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## A Review and Theoretical Study

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# HIGH ENERGY HYDROCARBON BOOSTER FUELS, A REVIEW AND THEORETICAL STUDY.

Final Report

Contract No. NAS 7-410

Period: October 4, 1965 - September 30, