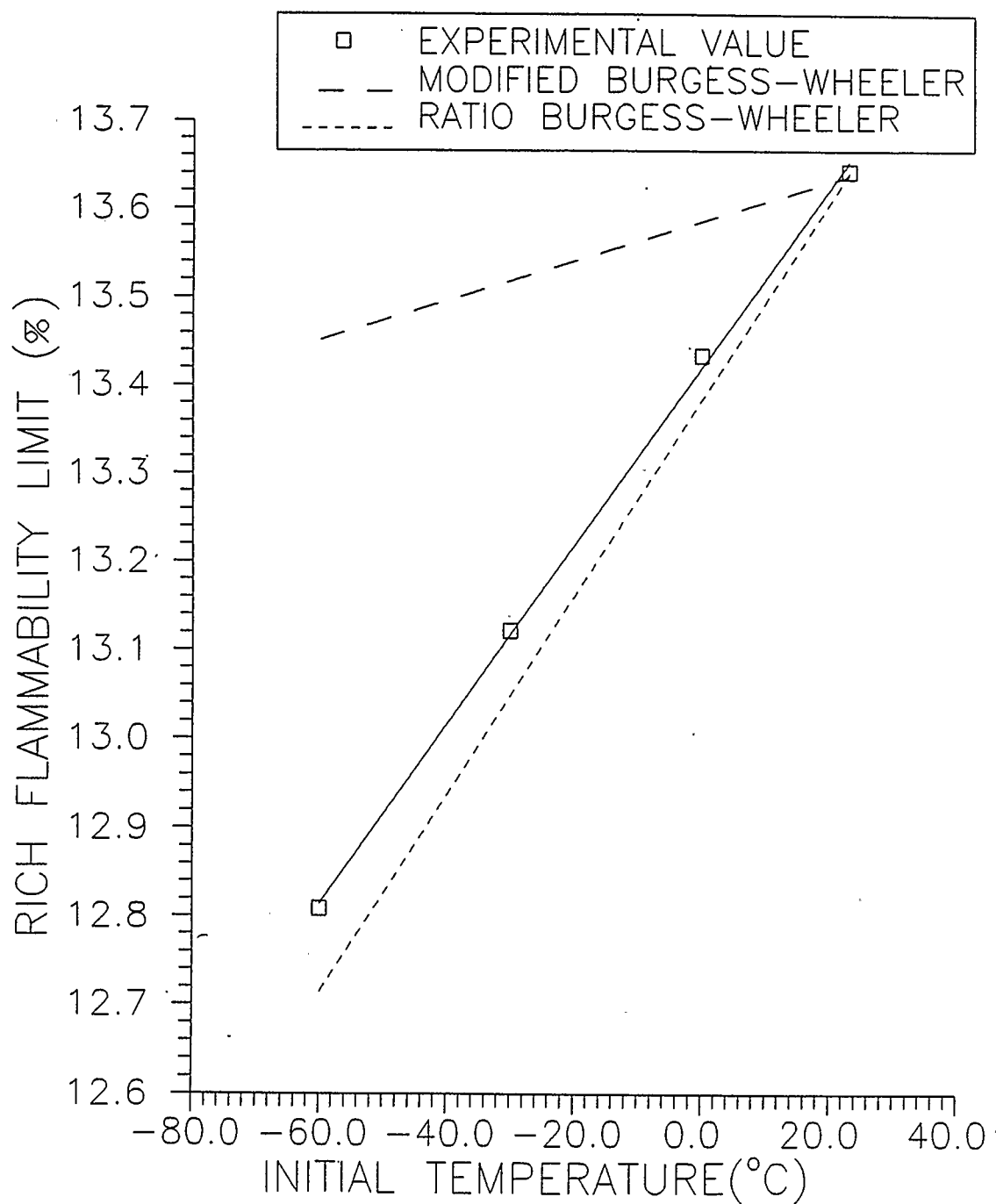


Figure 4.3.5 - A Comparison of the Rich Flammability Limits of Ethane at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law

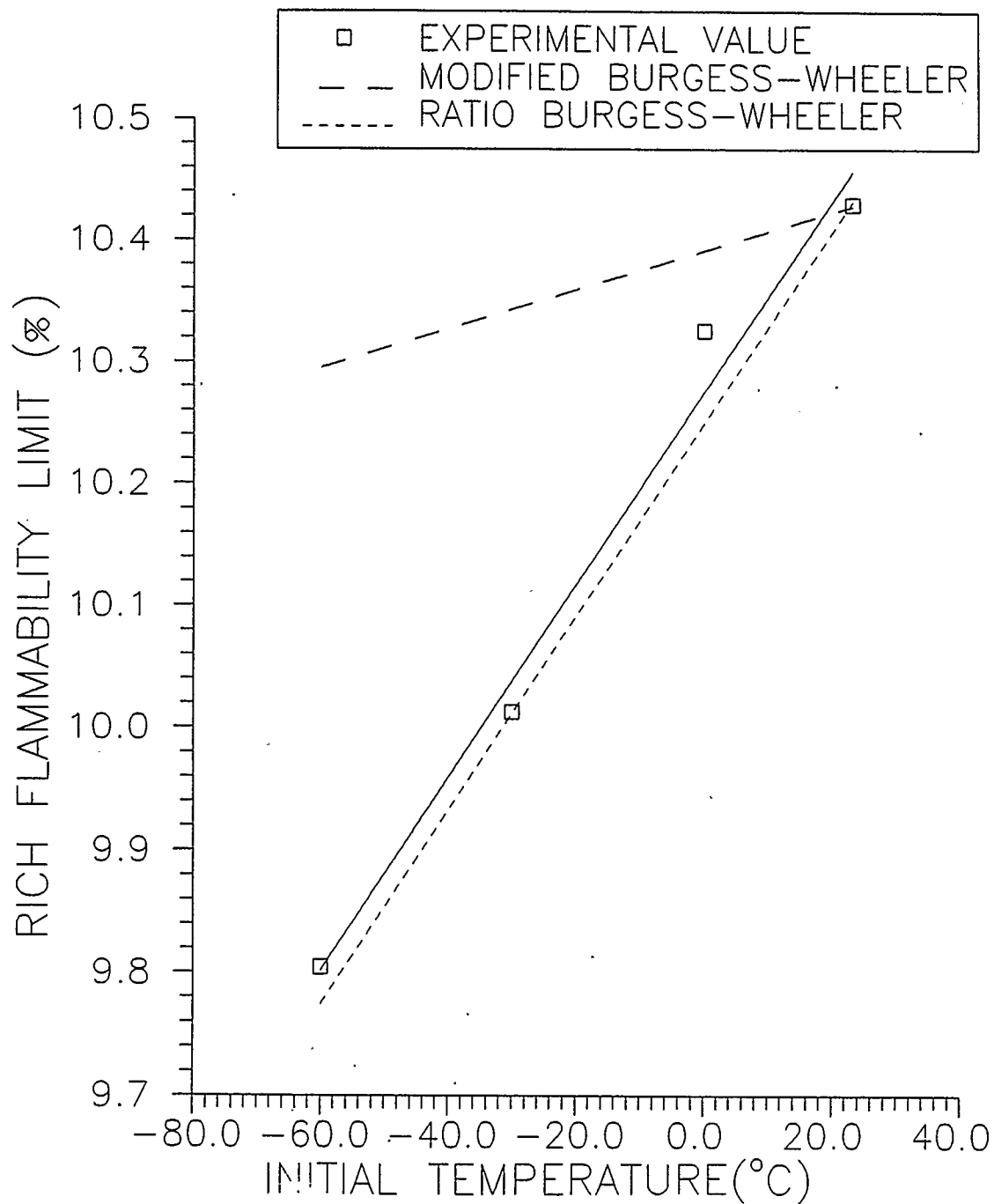


Figure 4.3.6 - A Comparison of the Rich Flammability Limits of Propane at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law

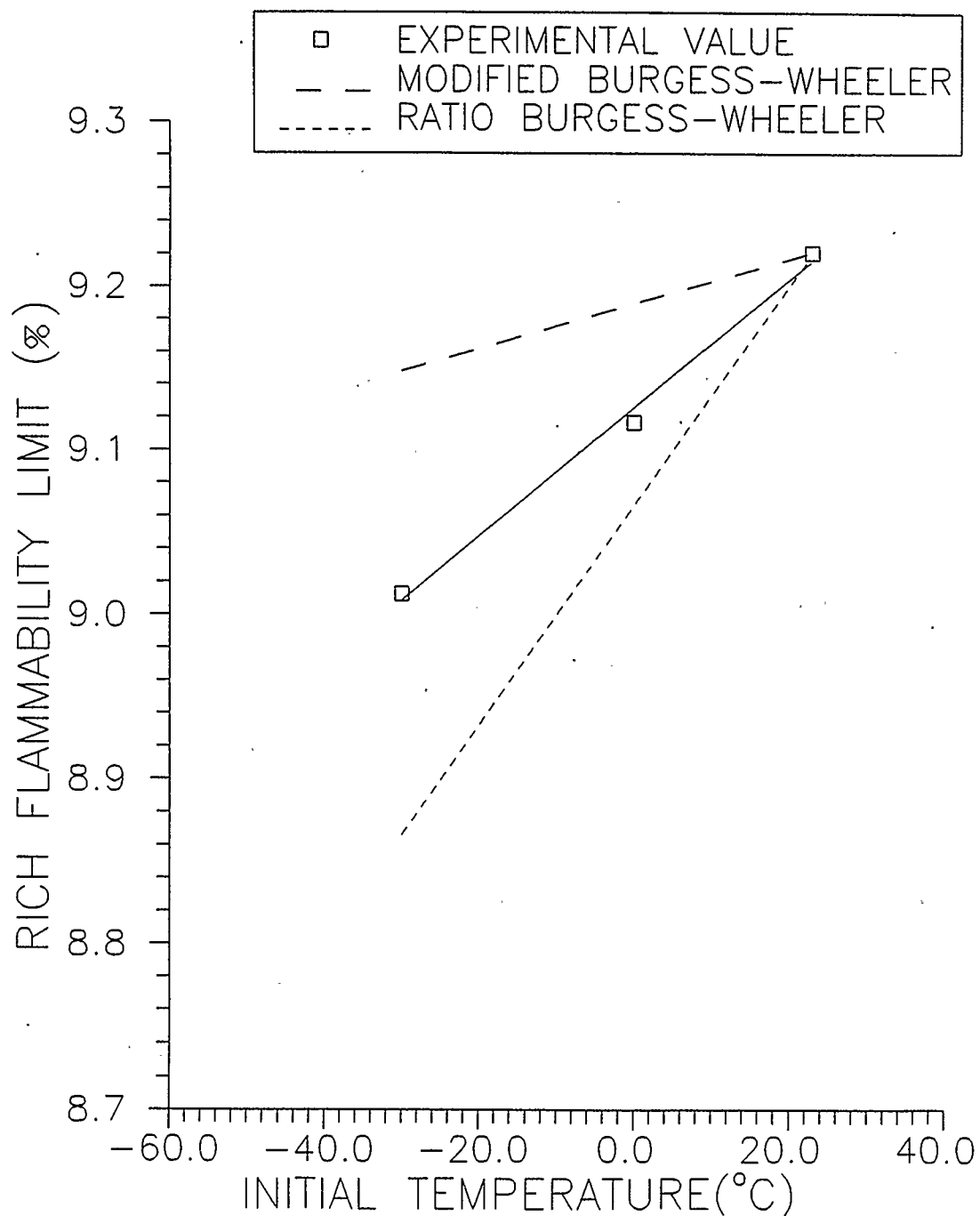


Figure 4.3.7 - A Comparison of the Rich Flammability Limits of Butane at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law



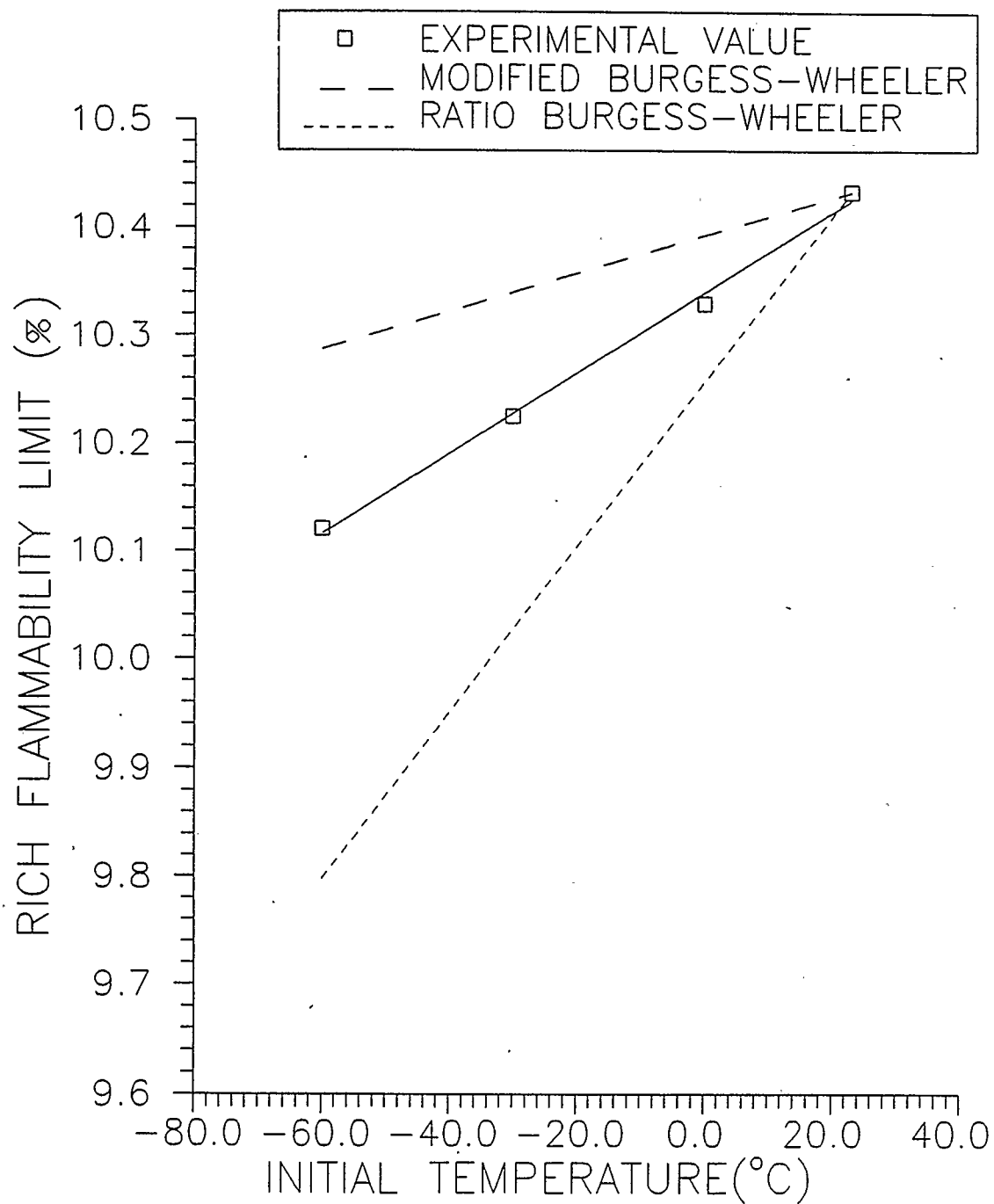


Figure 4.3.8 - A Comparison of the Rich Flammability Limits of Propylene at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law

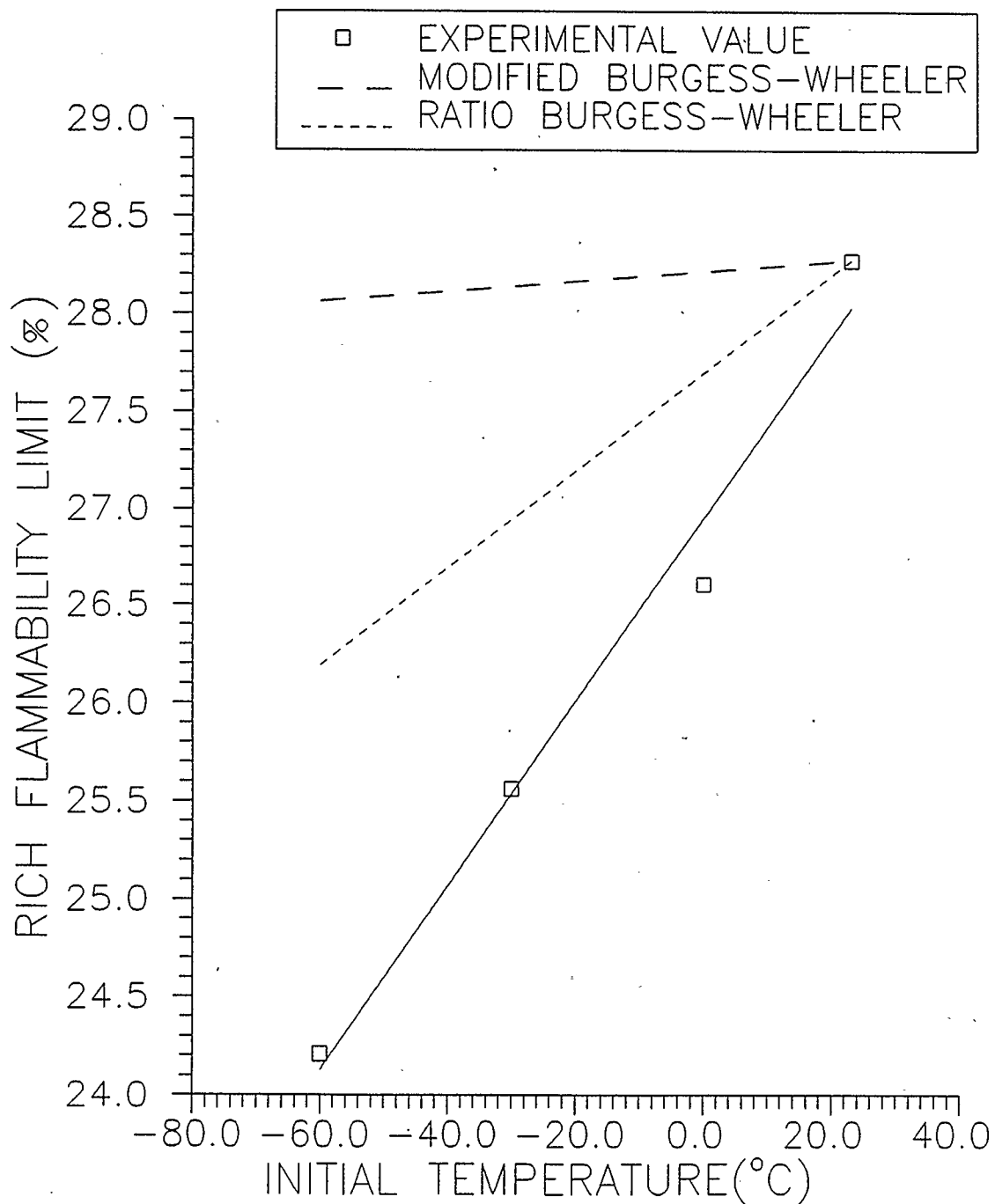


Figure 4.3.9 - A Comparison of the Rich Flammability Limits of Ethylene at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law

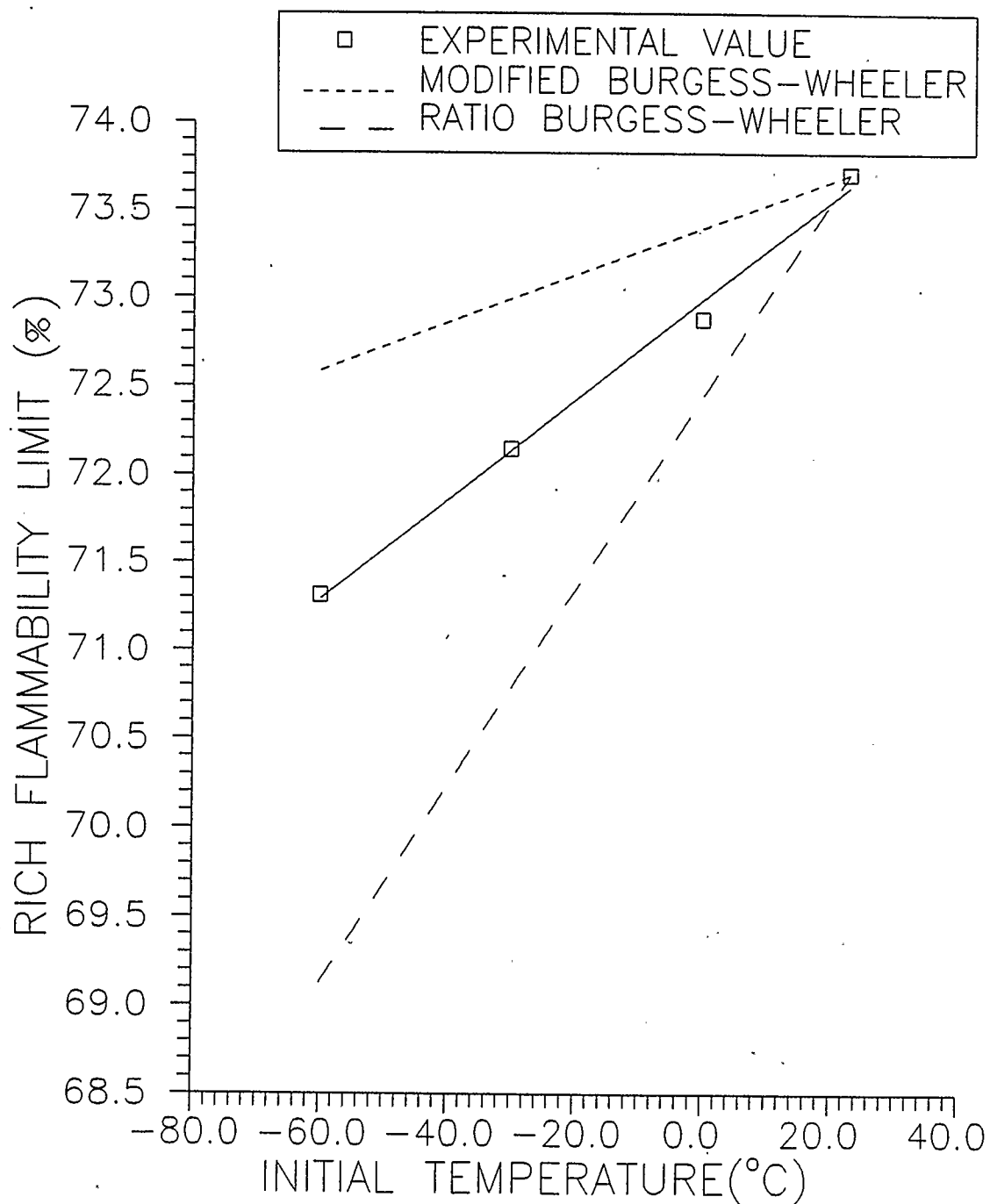


Figure 4.3.10 - A Comparison of the Rich Flammability Limits of Hydrogen at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law

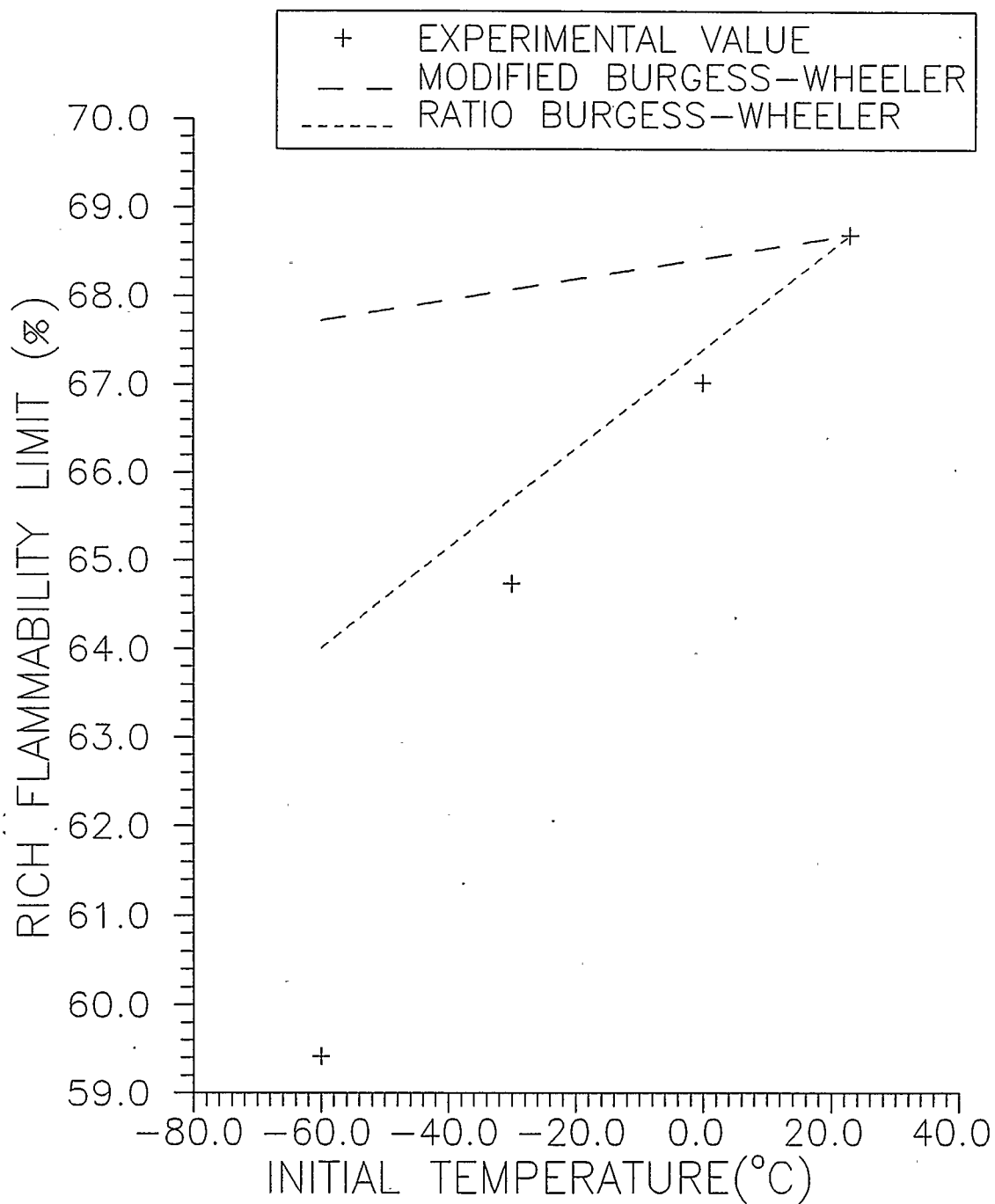


Figure 4.3.11 - A Comparison of the Rich Flammability Limits of Carbon Monoxide at Different Initial Temperatures, With Those Calculated Using the Modified Burgess-Wheeler Law

Ratio Burgess-Wheeler law gave predictions that were closer to experimental values than the Modified Burgess-Wheeler law (equation 4.3.1). This was also true for carbon monoxide over the 23°C to -30°C temperature range, below which the experimental rich limits were no longer a linear function of initial temperature. As in the case of the lean limits for hydrogen, equation 4.3.2 yielded very poor estimations for hydrogen rich limits and should not be used. When an average value of  $LL_{23}(\Delta H_c) = 1040$  kcal/mole for paraffins suggested by Zabetakis [70] was used in Equation 4.3.1, it produced the curve denoted as the Ratio Burgess-Wheeler law prediction displayed in Figure 4.3.10. The resulting prediction was still too low, so for safety purposes where a conservative estimate is desired, it would be safer to use equation 4.3.1 in its original form.

The rich and lean flammability limit data for butane from this study were used in conjunction with published vapor pressure data [53] to construct the flammability diagram in Figure 4.3.12. Point A in the figure is the point where the saturated vapor concentration and rich flammability limit curves meet. As Van Dolah et al. [58] originally noted, if the liquid and gas are in equilibrium, at temperatures below point A (-60°C), the rich flammability limit should not exist. To test this prediction, experiments were carried out to find the maximum temperature at which a fuel/air mixture containing 20% butane by volume would propagate a flame through the whole length of the tube. The temperature was found to be -57°C, which agreed quite well with Figure 4.3.12. Point B in the same diagram is usually referred to in the literature as the low temperature limit of flammability; and is normally

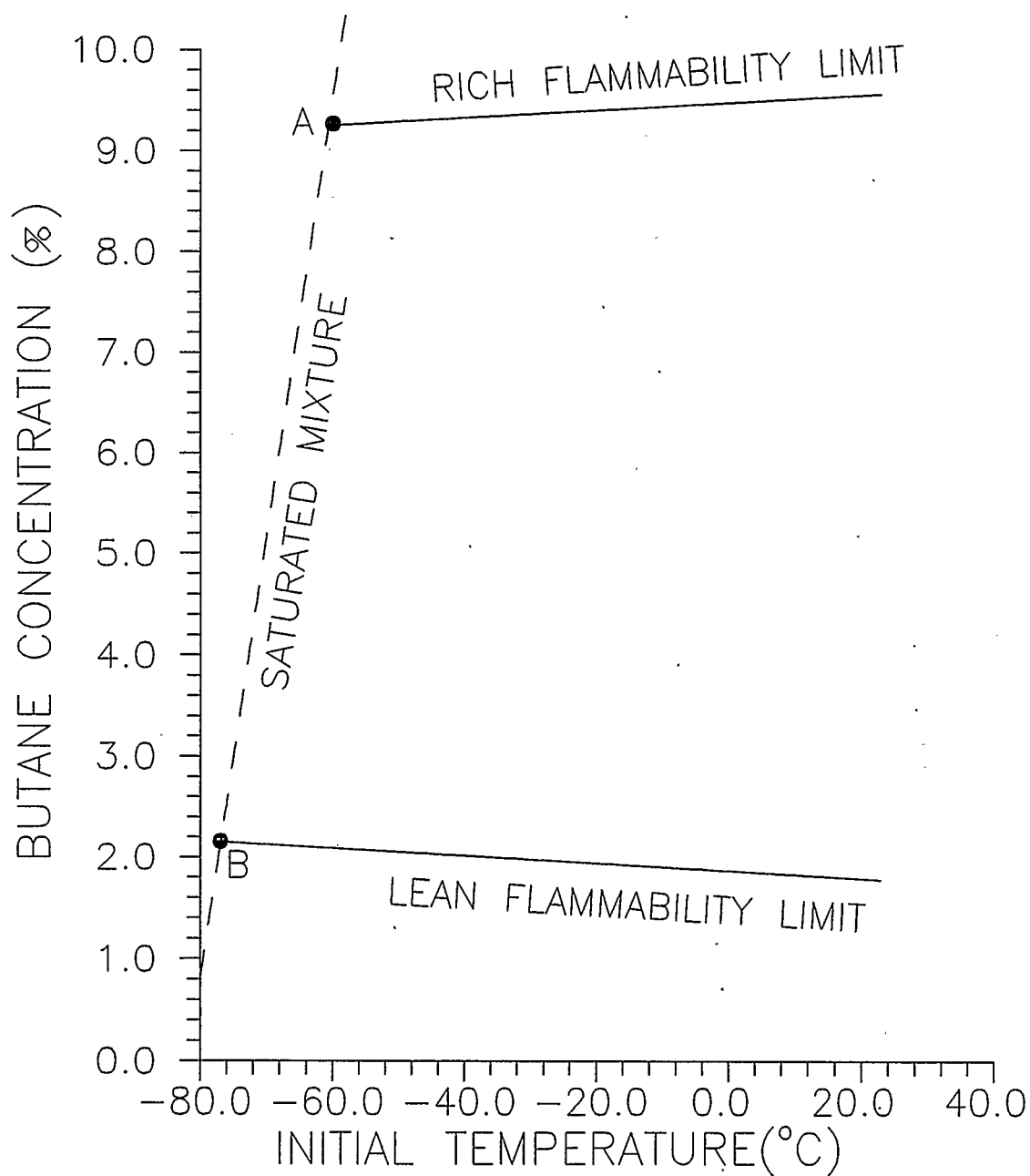


Figure 4.3.12 - Rich and Lean Flammability Limits of Butane as a Function of Initial Temperature

equal to or slightly lower than the flash point of the fuel [1,11,12,35, 58,70,71]. Once again, this is only true for fuel/air mixtures with the phases in equilibrium. Tests were performed to determine point B for butane, and it was found to be approximately  $-74^{\circ}\text{C}$  which also agreed quite well with Figure 4.3.12 and the calculated value of  $-72^{\circ}$  quoted in the literature [70]. This can be an important consideration for fuel storage at low temperatures, because it is possible that a fuel/air mixture that is too rich to burn at warmer temperatures may become flammable if the temperature is lowered. For situations where the liquid and gas phases are not in equilibrium, the situation is even more complex because some of the liquid phase will be distributed in the gas in the form of a mist. In the case of mists, the fuel/air mixture can be flammable over a very wide range of composition and temperature [70].

#### **4.4 Lean Flammability Limits of Some Binary Fuel Mixtures**

Lean flammability limit tests were performed for various binary fuel mixtures of methane and propane, methane and butane, and propane and propylene. The results of these tests are recorded in Table 4.4.1 and displayed graphically in Figures 4.4.1 through 4.4.3.

Figure 4.4.1 compares the experimentally determined lean flammability limits of methane/propane fuel mixtures with flammability limits calculated using Le Chatelier's rule. The accuracy of the Le Chatelier predictions for these lean mixtures was good, being of the order of the experimental error. Any errors tended to be on the low side, which is desirable for safety applications where conservative predictions are needed.

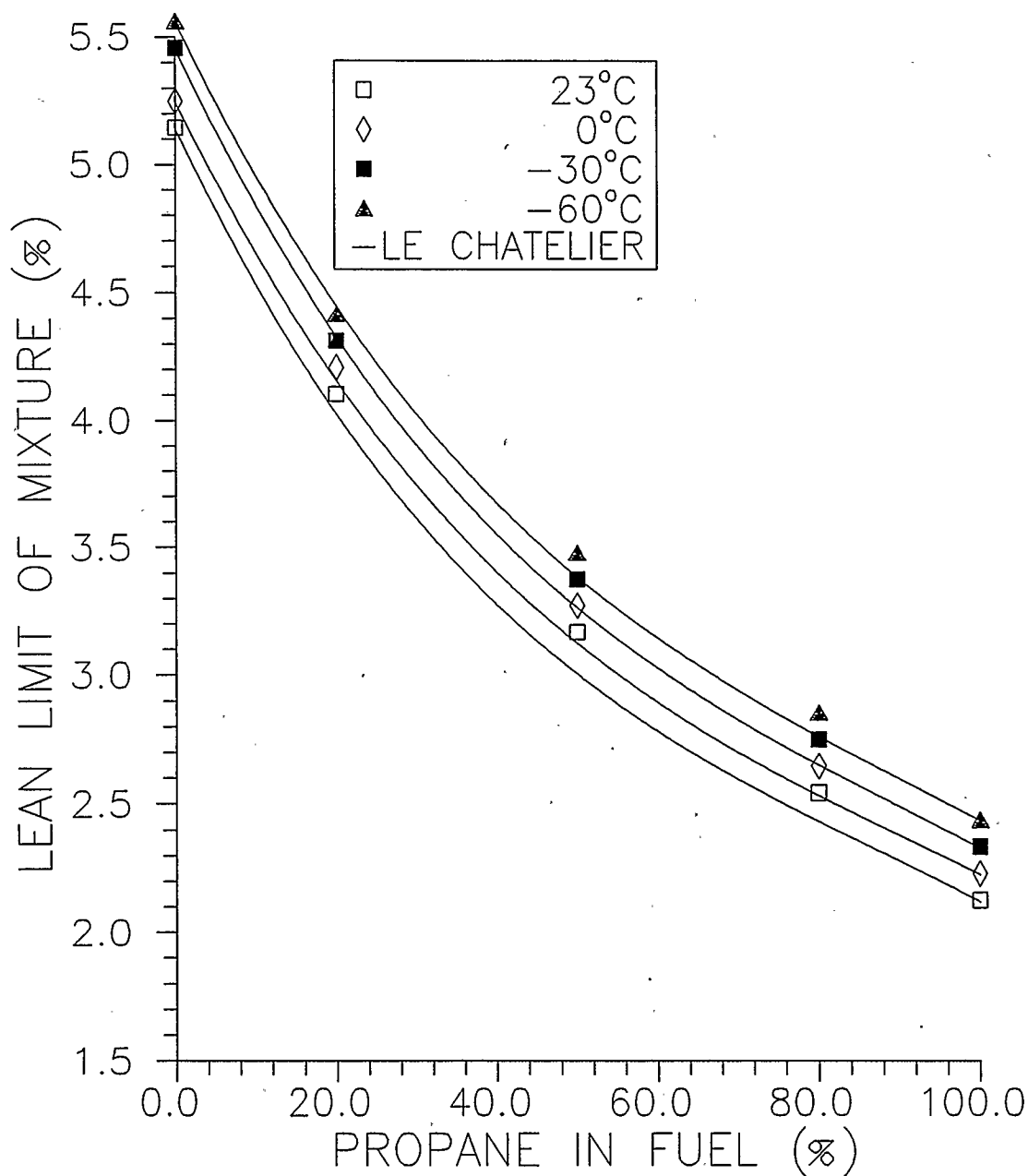


Figure 4.4.1 - A Comparison of the Lean Flammability Limits of Methane/Propane Mixtures at Various Initial Temperatures With Predictions From Le Chatelier's Rule, as a Function of Percent Propane Content



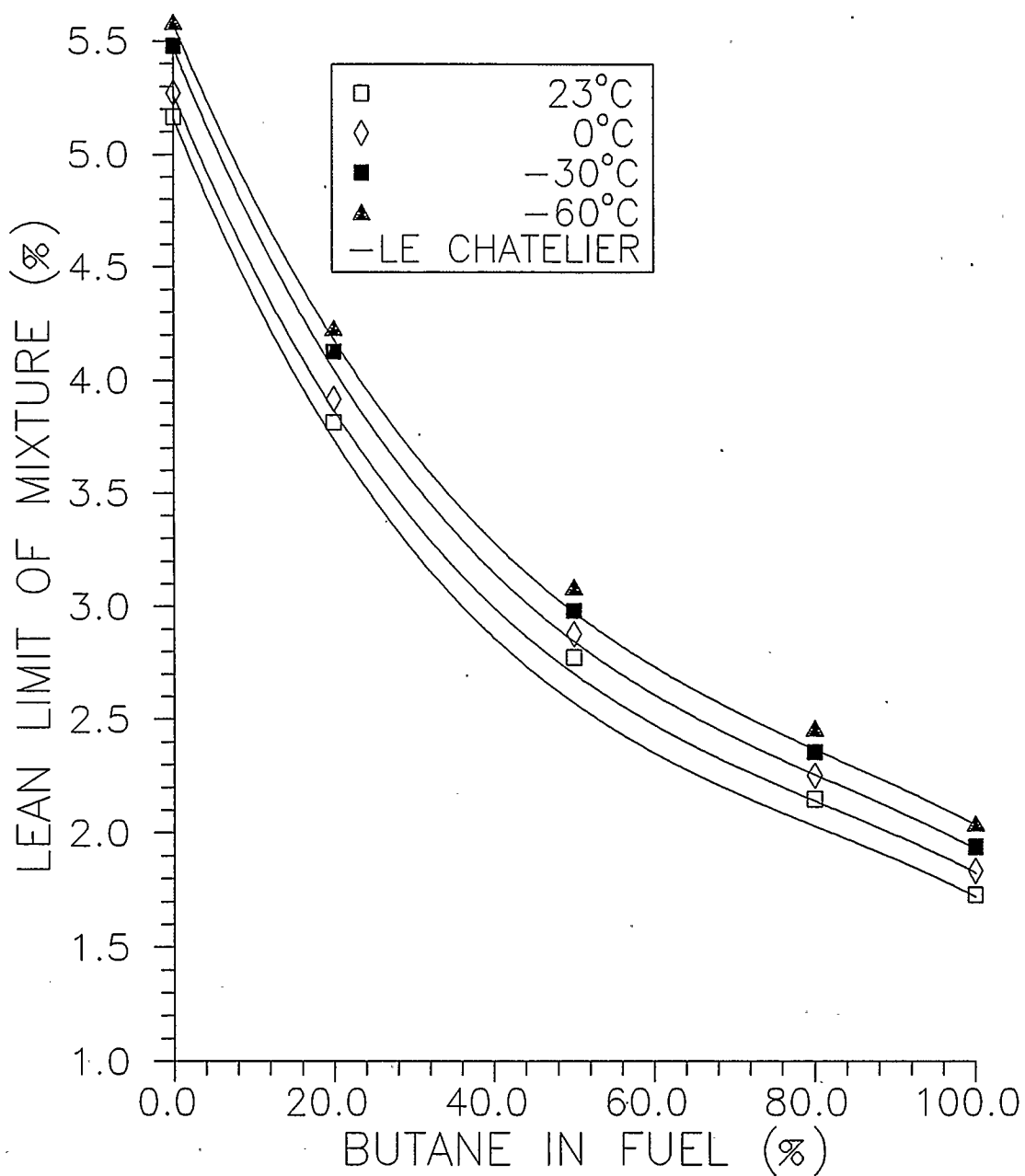


Figure 4.4.2 - A Comparison of the Lean Flammability Limits of Methane/Butane Mixtures at Various Initial Temperatures With Predictions From Le Chatelier's Rule, as a Function of Percent Butane Content

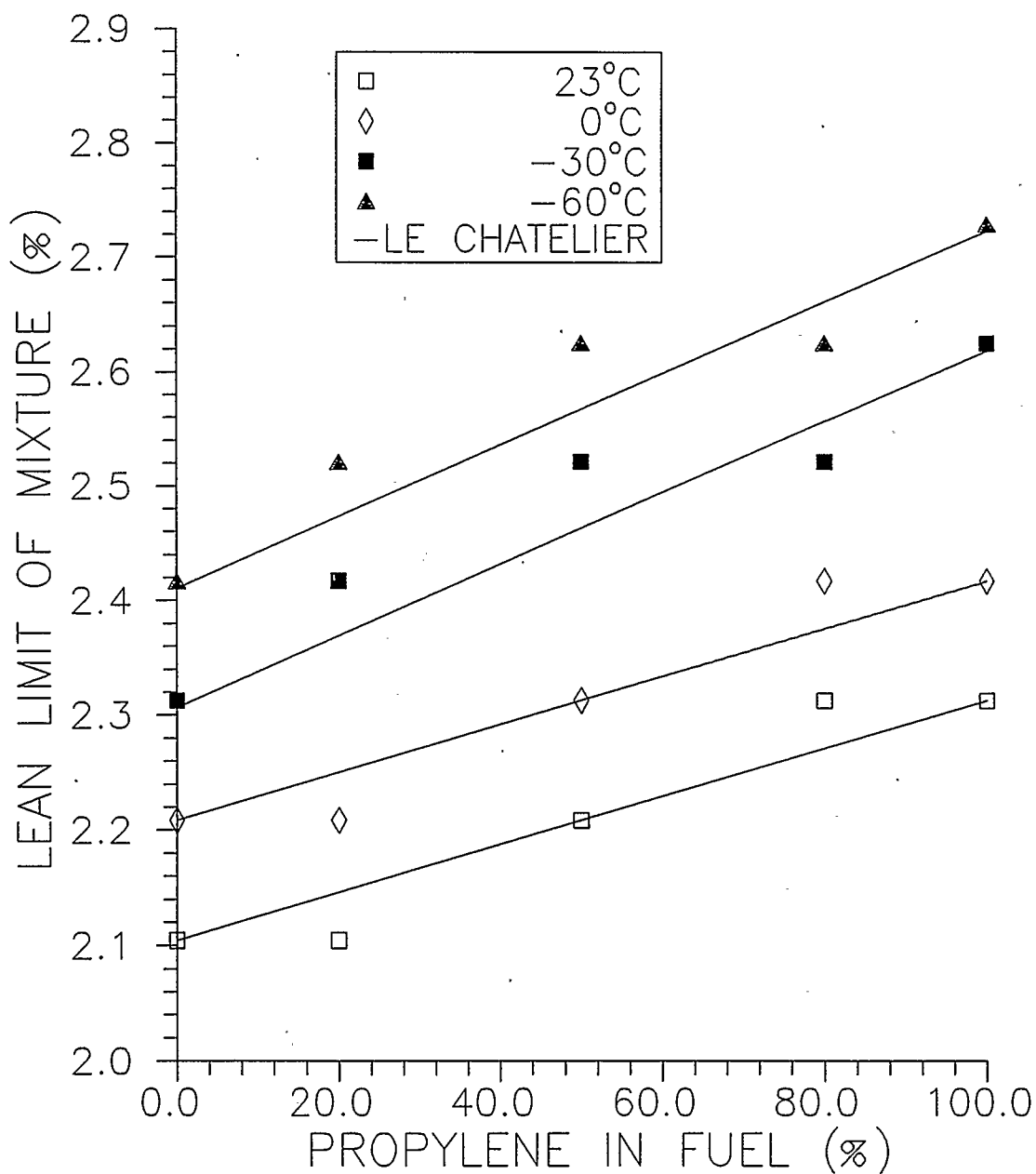


Figure 4.4.3 - A Comparison of the Lean Flammability Limits of Propane/Propylene Mixtures at Various Initial Temperatures With Predictions From Le Chatelier's Rule, as a Function of Percent Propylene Content

Table 4.4.1 - Lean Limits of Binary Mixtures Involving Methane or Propane.

Fuel Composition % by Volume				Experimental Lean Limit % by Volume			
				Initial Mixture Temperature °C			
C <sub>3</sub> H <sub>6</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	23	0	-30	-60
-	20.0	80.0	-	2.5	2.6	2.7	2.8
-	50.0	50.0	-	3.1	3.2	3.3	3.4
-	80.0	20.0	-	4.0	4.1	4.2	4.3
-	20.0	-	80.0	2.1	2.2	2.3	2.4
-	50.0	-	50.0	2.7	2.8	2.9	3.0
-	80.0	-	20.0	3.7	3.8	4.0	4.1
80.0	-	20.0	-	2.3	2.4	2.5	2.6
50.0	-	50.0	-	2.2	2.3	2.5	2.6
20.0	-	80.0	-	2.1	2.2	2.4	2.5

The constant adiabatic flame temperature method can be used to calculate the lean limit of various hydrocarbon mixtures over a range of initial temperatures if the limit is known at a reference temperature. This was done for the mixtures listed in Table 4.4.1 and the resulting calculated limits were in good agreement with the experimental results. In the interest of brevity, these calculated results have been omitted:

#### 4.5 Rich Flammability Limits of Some Binary Fuel Mixtures

Rich flammability limits were determined for a variety of binary mixtures of methane with propane, butane, and ethylene and are presented in Table 4.5.1 and Figures 4.5.1 through 4.5.3. Rich limits were also

found for binary mixtures of hydrogen and ethylene, hydrogen and methane, hydrogen and propane, and propane and propylene and are presented in Table 4.5.2 and Figures 4.5.4 and 4.5.5. It can be seen from Figure 4.5.1 that predictions from Le Chatelier's rule were quite close to the rich flammability limits of methane/propane mixtures at various temperatures. The deviations were slightly larger than the experimental error and they are listed in Table 4.5.3. From Table 4.5.3, it can be seen that fuel mixtures not involving hydrogen obey Le Chatelier's rule quite closely, with the highest deviation being 4.7%.

Table 4.5.1 - Rich Limits of Binary Mixtures Involving Methane.

Fuel Composition % by Volume				Experimental Rich Limit % by Volume			
				Initial Mixture Temperature °C			
C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	23	0	-30	-60
-	20.0	80.0	-	11.0	10.9	10.6	10.3
-	50.0	50.0	-	12.1	11.8	11.5	11.1
-	80.0	20.0	-	13.4	13.2	13.0	12.6
-	20.0	-	80.0	9.8	9.7	9.6	-
-	50.0	-	50.0	11.0	10.8	10.6	10.4
-	80.0	-	20.0	12.7	12.4	12.0	11.7
80.0	20.0	-	-	22.4	22.0	21.5	20.6
42.0	58.0	-	-	17.2	16.9	16.6	16.1
20.0	80.0	-	-	15.7	15.4	15.1	14.7

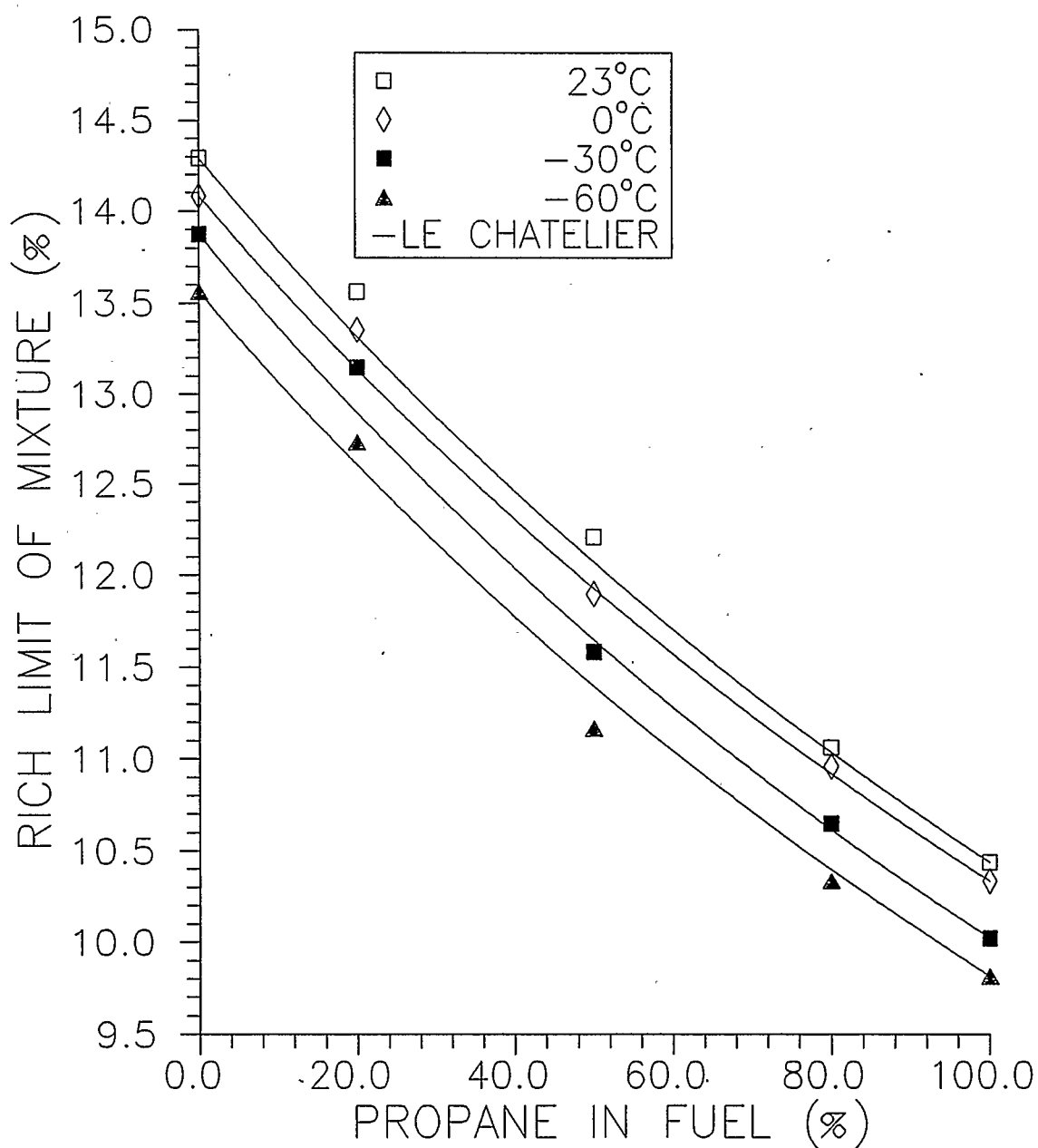


Figure 4.5.1 - A Comparison of the Rich Flammability Limits of Methane/Propane Mixtures at Various Initial Temperatures With Predictions From Le Chatelier's Rule, as a Function of Percent Propane Content

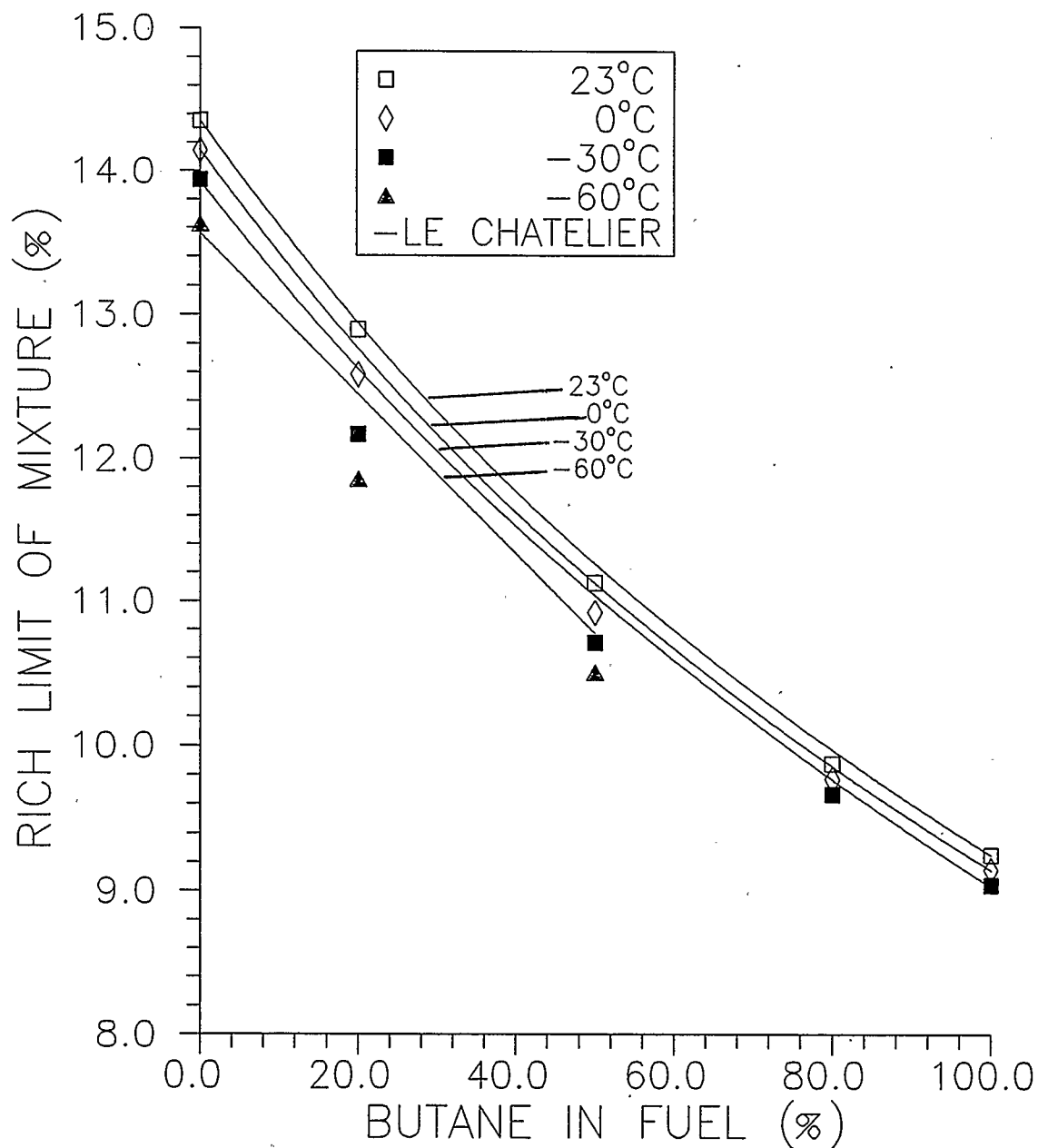


Figure 4.5.2 - A Comparison of the Rich Flammability Limits of Methane/Butane Mixtures at Various Initial Temperatures With Predictions From Le Chatelier's Rule, as a Function of Percent Butane Content

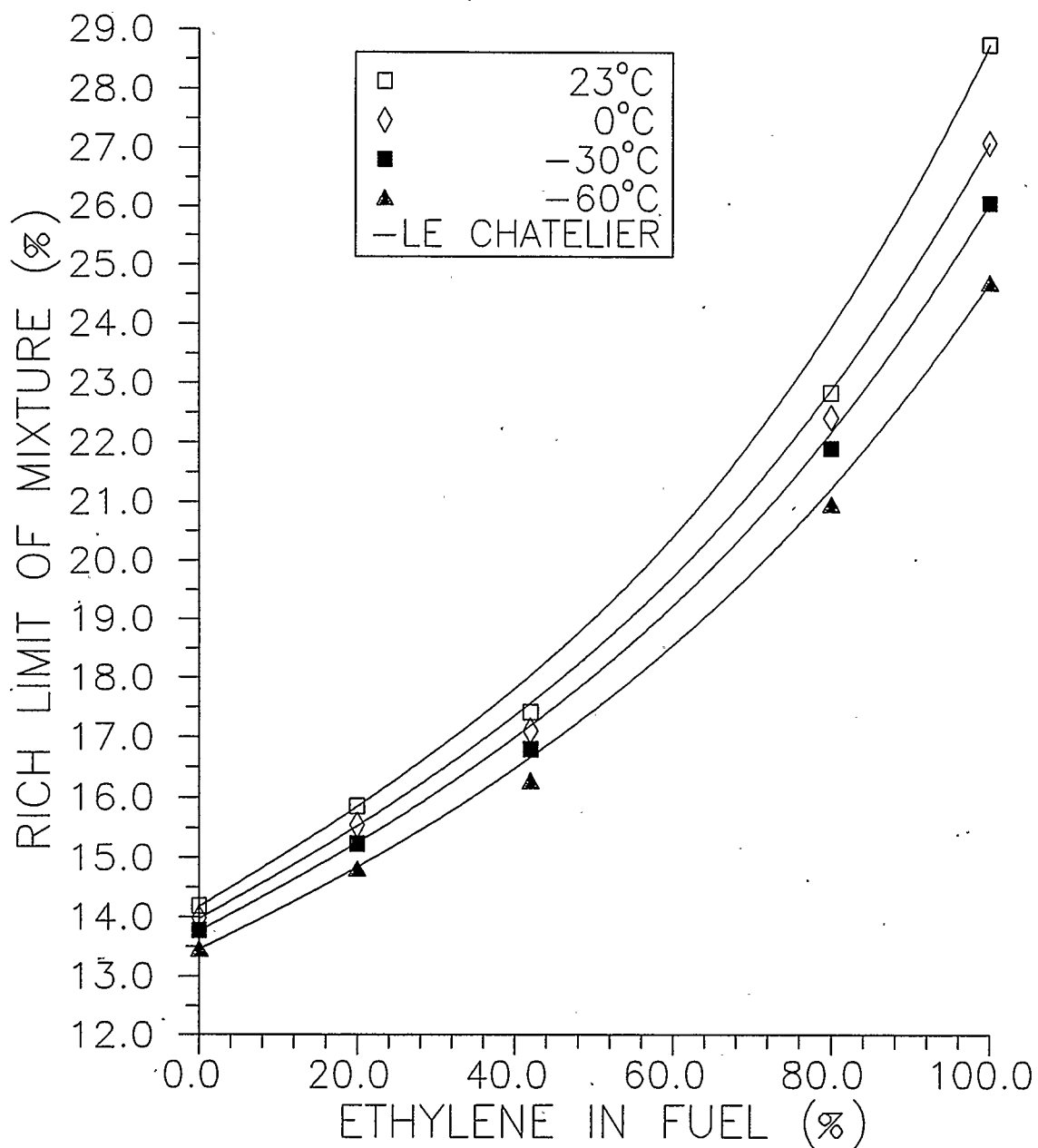


Figure 4.5.3 - A Comparison of the Rich Flammability Limits of Methane/Ethylene Mixtures at Various Initial Temperatures With Predictions From Le Chatelier's Rule, as a Function of Percent Ethylene Content

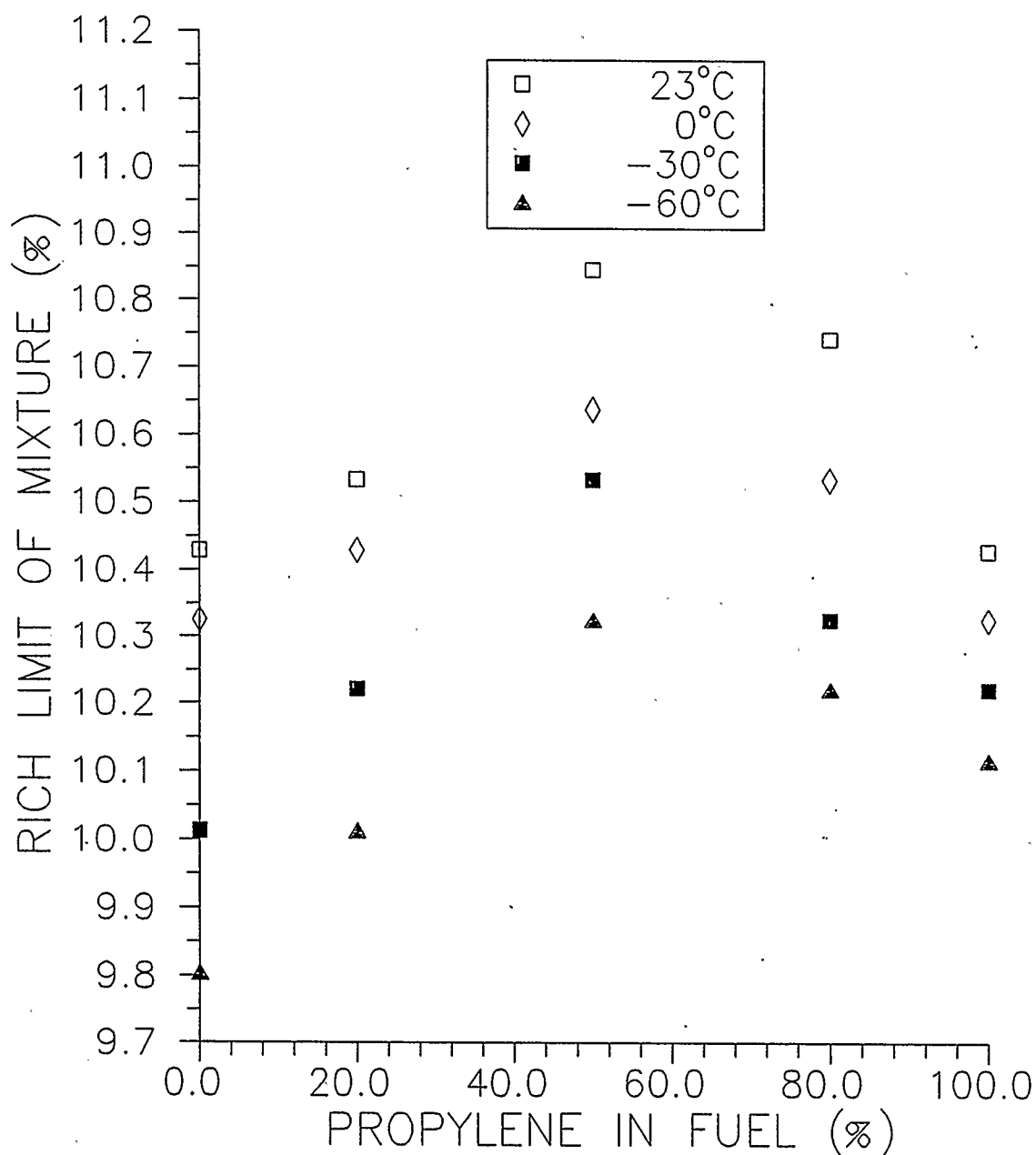


Figure 4.5.4 - Rich Flammability Limits of Propane/Propylene Mixtures Versus the Amount of Propylene in the Fuel for Different Initial Temperatures



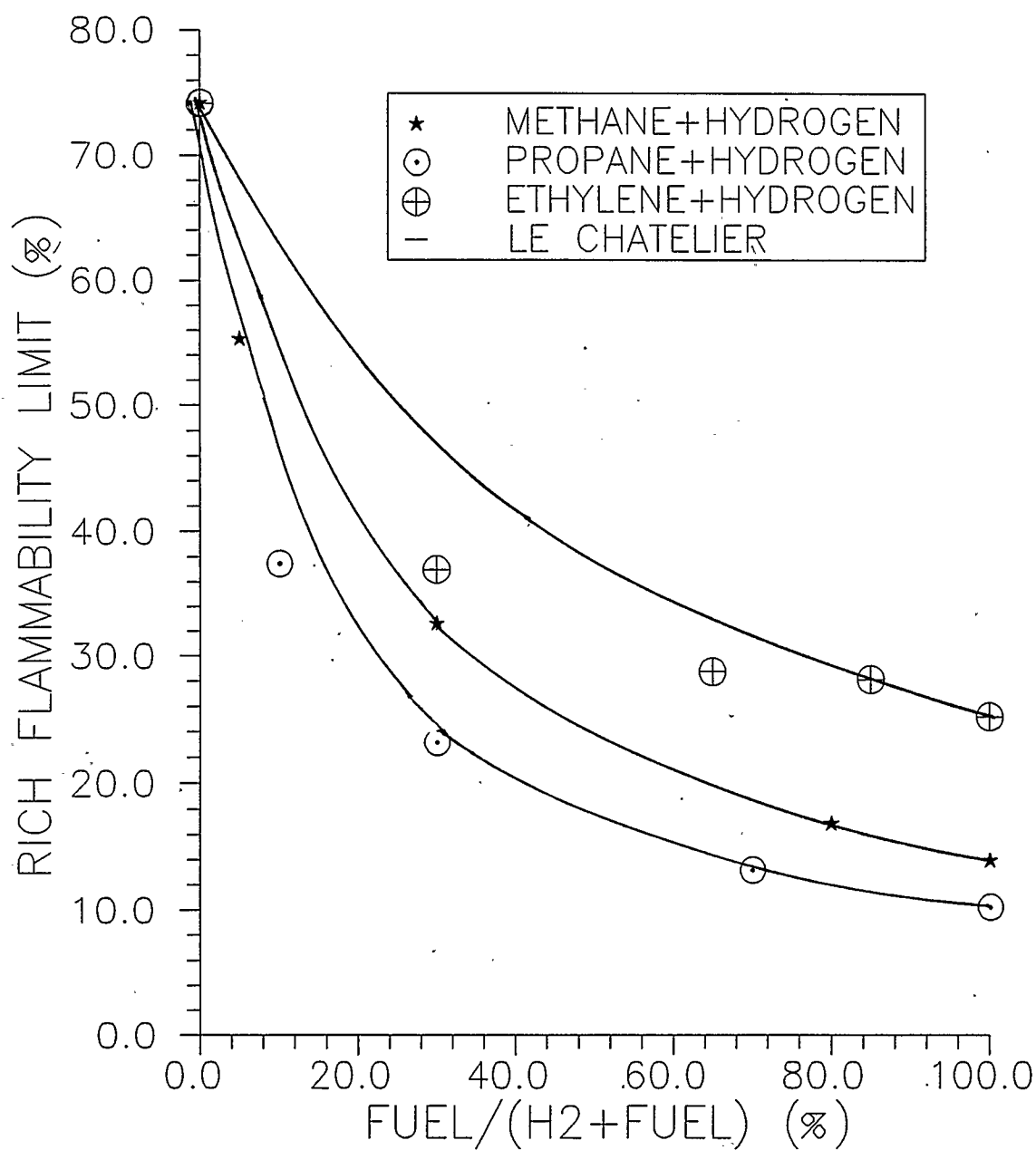


Figure 4.5.5 - Rich Flammability Limits of Binary Mixtures of Hydrogen With Methane, Ethylene, and Propane, Compared to Predictions From Le Chatelier's Rule at an Initial Temperature of -60°C.

Table 4.5.2 - Rich Limits of Binary Mixtures Involving Propane or Hydrogen.

Fuel Composition % by Volume					Experimental Rich Limit % by Volume			
					Initial Mixture Temperature °C			
CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	23	0	-30	-60
-	-	90.0	10.0	-	-	-	-	35.9
-	-	70.0	30.0	-	-	-	-	22.2
-	-	30.0	70.0	-	-	-	-	12.6
-	-	-	20.0	80.0	10.7	10.5	10.3	10.2
-	-	-	50.0	50.0	10.8	10.6	10.5	10.3
-	-	-	80.0	20.0	10.5	10.4	10.2	10.0
80.0	-	20.0	-	-	-	-	-	16.2
30.0	-	70.0	-	-	-	-	-	31.3
5.0	-	95.0	-	-	-	-	-	53.1
-	30.0	70.0	-	-	38.8	-	-	35.5
-	65.0	35.0	-	-	31.0	-	-	27.6 <sup>1</sup>
-	85.0	15.0	-	-	-	-	-	27.0 <sup>1</sup>

<sup>1</sup>Tests where there was no detectable ignition at the measured flammability limit

The rich limits of propane/propylene mixtures are shown in Figure 4.5.4. It can be seen that the rich flammability limits of many of the propane/propylene mixtures were higher than the limit of either of these fuels individually. Even though propane and propylene were found to have the same rich limit (10.4%) at 23°C, a 50%/50% mixture had a higher limit of 10.8%. As mentioned earlier, mixtures of saturated and unsaturated

hydrocarbons tend to deviate more from the Le Chatelier estimations than mixtures of saturated hydrocarbons. As expected, the percent deviations listed in Table 4.5.3 for propane/propylene mixtures were slightly higher than for methane/propane mixtures, and although they were still less than 4%, this still shows that Le Chatelier's rule cannot predict this behavior.

The rich flammability limit of binary mixtures of hydrogen with methane, propane, and ethylene were determined experimentally at an initial temperature of  $-60^{\circ}\text{C}$  and are shown in Table 4.5.2 and Figure 4.5.5. As it can be seen, deviations from the rich limits estimated using Le Chatelier's rule were significant for some of the mixtures. The deviations from Le Chatelier estimations seemed to be particularly large for mixtures containing large quantities of hydrogen as shown in Table 4.5.3, which also agrees with the results of Cheng [14] for tests done with similar mixtures at room temperature. The extent of the relative deviation seemed to be independent of the initial mixture temperature for the mixtures considered. It is evident that Le Chatelier's rule must be applied cautiously to mixtures whose main constituent is hydrogen, although it should be pointed out that the Le Chatelier estimates were almost exclusively on the high side.

Table 4.5.3 - Comparison of Experimental Rich Flammability Limits of Binary Fuel Mixtures With Those Predicted by Le Chatelier's Rule.

Fuel Composition % by Volume						(RL <sub>c</sub> - RL)/RL (%) Initial Temperature°C			
CH <sub>4</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	23	0	-30	-60
80.0	-	-	20.0	-	-	-1.8	-1.6	-1.9	-0.9
50.0	-	-	50.0	-	-	-0.1	0.3	0.5	2.0
20.0	-	-	80.0	-	-	-0.2	-0.3	-0.3	0.6
-	-	-	20.0	80.0	-	-2.8	-1.9	-1.4	-1.6
-	-	-	50.0	50.0	-	-3.7	-2.8	-3.8	-3.4
-	-	-	80.0	20.0	-	-1.0	-1.0	-1.6	-1.4
80.0	-	20.0	-	-	-	-0.3	-0.3	0.0	0.1
58.0	-	42.0	-	-	-	3.7	2.8	2.4	2.0
20.0	-	80.0	-	-	-	4.7	2.0	1.2	0.6
80.0	20.0	-	-	-	-	0.3	1.4	3.3	4.0
50.0	50.0	-	-	-	-	1.2	1.9	3.1	2.9
20.0	80.0	-	-	-	-	0.9	0.8	0.6	-
80.0	-	-	-	-	20.0	-	-	-	-1.2
30.0	-	-	-	-	70.0	-	-	-	-0.8
5.0	-	-	-	-	95.0	-	-	-	10.3
-	-	30.0	-	-	70.0	27.6	-	-	26.7
-	-	65.0	-	-	35.0	15.7	-	-	14.0
-	-	85.0	-	-	15.0	-	-	-	-0.5
-	-	-	10.0	-	90.0	-	-	-	21.9
-	-	-	30.0	-	70.0	-	-	-	11.3
-	-	-	70.0	-	30.0	-	-	-	4.9

#### 4.6 Lean Flammability Limits of Some Fuel Mixtures Containing Diluents

The results of measurements of the lean flammability limits made for a variety of mixtures of methane with either nitrogen or carbon dioxide are shown in Table 4.6.1.

In general, as the quantity of inert diluent in the fuel increases, the lean limit of the mixture also increases until a point is reached where the fuel is no longer flammable. Figures 4.6.1 and 4.6.2 show the rich and lean limits of methane/nitrogen and methane/carbon dioxide mixtures as a function of the percentage of diluent in the fuel. A comparison of the lean limit curves in the two figures shows that mixtures containing given quantities of carbon dioxide had higher lean limits than mixtures containing equal amounts of nitrogen.

Table 4.6.1 - Lean Limits of Methane/Diluent Mixtures.

Fuel Composition % by Volume			Experimental Lean Limit % by Volume			
			Initial Mixture Temperature °C			
CH <sub>4</sub>	N <sub>2</sub>	CO <sub>2</sub>	23	0	-30	-60
20.0	80.0	-	24.9	25.4	26.4	27.2
50.0	50.0	-	9.9	10.2	10.5	10.8
80.0	20.0	-	6.2	6.3	6.5	6.8
30.0	-	70.0	18.4	19.1	20.0	21.0
50.0	-	50.0	10.4	10.8	11.2	11.7
80.0	-	20.0	6.3	6.5	6.8	7.0

Theoretical adiabatic flame temperatures were calculated for the methane/diluent mixtures, and are plotted in Figure 4.6.3. It can be seen that flame temperatures were a linear function of the initial temperature for the mixtures tested, and that flame temperature increased as initial temperature decreased. For lean methane/nitrogen mixtures, the curves plotted for the various component combinations were quite close together, indicating that for a given initial temperature, the calculated flame temperatures of the lean methane/nitrogen mixtures were not constant, but did fall into a narrow range. It is also evident that this range of flame temperature was larger for methane/carbon dioxide mixtures than it was for methane/nitrogen mixtures. It was suggested [62] that the flammability limits are associated with a certain value of flame temperature. Assuming that this flame temperature remains constant with addition of nitrogen or carbon dioxide to the methane makes it possible to calculate the lean limits of "diluted" fuel mixtures. The limits in Figure 4.6.4 for methane/nitrogen mixtures and for methane/carbon dioxide mixtures in Figure 4.6.5 were found using the methane lean limit mixture flame temperature, and the results are compared with the experimental values. Predictions of methane/nitrogen lean limits were very accurate using this method, while those for methane/carbon dioxide limits were not as good, but still reasonable for mixtures containing up to 50% carbon dioxide.

Another method of predicting lean limits of fuel/diluent mixtures is to create diagrams such as Figures 4.6.6 and 4.6.7, as suggested by Wierzba and Karim [65]. For the lean methane/nitrogen mixtures in Figure 4.6.6, the lean limit curves (right hand side) can be plotted by drawing straight lines between the origin and the points for the pure methane lean

limits at particular initial temperatures. Alternatively, these lean limits can be calculated using the expression:

$$LL_m = 100(LL_{CH_4})/Y_F \quad (4.6.1)$$

Where,

- $LL_m$  is the lean flammability limit of the methane/nitrogen mixture, % by volume.
- $LL_{CH_4}$  is the corresponding lean flammability limit for methane, % by volume.
- $Y_F$  is the concentration of the methane in the fuel mixture, expressed in % by volume.

Equation 4.6.1 cannot be applied directly to methane/carbon dioxide mixtures because unlike nitrogen, carbon dioxide has thermal/transport properties that are substantially different from those of air. This explains why the lean limit curves in Figure 4.6.7 did not pass through the origin. It was reported earlier [64] that the flammability of fuel/diluent mixtures can be correlated using the following relationship:

$$LL_m = 100/((Y_F/LL_{CH_4}) + a_F(100-Y_F)) \quad (4.6.2)$$

Where,

- $LL_m$  is the lean flammability limit of the methane/diluent mixture, % by volume.
- $LL_{CH_4}$  is the corresponding lean flammability limit for methane, % by volume.
- $Y_F$  is the concentration of the methane in the fuel mixture, % by volume.
- $a_F$  is the corresponding empirical constant.

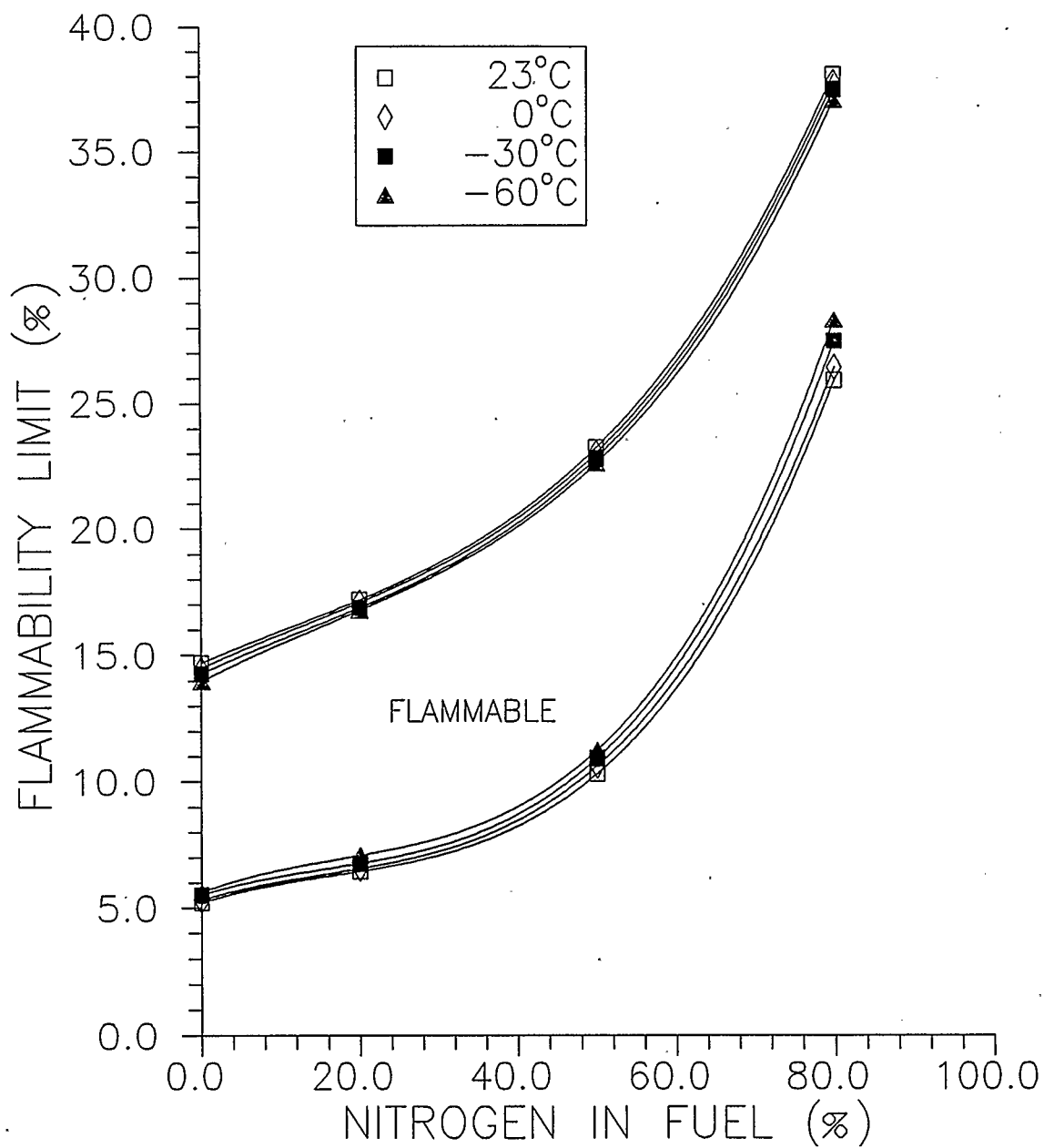


Figure 4.6.1 - Rich and Lean Flammability Limits of Methane/Nitrogen Mixtures Versus the Amount of Nitrogen in the Fuel, for Different Initial Temperatures



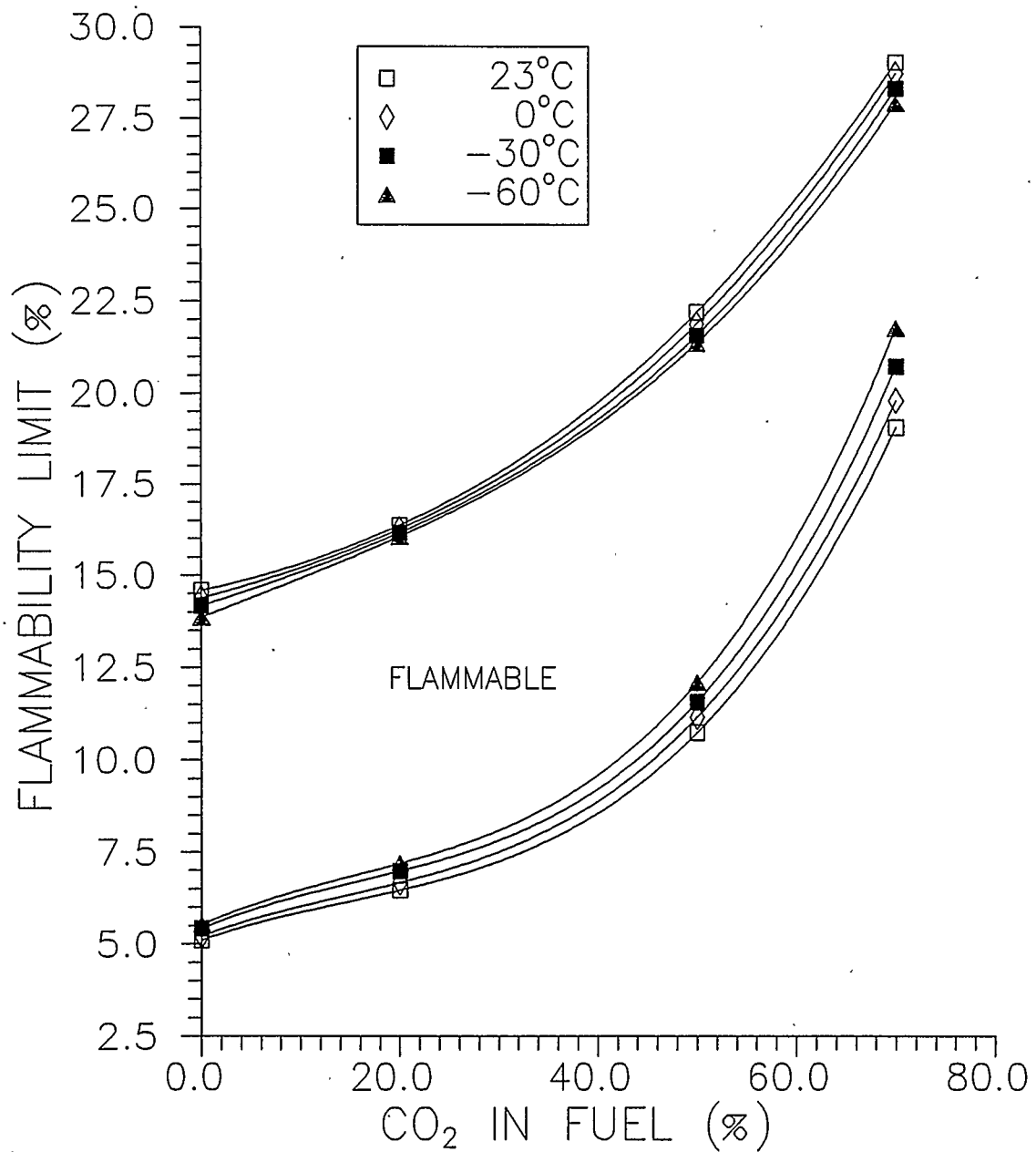


Figure 4.6.2 - Rich and Lean Flammability Limits of Methane/Carbon Dioxide Mixtures Versus the Amount of Carbon Dioxide in the Fuel, for Different Initial Temperatures

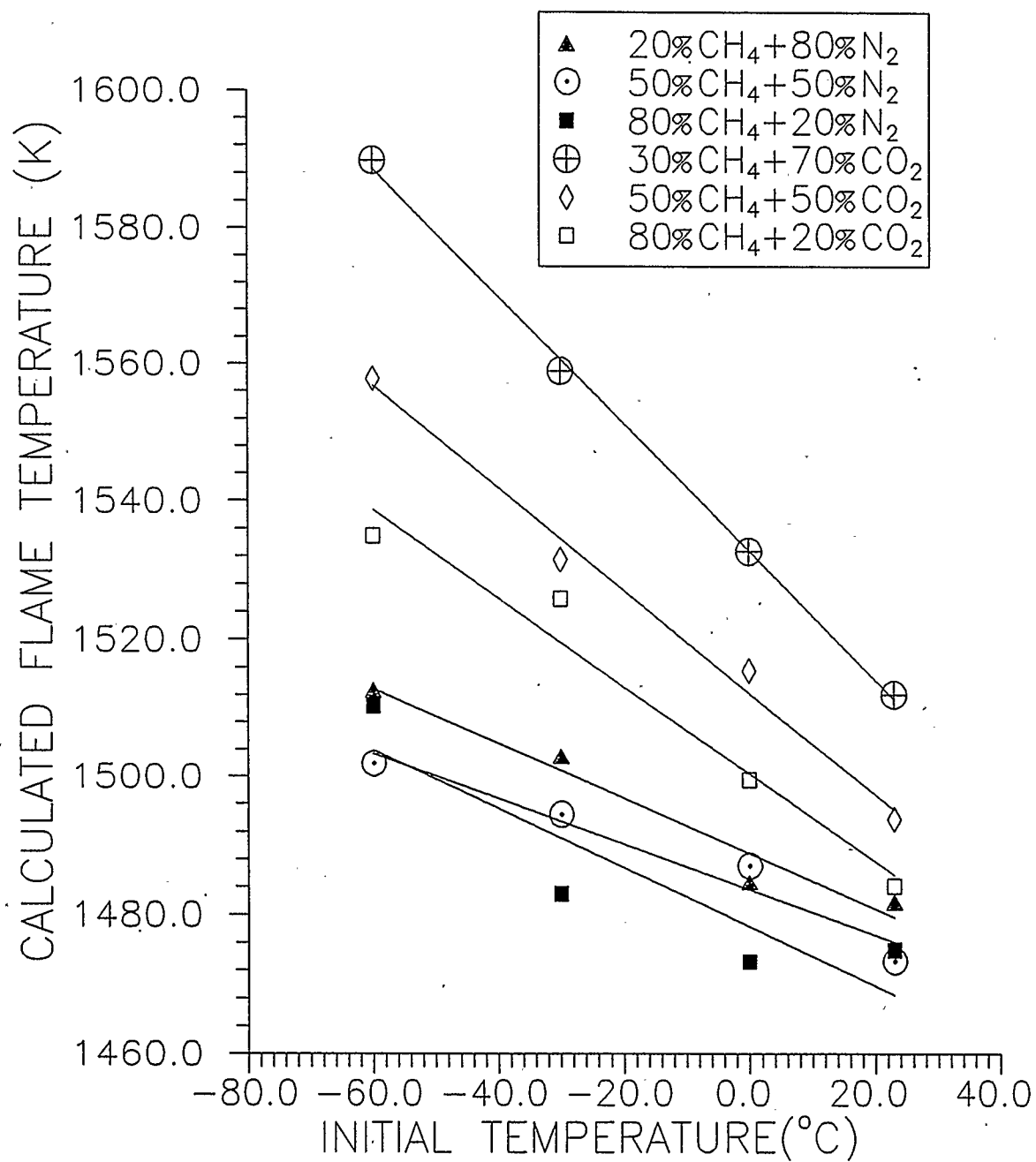


Figure 4.6.3 - Calculated Adiabatic Flame Temperature of Methane/Diluent Lean Limit Mixtures as a Function of Initial Temperature

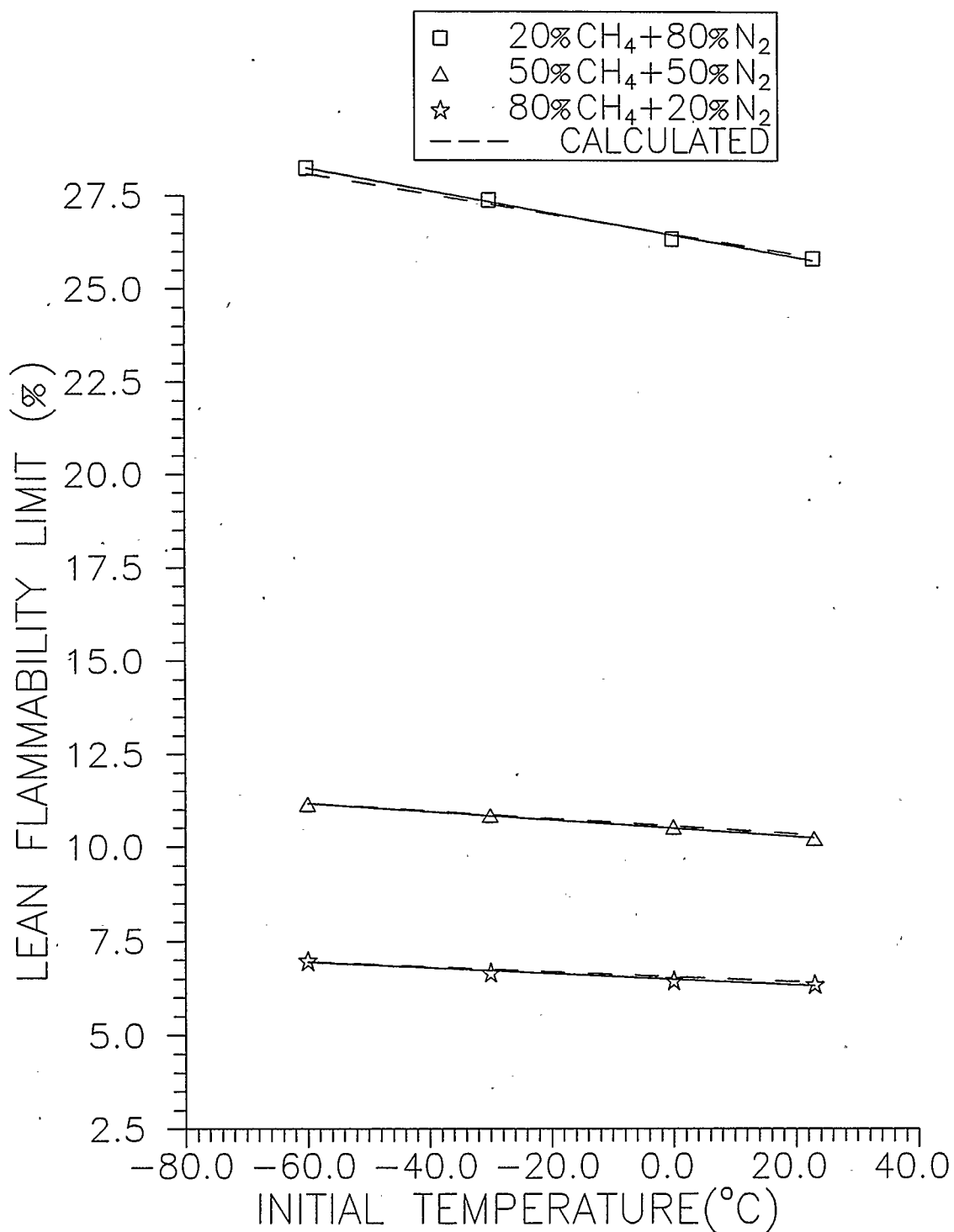


Figure 4.6.4 - Lean Flammability Limits of Methane/Nitrogen Mixtures Versus Initial Temperature for Both Experimental Limits and Those Calculated Using the Adiabatic Flame Temperature of Pure Methane at the Same Initial Temperature

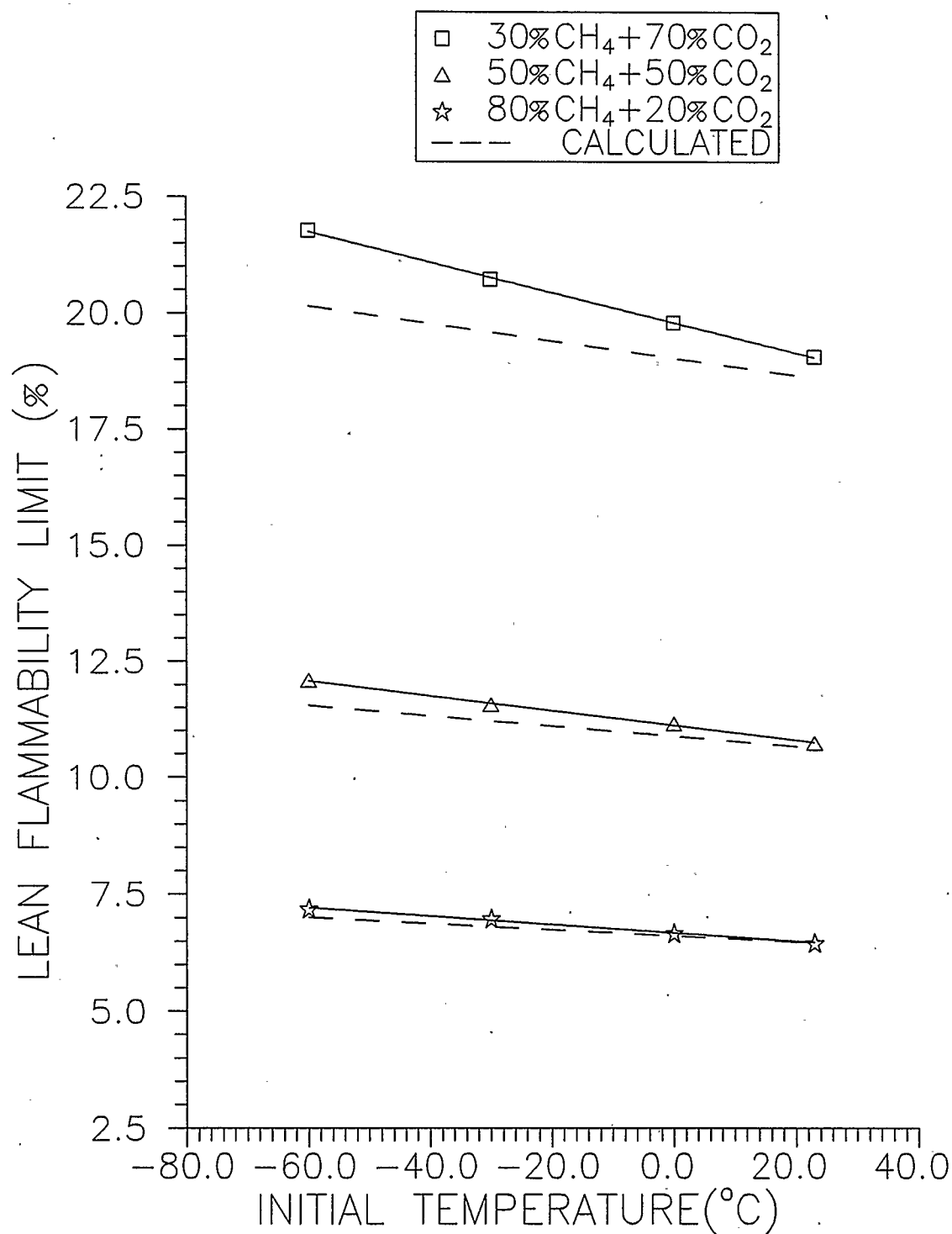


Figure 4.6.5 - Lean Flammability Limits of Methane/Carbon Dioxide Mixtures Versus Initial Temperature for Both Experimental Limits and Those Calculated Using the Adiabatic Flame Temperature of Pure Methane at the Same Initial Temperature

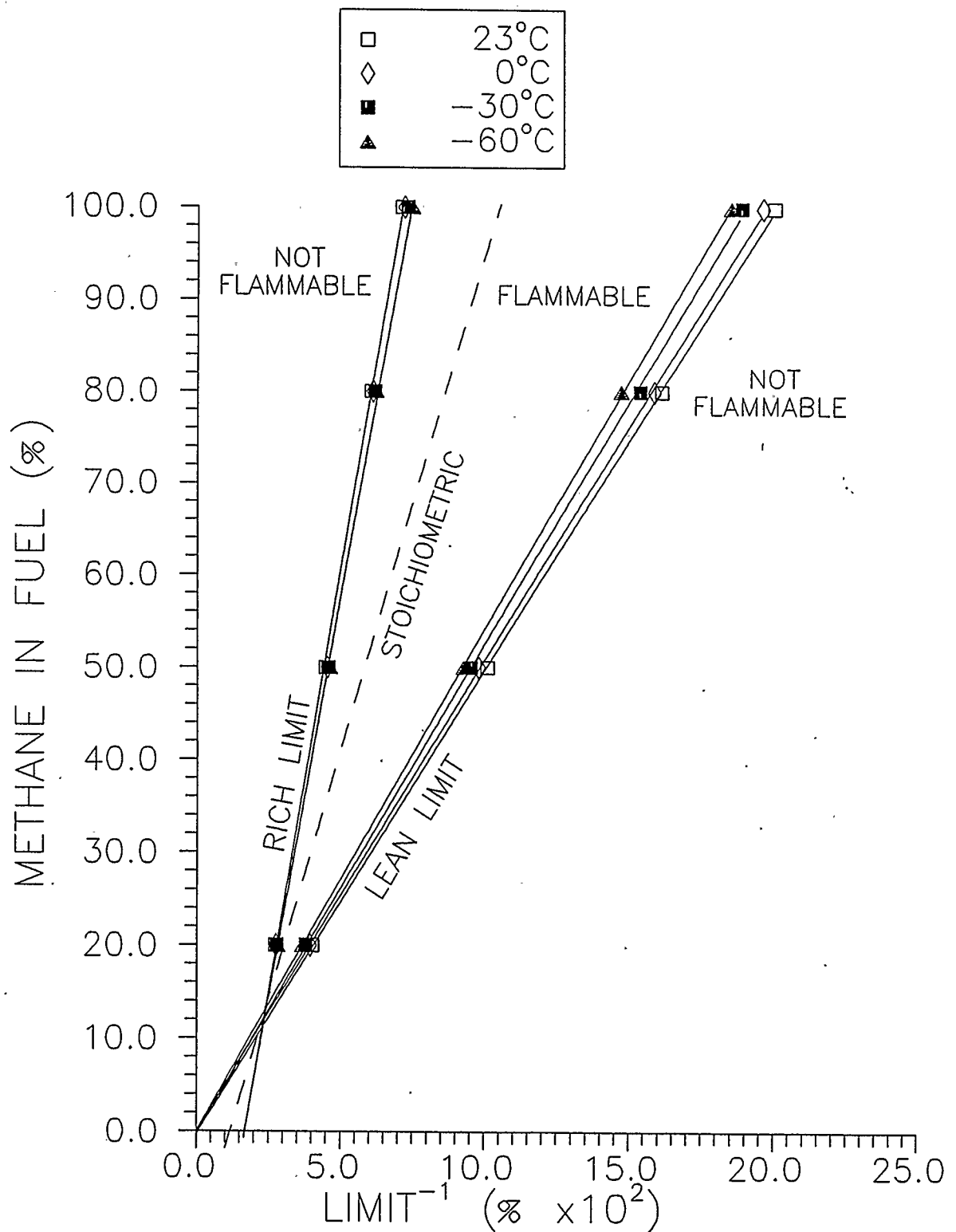


Figure 4.6.6 - The Amount of Methane in Methane/Nitrogen Fuel Mixtures Versus  $1/\text{Limit}$  for Both Rich and Lean Flammability Limits at Various Initial Temperatures

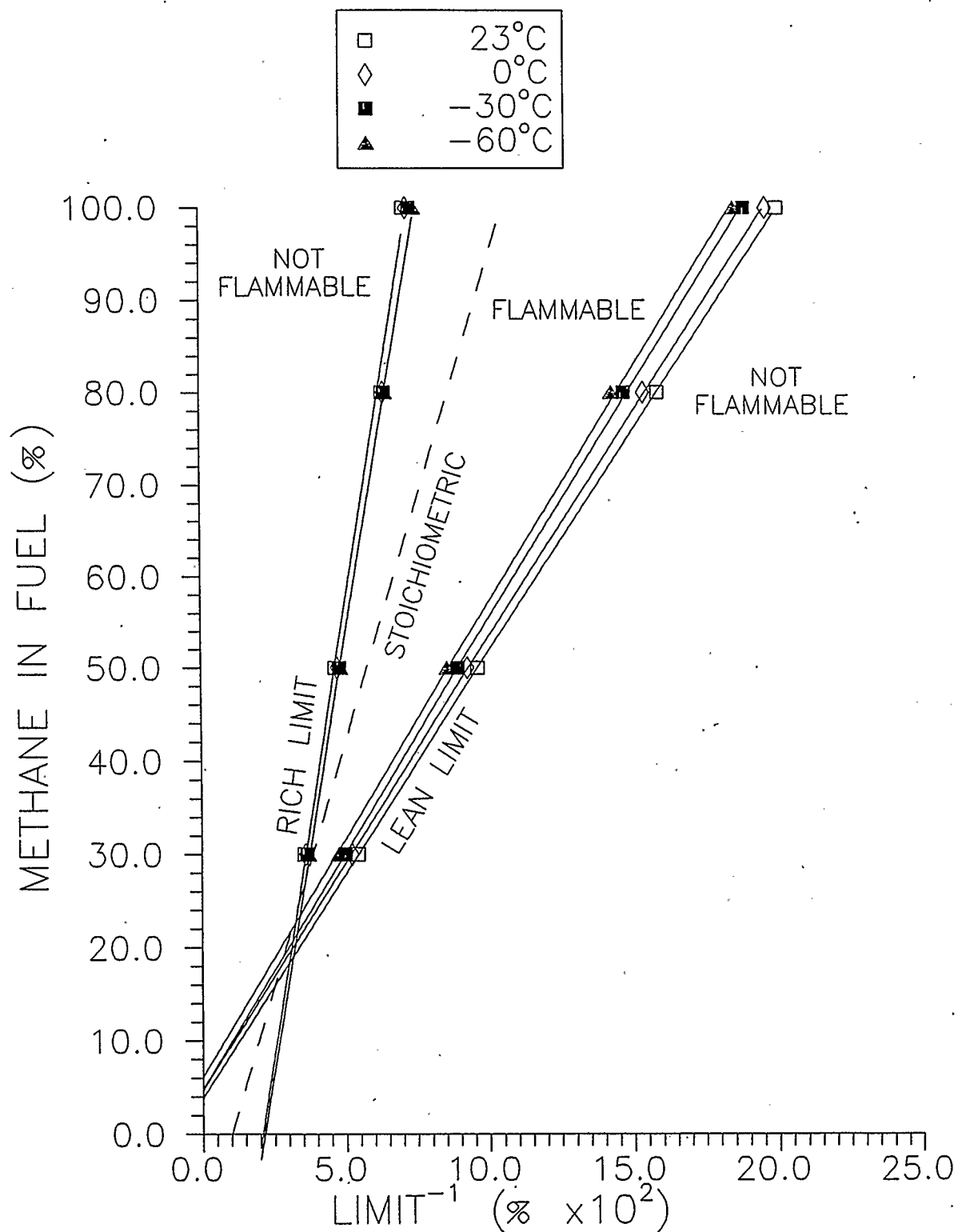


Figure 4.6.7 - The Amount of Methane in Methane/Carbon Dioxide Fuel Mixtures Versus 1/Limit for Both Rich and Lean Flammability Limits at Various Initial Temperatures

The empirical constant  $a_f$  depends on the type of fuel and diluent, and is approximately zero for nitrogen. Analysis of the experimental data on lean limits of methane/carbon dioxide fuel mixtures indicated that  $a_f$  values depend on the initial temperatures and are as follows: -0.0075 at 23°C, -0.0100 at 0°C and -30°C, and -0.1250 at -60°C. Equations 4.6.1 and 4.6.2 were used to calculate the lean flammability limits of the methane/diluent mixtures tested, and the results are compared with the experimental values in Table 4.6.2.

Table 4.6.2 - Comparison of Experimental and Calculated Lean Flammability Limits for Methane/Diluent Mixtures.

Fuel Composition % by Volume			(LL <sub>c</sub> - LL) / LL (%)			
			Initial Mixture Temperature °C			
CH <sub>4</sub>	N <sub>2</sub>	CO <sub>2</sub>	23	0	-30	-60
20.0	80.0	-	0.4	0.4	0.4	-0.7
50.0	50.0	-	1.0	0.0	0.9	0.0
80.0	20.0	-	0.8	1.3	2.0	-0.7
30.0	-	70.0	-0.8	1.0	0.8	1.7
50.0	-	50.0	-0.1	0.5	-0.1	-1.0
80.0	-	20.0	0.2	-0.6	-1.3	-1.9

The differences between the calculated and experimental results in Table 4.6.2 are all quite small. Calculations for methane/nitrogen mixtures made using Equation 4.6.1 agreed very well with the experimental limits, and those for methane/carbon dioxide that utilized Equation 4.6.2 were also quite good.

#### 4.7 Rich Flammability Limits of Some Fuel Mixtures Containing Diluents

The rich flammability limits of a variety of mixtures of methane with either nitrogen or carbon dioxide are given in Table 4.7.1 and are also shown in Figures 4.6.1 and 4.6.2. The rich limits obtained for ethylene/carbon dioxide mixtures at an initial temperature of  $-60^{\circ}\text{C}$  are also included in Table 4.7.1 and Figure 4.7.1.

Table 4.7.1 - Rich Limits of Some Fuel/Diluent Mixtures.

Fuel Composition % by Volume				Experimental Rich Limit % by Volume			
				Initial Mixture Temperature $^{\circ}\text{C}$			
$\text{C}_2\text{H}_4$	$\text{CH}_4$	$\text{N}_2$	$\text{CO}_2$	23	0	-30	-60
-	20.0	80.0	-	36.6	36.3	36.0	35.6
-	50.0	50.0	-	22.3	22.1	21.9	21.7
-	80.0	20.0	-	16.5	16.4	16.2	16.1
-	30.0	-	70.0	28.0	27.7	27.3	26.9
-	50.0	-	50.0	21.4	21.1	20.8	20.6
-	80.0	-	20.0	15.8	15.7	15.6	15.5
80.0	-	-	20.0	-	-	-	<sup>1</sup> 26.1
50.0	-	-	50.0	-	-	-	27.2
20.0	-	-	80.0	-	-	-	34.3

<sup>1</sup>Tests where there was no detectable ignition at the measured flammability limit.

It can be perceived that the addition of diluents to methane increased the rich limit of the resulting fuel mixture. The resulting increase was greater in the case where the added diluent was nitrogen



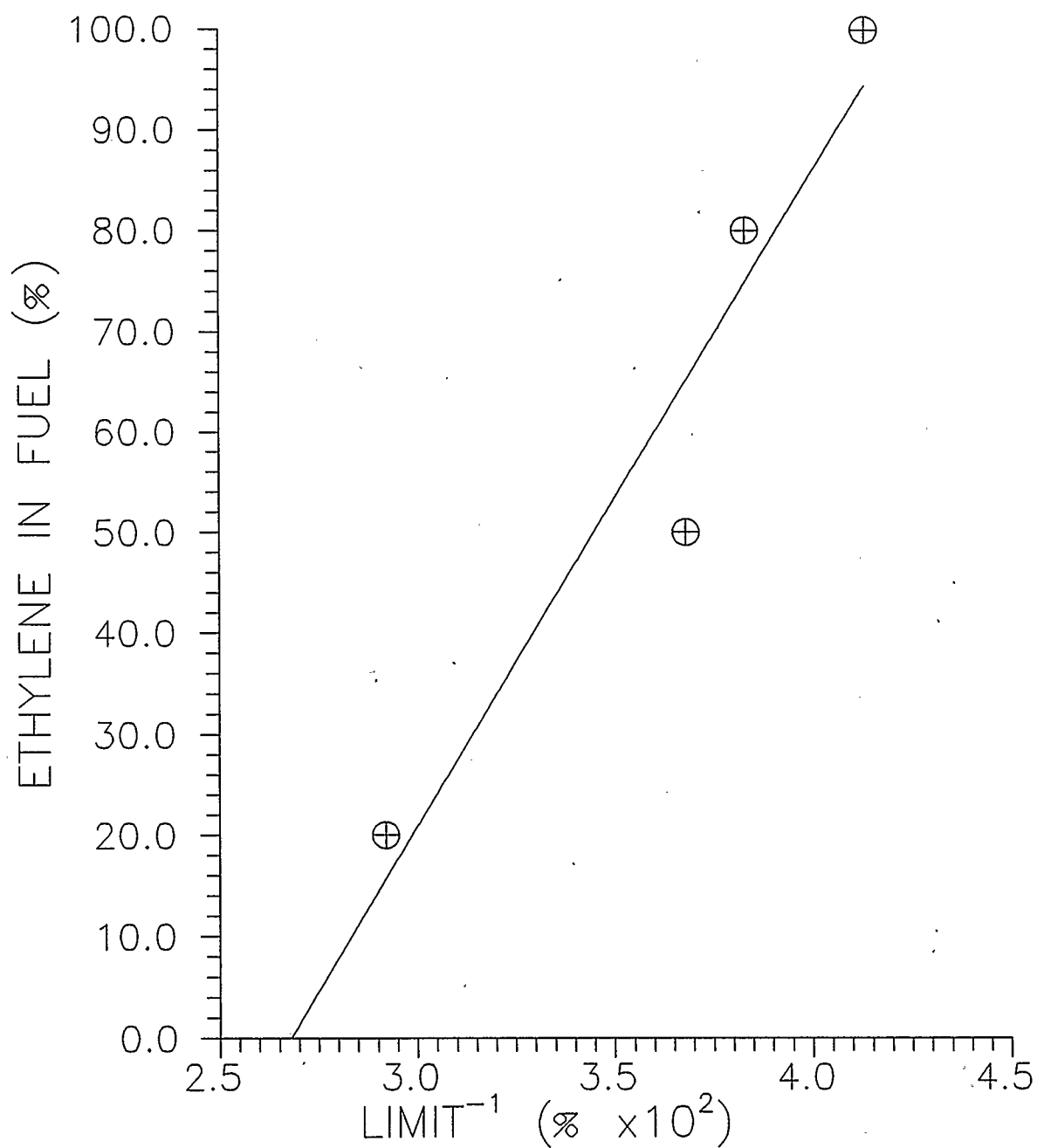


Figure 4.7.1 - The Amount of Ethylene in Ethylene/Carbon Dioxide Rich Limit Mixtures Versus 1/Rich Limit at an Initial Temperature of -60°C

rather than carbon dioxide.

Differences in the effects of nitrogen and carbon dioxide are attributable to their dissimilar thermal and transport properties as well as possible differences in chemical kinetics. As expected, the rich limit of each methane/diluent mixture decreased linearly with initial temperature decrease, although the change was quite small.

Close inspection of Figures 4.6.6 and 4.6.7 shows that the point of intersection of the rich and lean limit lines was also a stoichiometric mixture. This observation was true for both methane/nitrogen and methane/carbon dioxide mixtures. If the lean and rich flammability limits of pure methane in air are known, they can be used to calculate the rich and lean limits of methane/nitrogen mixtures. Equation 4.6.1 was discussed earlier, and it was shown that it could be used to represent the lean limit curve of methane/nitrogen mixtures in Figure 4.6.6. It is also possible to calculate the point on the lean limit curve where the fuel/air mixture contains fuel and oxygen in stoichiometric proportions. Connecting this stoichiometric point to the pure methane rich limit point with a straight line will define the possible rich limit mixtures of methane and nitrogen [65]. In equation form, the calculation process is as follows [65]:

$$RL_m = 100 / ((Y_F / RL_{CH_4}) + (1 - LL_{CH_4} / RL_{CH_4}) (100 - Y_F) / (100 - 10.52 (LL_{CH_4}))) \quad (4.7.1)$$

Where,

$RL_m$  is the rich flammability limit of the methane/nitrogen mixture, % by volume.

$LL_{CH_4}$  is the corresponding lean flammability limit for methane, expressed in % by volume.

$y_F$  is the concentration of the methane in the fuel mixture, % by volume.

$RL_{CH_4}$  is the corresponding rich flammability limit for methane, % by volume.

The same procedure can be followed for the rich limits of methane/carbon dioxide mixtures shown in Figure 4.6.7, except this time Equation 4.6.2 is used to define the lean limit line. An average value for  $a_f$  of -0.01 was used for all the initial temperatures because calculations indicated that this resulted in only small changes in the percent errors given in Table 4.6.2. The resulting equation follows:

$$RL_m = m / (y_F - 100 + m / RL_{CH_4}) \quad (4.7.2)$$

Where,

$$m = (100 / LL_{CH_4} - 10.524) / ((1 / LL_{CH_4} - 0.08524) / RL_{CH_4} - 0.01 / LL_{CH_4} - 0.0010524)$$

$RL_m$  is the rich flammability limit of the methane/nitrogen mixture, % by volume.

$RL_{CH_4}$  is the corresponding rich flammability limit for methane, % by volume.

$LL_{CH_4}$  is the corresponding lean flammability limit for methane, % by volume.

$y_F$  is the concentration of the methane in the fuel mixture, % by volume.

Equations 4.7.1 and 4.7.2 were used to calculate the rich limits of flammability for methane diluted with nitrogen or carbon dioxide. Calculated limits are compared to the experimental values in Table 4.7.2.

Table 4.7.2 - Comparison of Experimental and Calculated Rich Flammability Limits for Methane/Diluent Mixtures.

Fuel Composition % by Volume			(RL <sub>c</sub> - RL)/RL (%)			
			Initial Mixture Temperature °C			
CH <sub>4</sub>	N <sub>2</sub>	CO <sub>2</sub>	23	0	-30	-60
20.0	80.0	-	9.0	8.8	8.1	8.1
50.0	50.0	-	6.1	5.7	5.1	4.1
80.0	20.0	-	1.9	1.2	0.9	-0.6
30.0	-	70.0	7.1	7.1	6.8	7.0
50.0	-	50.0	6.0	6.2	5.8	5.2
80.0	-	20.0	5.2	4.4	3.5	2.0

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

1. The rich and lean flammability limits for the following pure gaseous fuels: methane, ethane, propane, n-butane, ethylene, propylene, carbon monoxide, and hydrogen, were obtained over a temperature range of 23°C to -60°C. Lean flammability limits for hydrogen were determined down to -100°C. In addition, the rich and lean limits were determined for the vapors of selected liquid fuels at 23°C including pentane, hexane, and heptane.
2. It was found that for the fuels tested, the lean limit of flammability increased linearly as initial temperature decreased. Good prediction of this linear relationship for the various gases was obtained with the Modified Burgess-Wheeler law or by assuming that the adiabatic flame temperature was constant. The constant flame temperature method yielded the best predictions for most fuels tested, with the exception of hydrogen.
3. The rich flammability limits of the fuels tested were reduced linearly with temperature decrease. Reasonable prediction of this behavior was achieved using the Modified Burgess-Wheeler law. One exception to this linear behavior was in the case of the carbon monoxide rich limit, which was non-linear at temperatures below -30°C. It was suggested that this may have been an indication that the tube diameter was insufficient to test the carbon monoxide rich limit at

temperatures this low or that the water vapor content of the air was changing as the temperature was lowered.

4. The rich and lean flammability limits were determined for a variety of binary fuel mixtures over the same temperature range used for pure fuels. Mixtures that were tested included:  $(\text{CH}_4 + \text{C}_3\text{H}_8)$ ,  $(\text{CH}_4 + \text{C}_4\text{H}_{10})$ ,  $(\text{CH}_4 + \text{C}_2\text{H}_4)$ ,  $(\text{CH}_4 + \text{H}_2)$ ,  $(\text{C}_3\text{H}_8 + \text{C}_3\text{H}_6)$ ,  $(\text{C}_3\text{H}_8 + \text{H}_2)$ , and  $(\text{H}_2 + \text{C}_2\text{H}_4)$ . Calculations showed that the lean limits of these mixtures could be adequately predicted using Le Chatelier's rule. The lean limits of these mixtures also increased linearly with initial temperature decrease and this relationship for the lean mixtures tested was estimated accurately by assuming that the adiabatic flame temperature of the limit mixture was independent of initial temperature.
5. Le Chatelier's rule was used successfully to estimate the rich limits of the mixtures tested. Good agreement between experimental and estimated limits was observed with the exception of mixtures containing large quantities of hydrogen mixed with small amounts of other fuels. For some of these mixtures, the relative deviations were substantial. Comparison with results from other investigations suggested that for these mixtures containing hydrogen, the relative deviations are essentially independent of initial temperature in the range considered.
6. Both rich and lean flammability limits were determined for a range of mixtures of methane diluted with either nitrogen or carbon dioxide, over the same temperature range. In addition, rich limits for some ethylene/carbon dioxide mixtures were found at  $-60^\circ\text{C}$ .
7. The addition of either nitrogen or carbon dioxide to methane

increased both the lean and rich limits of flammability with carbon dioxide having the greater effect. These limits correlated well on the basis of the mixture composition and the corresponding lean and rich limits of methane over the range of initial mixture temperatures tested.

## 5.2 Recommendations for Future Work

Initial fundamental aspects of the behavior of rich and lean limits of flammability were investigated in the present research. Much work remains to be done in this area. Further investigations in the following areas are required:

1. Additional studies on ignition systems are needed, especially in the area of rich limits of fuels such as ethylene. The results of this study indicated that for this apparatus, the ignition energy was insufficient to provide rich flammability limits for ethylene that were independent of ignition energy. Possible solutions include changing the geometry of the ignition electrodes and electrode holders or modifying the ignition power source. Because the ignition transformer can provide only limited current, a capacitive discharge system would be an improvement since these systems can supply much higher current levels.
2. Research to investigate the effect of tube size on the rich flammability limit of carbon monoxide at low temperatures is recommended. Observation of the mechanisms of flame extinction

under these conditions might provide valuable information on the role of heat losses in rich carbon monoxide flames.

3. Extended theoretical studies on the role of such processes as heat losses, flame stretch, selective diffusion, reaction kinetics, etc. in the combustion of limit mixtures are needed.
4. Before any further low temperature research is conducted in this area, the apparatus should be improved to reduce the quantity of liquid nitrogen used in cooling the tube. One possible modification would be to surround the cooling system with a cylindrical chamber which could be evacuated to reduce heat transfer from the cooling system.
5. Work should be conducted on the flammability limits at low temperatures of fuel/air mixtures with the fuel in two phases (liquid and gaseous), in order to investigate the behavior of mists etc. Particular attention should be paid to mixtures of multiple fuels, for which there is little phase behavior information at low temperatures.



## REFERENCES

1. Affens, W.A., Carhart, H.W. and McLaren, G.W., "Variation of Flammability Index with Temperature and the Relationship to Flash Point of Liquid Hydrocarbons", Journal of Fire & Flammability, Vol. 8, pp. 152-157, 1977.
2. American National Standard ASTM E681-79, "Standard Test Method for Limits of Flammability of Chemicals", American Society for Testing and Materials, Part 41, pp. 924-932, Philadelphia, Pennsylvania, 1979.
3. Andrews, G.E. and Bradley, D., "Limits of Flammability and Natural Convection for Methane-Air Mixtures", Fourteenth Symposium (International) on Combustion, pp. 119-128, The Combustion Institute, Pittsburgh, Pennsylvania, 1973.
4. Barnett, H.C. and Hibbard, R.R., "Basic Considerations in the Combustion of Hydrocarbon Fuels With Air", National Advisory Committee for Aeronautics, Report 1300, Washington, D.C. 1957.
5. Benkhaldoun, F., Larrousturou, B. and Denet, B., "Numerical Investigation of the Extinction Limit of Curved Flames", Combustion Science and Technology, Vol. 64, pp. 187-198, 1989.
6. Blanc, M.V., Guest, P.G., von Elbe, G. and Lewis, B., "Ignition of Explosive Gas Mixtures by Electric Sparks - III. Minimum Ignition Energies and Quenching Distances of Mixtures of Hydrocarbons and Ether with Oxygen and Inert Gases", Third Symposium (International) on Combustion, pp. 363-367, The Combustion Institute, Pittsburgh, Pennsylvania, 1949.
7. Boon, S.L., "An Experimental Study of the Lean Flammability Limits of Some Gaseous Fuels and Their Mixtures", M.Sc. Thesis, Department of Mechanical Engineering, The University of Calgary, Calgary, Alberta, 1982.
8. Boston, P.M., Bradley, D., Lung, F.K-K., Vince, I.M. and Weinberg, F.J., "Flame Initiation in Lean, Quiescent and Turbulent Mixtures With Various Igniters", Twentieth Symposium (International) on Combustion, pp. 141-149, The Combustion Institute, Pittsburgh, Pennsylvania, 1984.
9. Buckmaster, J. and Mikolaitis, D., "A Flammability Limit Model for Upward Propagation Through Lean Methane/Air Mixtures in a Standard Flammability Tube", Combustion and Flame, Vol. 45, pp. 109-119, 1982.
10. Burgess, D.S., Furno, A.L., Kuchta, J.M. and Mura, K.E., "Flammability of Mixed Gases", U.S. Bureau of Mines Bulletin 8709, Pittsburgh, Pennsylvania, 1983.

11. Burgess, D.S. and Zabetakis, M.G., "Fire and Explosion Hazards Associated with Liquified Natural Gas", U.S. Bureau of Mines Report of Investigation 6099, Pittsburgh, Pennsylvania, 1962.
12. Burgoyne, J.H., Roberts, A.F. and Alexander, J.L., "The Significance of Open Flash Points", Journal of the Institute of Petroleum, Vol. 53, No. 526, pp. 338-342, 1967.
13. Cassutt, L.H., Maddocks, F.E. and Sawyer, W.A., "A Study of the Hazards in the Storage and Handling of Liquid Hydrogen", Advances in Cryogenic Engineering, Vol. 8, pp. 236-241, 1963.
14. Cheng, T.K.H., "An Experimental Study of the Rich Flammability Limits of Some Gaseous Fuels and Their Mixtures in Air", M.Sc. Thesis, Department of Mechanical Engineering, The University of Calgary, Calgary, Alberta, 1985.
15. Coward, H.F. and Jones, G.W., "Limits of Flammability of Gases and Vapors", U.S. Bureau of Mines, Bulletin 503, Pittsburgh, Pennsylvania, 1952.
16. Davis, L.N., "Frozen Fire", Hurtig Publishers, Edmonton, Alberta, 1979.
17. Dixon-Lewis, G. and Isles, G.L., "Limits of Inflammability", Seventh Symposium (International) on Combustion, pp. 475-483, The Combustion Institute, Pittsburgh, Pennsylvania, 1959.
18. Ducros, M. and Sannier, H. "Application du Programme Chetah a l'Etude de la Sensibilisation de Composes Oxygenes et a l'Estimation des Limites Inferieures d'Inflammabilite", Journal of Hazardous Material, Vol. 19, pp. 33-49, 1988.
19. Egerton, A.C., "Limits of Inflammability", Fourth Symposium (International) on Combustion, pp. 4-13, The Combustion Institute, Pittsburgh, Pennsylvania, 1953.
20. Everett, A.J. and Minkoff, G.J., "Some Aspects of the Combustion of Methane at Low Pressures", Third Symposium (International) on Combustion, pp. 390-397, The Combustion Institute, Pittsburgh, Pennsylvania, 1949.
21. Fenn, J.B., "Lean Flammability Limit and Minimum Spark Ignition Energy", Industrial and Engineering Chemistry, Vol. 43, No. 12, pp. 2865-2869, 1951.
22. Furno, A.L., Cook, E.B., Kuchta, J.M. and Burgess, D.S., "Some Observations on Near-Limit Flames", Thirteenth Symposium (International) on Combustion, pp. 593-599, The Combustion Institute, Pittsburgh, Pennsylvania, 1971.

23. Hauser, R.L. and Rumpel, W.F., "Reactions of Organic Materials with Liquid Oxygen", *Advances in Cryogenic Engineering*, Vol. 8, pp. 242-249, 1963.
24. Heffington, W.M. and Gaines, W.R., "Flammability Calculations for Gas Mixtures", *Oil & Gas Journal*, Vol. 79, No. 46, pp. 87-90, 1981.
25. Hertzberg, M., "The Theory of Flammability Limits - Natural Convection", U.S. Bureau of Mines, Report of Investigation 8127, Pittsburgh, Pennsylvania, 1976.
26. Hertzberg, M., "The Theory of Flammability Limits - Conductive-Convective Wall Losses and Thermal Quenching", U.S. Bureau of Mines, Report of Investigation 8469, Pittsburgh, Pennsylvania, 1980.
27. Hertzberg, M., "The Theory of Flammability Limits - Radiative Losses and Selective Diffusional Demixing", U.S. Bureau of Mines, Report of Investigation 8607, Pittsburgh, Pennsylvania, 1982.
28. Hertzberg, M., "Flame Stretch Extinction in Flow Gradients, Flammability Limits Under Natural Convection", Twentieth Symposium (International) on Combustion, pp. 1967-1974, The Combustion Institute, Pittsburgh, Pennsylvania, 1984.
29. Hertzberg, M., Cashdollar, K.L. and Zlochower, I.A. "Flammability Limit Measurements for Dusts and Gases: Ignition Energy Requirements and Pressure Dependences", Twenty-First Symposium (International) on Combustion, pp. 303-311, The Combustion Institute, Pittsburgh, Pennsylvania, 1986.
30. Hilado, C.J. and Cumming, H.J., "Limits of Flammability of Organic Chemicals", *Journal of Fire & Flammability*, Vol. 10, pp. 252-260, 1979.
31. Ishizuka, S. and Law, C.K., "An Experimental Study on Extinction and Stability of Stretched Premixed Flames", Nineteenth Symposium (International) on Combustion, pp. 327-335, The Combustion Institute, Pittsburgh, Pennsylvania, 1982.
32. "JANAF Thermochemical Tables", Third Edition, American Chemical Society for the National Bureau of Standards, Washington, D.C., 1985.
33. Jarosinski, J., "A Survey of Recent Studies on Flame Extinction", *Progress in Energy and Combustion Science*, Vol. 12, pp. 81-116, 1986.
34. Jarosinski, J., Strehlow, R.A. and Azarbarzin, A., "The Mechanisms of Lean Limit Extinguishment of an Upward and Downward Propagating Flame in a Standard Flammability Tube", Nineteenth Symposium (International) on Combustion, pp. 1549-1557, The Combustion Institute, Pittsburgh, Pennsylvania, 1982.

35. Kanury, A.M., "A Relationship Between the Flash Point, Boiling Point and Lean Limit of Flammability of Liquid Fuels", *Combustion Science and Technology*, Vol. 31, pp. 297-302, 1983.
36. Lakshmisha, K.N., Paul, P.J., Rajan, N.K.S., Goyal, G. and Mukunda, H.S., "Behavior of Methane-Oxygen-Nitrogen Mixtures Near Flammability Limits", *Twenty-Second Symposium (International) on Combustion*, pp. 1573-1578, The Combustion Institute, Pittsburgh, Pennsylvania, 1988.
37. Law, C.K., "Dynamics of Stretched Flames", *Twenty-Second Symposium (International) on Combustion*, pp. 1381-1402, The Combustion Institute, Pittsburgh, Pennsylvania, 1988.
38. Le Chatelier, H. and Boudouard, O., "Limits of Flammability of Gaseous Mixtures", *Journal of the Chemical Society (Paris)*, Vol. 19, pp. 483-488, 1898.
39. Levy, A., "An Optical Study of Flammability Limits", *Proceedings of the Royal Society (London)*, Series A, Vol. 283, pp. 134-144, 1965.
40. Lovachev, L.A., "The Theory of Limits on Flame Propagation in Gases", *Combustion and Flame*, Vol. 17, pp. 275-278, 1971.
41. Lovachev, L.A., Babkin, V.S., Bunev, V.A., V'yun, A.V., Krivulin, V.N. and Baratov, A.N., "Flammability Limits - An Invited Review", *Combustion and Flame*, Vol. 20, pp. 259-289, 1973.
42. Lovachev, L.A., "Flammability Limits - a Review", *Combustion Science and Technology*, Vol. 20, pp. 209-224, 1979.
43. Lovachev, L.A., "Chemical Kinetics in Flames - a Review", *Combustion Science and Technology*, Vol. 25, pp. 49-69, 1981.
44. Macek, A., "Flammability Limits: A Re-examination", *Combustion Science and Technology*, Vol. 21, pp. 43-52, 1979.
45. Mason, W. and Wheeler, R.V., "The Effect of Temperature and of Pressure on the Limits of Inflammability of Mixtures of Methane and Air", *Journal of the Chemical Society*, Vol. 113, pp. 45-57, 1918.
46. Morris, H., "Ignition of Gas Mixtures by Electric Sparks", *Third Symposium (International) on Combustion*, pp. 361-362, The Combustion Institute, Pittsburgh, Pennsylvania, 1949.
47. Mullins, B.P. and Penner, S.S., "Explosions, Detonations, Flammability and Ignition", Pergamon Press, London, 1959.
48. Odgers, J., Kretschmer, D. and Halpin, J., "Weak Limits of Premixed Gases", *Journal of Engineering for Gas Turbines and Power*, Vol. 107, pp. 10-17, 1985.

49. Odgers, J., White, I. and Kretschmer, D., "The Experimental Behavior of Premixed Gases in Tubes: The Effect of Diluent Gases", ASME Journal of Engineering for Power, Vol. 102, No. 2, pp. , 1980.
50. Plett, E.G., "Flammability of Mixtures of Ethylene Oxide, Nitrogen, and Air", Plant/Operations Progress, Vol. 3, No. 3, pp. 190-194, 1984.
51. Reid, R.C., Prausnitz, J.M. and Poling, B.E., "The Properties of Gases and Liquids", Fourth Edition, McGraw-Hill, New York, 1987.
52. Ronney, P.D., "On the Mechanisms of Flame Propagation Limits and Extinguishment Processes at Microgravity", Twenty-Second Symposium (International) on Combustion, pp. 1615-1623, The Combustion Institute, Pittsburgh, Pennsylvania, 1988.
53. Rose, J.W. and Cooper, J.R., "Technical Data on Fuel", Seventh Edition, The British National Committee, World Energy Conference, London, 1977.
54. Schultz, N., "Fire and Flammability Handbook", Van Nostrand Reinhold, New York, 1985.
55. Spalding, D.B., "A Theory of Inflammability Limits and Flame-Quenching", Proceedings of the Royal Society (London), Series A, Vol. 240, pp. 83-100, 1957.
56. Strehlow, R.A. and Reuss, D.L., "Effect of a Zero g Environment on Flammability Limits as Determined Using a Standard Flammability Tube Apparatus", NASA Contractor Report 3259, Cleveland, Ohio, 1980.
57. Strehlow, R.A., Noe, K.A. and Wherley, B.L., "The Effect of Gravity on Premixed Flame Propagation and Extinction in a Vertical Standard Flammability Tube", Twenty-First Symposium (International) on Combustion, pp. 1899-1907, The Combustion Institute, Pittsburgh, Pennsylvania, 1986.
58. Van Dolah, R.W., Zabetakis, M.G., Burgess, S. and Scott, G.S., "Review of Fire and Explosion Hazards of Flight Vehicle Combustibles", U.S. Bureau of Mines, Information Circular 8137, Pittsburgh, Pennsylvania, 1962.
59. Van Wylen, G.J. and Sonntag, R.E., "Fundamentals of Classical Thermodynamics", Third Edition, John Wiley & Sons, New York, 1985.
60. Vince, I.M., Vovelle, C. and Weinberg, F.J., "The Effect of Plasma Jet Ignition on Flame Propagation and Sooting at the Rich Limit of Flammability", Combustion and Flame, Vol. 56, pp. 105-112, 1984.
61. Ward, D.L., Pearce, D.G., and Merrett, D.J., "Liquid Hydrogen Explosions in Closed Vessels", Advances in Cryogenic Engineering, Vol. 9, pp. 390-400, 1964.

62. White, A.G., "Limits for Propagation of Flame in Inflammable Gas-Air Mixtures. Part III. The Effect of Temperature on the Limits", *Journal of the Chemical Society*, Vol. 127, pp. 672-684, 1925.
63. Wierzba, I., Harris, K. and Karim, G.A., "Effect of Low Temperature on the Rich Flammability Limits of Some Gaseous Fuels and Their Mixtures", Accepted for Presentation at the Second International Specialists Meeting on Major Hazards in the Transport and Storage of Pressure Liquified Gases, Queen's University, Kingston, Ontario, (To be Published May 1990).
64. Wierzba, I., Harris, K. and Karim, G.A., "Effect of Low Temperature on the Rich Flammability Limits in Air of Hydrogen and Fuel Mixtures Containing Hydrogen", Accepted for Presentation at the Eighth World Hydrogen Energy Conference, Hawaii, (To be Published July, 1990).
65. Wierzba, I. and Karim, G.A., "A Predictive Approach for the Flammability Limits of Methane-Nitrogen Mixtures", Thirteenth Annual ETCE/ASME Conference, Fossil Fuel Combustion Symposium, New Orleans, Louisiana, January, 1990.
66. Williams, F.A., "Combustion Theory", Second Edition, Addison-Wesley, New York, 1985.
67. Zabetakis, M.G. and Richmond, J.K., "The Determination and Graphic Representation of the Limits of Flammability of Complex Hydrocarbon Fuels at Low temperatures and Pressures", Fourth Symposium (International) on Combustion, pp. 121-126, The Combustion Institute, Pittsburgh, Pennsylvania, 1953.
68. Zabetakis, M.G., Lambiris, S. and Scott, G.S., "Flame Temperatures of Limit Mixtures", Seventh Symposium (International) on Combustion, pp. 484-487, The Combustion Institute, Pittsburgh, Pennsylvania, 1959.
69. Zabetakis, M.G., "Hazards in the Handling of Cryogenic Fluids", *Advances in Cryogenic Engineering*, Vol. 8, pp. 236-241, 1963.
70. Zabetakis, M.G., "Flammability Characteristics of Combustible Gases and Vapors", U.S. Bureau of Mines, Bulletin 627, Pittsburgh, Pennsylvania, 1965.
71. Zabetakis, M.G., "Safety With Cryogenic Fluids", Plenum Press, New York, 1967.
72. Ziegler, G.F.W., Wagner, E.P. and Maly, R.R., "Ignition of Lean Methane-Air Mixtures by High Pressure Glow and Arc Discharges", Twentieth Symposium (International) on Combustion, pp. 1817-1824, The Combustion Institute, Pittsburgh, Pennsylvania, 1984.

## APPENDIX A

### CALCULATION OF PARTIAL PRESSURES

The partial pressures used in measuring the quantities of each gas needed in the fuel/air mixture of a certain composition were calculated using equation A.1, which is given below. This equation takes into account both the atmospheric pressure and also the amount of residual air in the system that the vacuum pump could not remove (approximately 1% of atmospheric pressure). Before each test, the system was evacuated and filled with air three times to ensure that the residual air remaining upon evacuation was of high purity.

$$PP_i = (P_{atm} + P_{max}) (P_{atm}/P_{vac}) (L_m/100) (Y_i/100) \quad (A.1)$$

where,

$PP_i$	is the calculated partial pressure of the $i^{th}$ gaseous fuel in the gaseous fuel mixture, in mm Hg.
$P_{atm}$	is the atmospheric pressure, in mm Hg.
$P_{max}$	is the maximum gauge pressure to which the mixing chamber was filled when it contained the entire fuel/air mixture, in mm Hg.
$P_{vac}$	is the pressure differential between the highest level of vacuum available and atmospheric pressure, in mm Hg.
$Y_i$	is the volumetric fraction of the $i^{th}$ gaseous fuel in the gaseous fuel mixture, in % by volume.
$L_m$	is the flammability limit of the gaseous fuel mixture to be tested, in % by volume.

After each fuel component had been added to the mixing chamber, air was added until the mixing chamber pressure was at  $P_{max}$ .

## APPENDIX B

### CALCULATION OF LIMITS USING THE BURGESS-WHEELER LAW

When equation 4.2.1 on page 49 was used to calculate the lean flammability limit at temperature  $T$  ( $LL_T$ ), the reference temperature lean flammability limit values were at  $23^\circ\text{C}$ , as determined during the research. Net heat of combustion ( $\Delta H_c$ ) values were taken from [53] at  $25^\circ\text{C}$  and were quoted for constant (atmospheric) pressure in kcal per mole. Constant pressure values were chosen instead of constant volume heats of combustion, because the flame tube pressure during the flammability limits tests was essentially constant, and equal to atmospheric pressure. No attempt was made to turn the value of  $LL_{23^\circ\text{C}}(\Delta H_c)$  into a fitting parameter to match the data. Actual values for net heat of combustion and experimental values for reference temperature lean flammability limit were used for each individual fuel because this yielded results that were closer to experimental values than if the value for  $LL_{23^\circ\text{C}}(\Delta H_c)$  of 1040 kcal per mole quoted by Zabetakis [70] was used. The only exception was in the case of the hydrogen lean limit, where the quoted value gave better predictions.

When the Modified Burgess-Wheeler law (equation 4.3.1) and the Ratio Burgess-Wheeler law (equation 4.3.2) on pages 64 and 66, were used to calculate the rich flammability limit at temperature  $T$  for various fuels, the same net heat of combustion values were used that had been utilized with equation 4.2.1 for lean limits.



## APPENDIX C

### CALCULATION OF LEAN LIMITS USING CONSTANT ADIABATIC FLAME TEMPERATURE

Constant adiabatic flame temperatures were calculated by using iteration to find the temperature at which the enthalpy of the products of combustion of the lean limit mixture was equal to the enthalpy of the lean limit mixture at its initial temperature. This calculation assumed that combustion was complete, there was no dissociation of the products of combustion, and that heat losses to the surroundings were non-existent.

In order to facilitate the calculation of a large number of flame temperatures, a computer program was written in Fortran 77. The program reads in values for initial mixture temperature in °C, lean flammability limit of the fuel or fuel mixture in % by volume, and the volumetric percentages of methane, ethane, propane, butane, ethylene, propylene, hydrogen, carbon monoxide, nitrogen, and carbon dioxide in the fuel mixture. The output of the program includes initial mixture temperature in °C, calculated flame temperature in K, the lean limit of the fuel, the stoichiometric fuel/air mixture on a volumetric basis, and the equivalence ratio of the lean limit mixture on a volumetric basis.

Values for enthalpy and enthalpy of formation are calculated with polynomials either obtained from or fitted using data from published sources [32,51,53,59]. Enthalpy of formation was taken at initial mixture temperature, and the polynomials for enthalpy of formation included in the program on the following page are only valid over the 0 K to 300 K temperature range.

```

c      PROGRAM TO CALCULATE THE ADIABATIC FLAME TEMPERATURE OF
c      A LEAN FLAMMABILITY LIMIT MIXTURE
c
c      OPEN FILES
      open(unit = 10, file = 'FIN')
      open(unit = 11, file = 'FOUT')
      write(11,*)'Tin(°C)      ', 'TF(K)      ', 'LIM(%)      ', 'Stoich(%)'
      +, 'equiv. ratio'
c
c      READ NUMBER OF DATA SETS IN INPUT FILE
      read(10,*)nn
c
c      START LOOP
      Do 50 i=1,nn
c
c      READ INPUT DATA
      read(10,*)Tin,XLIM,CH4,C2H6,C3H8,C4H10,C2H4,C3H6,H2,CO,XN2,CO2
      XLM = XLIM/100.
      Tinit = Tin + 273.15
      XCH4 = CH4/100.
      XC2H6 = C2H6/100.
      XC3H8 = C3H8/100.
      XC4H10 = C4H10/100.
      XC2H4 = C2H4/100.
      XC3H6 = C3H6/100.
      XH2 = H2/100.
      XCO = CO/100.
      XN2 = XN2/100.
      XCO2 = CO2/100.
c
c      CALCULATE COMPOSITION OF PRODUCTS OF COMBUSTION
      PXCO2=XLM*(XCO+XCH4+2.*XC2H6+3.*XC3H8+4.*XC4H10+3.*XC3H6+2.
+ *XC2H4+XCO2)
      PXH2O=XLM*(XH2+2.*XCH4+3.*XC2H6+4.*XC3H8+5.*XC4H10+2.*XC2H4+
+ 3.*XC3H6)
      PXO2=(1.-XLM)*0.21-PXCO2+XLM*XCO2-0.5*PXH2O+0.5*XCO
      PXN2=(1.-XLM)*0.79 + XLM*XN2
c
c      INITIALIZE VARIABLES
      Guess1 = 2300.
      Guess2 = 500.
      TF = 1600.
      ST = Tinit**2
      TZ = Tinit/100.
c
c      CALCULATE ENTHALPY OF REACTANTS
      XCH4EN=(-66913.-31.2033*Tinit+0.05250*ST-.00013*Tinit**3)*XCH4
      XCOEN=(-113805.+14.8779*Tinit-.00814*ST-0.000004*Tinit**3)*XCO
      XC2H4EN=(60983.8-29.86*Tinit+.02899*ST-0.00008*Tinit**3)*XC2H4
      XC3H8EN=(-213980.77+1000.*(-4.042*TZ+15.23*TZ**2-.52367*TZ**3+
+ .007925*TZ**4))*XC3H8
      XC4H10EN=(-287472.4+1000.*(3.954*TZ+18.56*TZ**2-.611*TZ**3+

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+ .008745*TZ**4))*XC4H10
  XC2H6EN=(-176500.42+1000.*(6.895*TZ+8.63*TZ**2-.2134*TZ**3
+ .00182*TZ**4))*XC2H6
  XC3H6EN=(9880.9+3.71*Tinit+.11725*ST-3.8666E-5*Tinit**3
+ +5.512E-9*Tinit**4)*XC3H6
  Renth=(XCOEN+XCH4EN+XC2H6EN+XC3H8EN+XC4H10EN+XC2H4EN+XC3H6EN)*XLM
C
C   CALCULATE ENTHALPY OF FORMATION
  HFORCO2=(PXCO2-XLM*XCO2)*(-393151.+84561*Tinit-.01776*ST+
+ .00004*Tinit**3)
  HFORH2O=PXH2O*(-238921.-14.921*Tinit+.0409*ST-.00008*Tinit**3)
C
C   FIND FLAME TEMPERATURE
  Do 40 j=1,200
C
C   CALCULATE CHANGE IN ENTHALPY
  DHCO2=PXCO2*(-6607.5+45.1085*TF+.00439*TF**2-29.4377*Tinit
+ .00872*ST-.00005*Tinit**3)
  DHH2O=PXH2O*(354.47+29.9265*TF+.00567*TF**2-32.8168*Tinit
+ -.00138*ST)
  DHO2=PXO2*(-1430.36+31.0208*TF+.00184*TF**2-28.9811*Tinit-
+ .00046*ST)
  DHN2=PXN2*(-235.05+28.2382*TF+.00218*TF**2-29.017*Tinit-
+ .00022*ST)
  Penth=HFORCO2+HFORH2O+DHCO2+DHH2O+DHO2+DHN2
C
C   COMPARE ENTHALPY OF PRODUCTS AND REACTANTS
  if((Renth-Penth).GT.0.) then
    Guess2 = TF
  else
    Guess1 = TF
  end if
  TF = (Guess1 + Guess2)/2.
  if(abs(Guess1 - Guess2).LT.1.) Goto 45
40 continue
C
C   WRITE OUTPUT
45 Stoich=XLM*100./((XLM*.21-PXO2)*4.762+XLM)
  phi = XLM/Stoich
  write(11,*) Tin, TF, XLIM, Stoich, phi
50 continue
C
C   CLOSE FILES
  close(10)
  close(11)
end

```

The lean limits of flammability in Figures 4.2.7 through 4.2.14 that are labelled "Constant Flame Temperature", were calculated by assuming that the calculated adiabatic flame temperature for each individual fuel at 23°C was also the flame temperature for the lean limit mixtures of that fuel at all other initial temperatures.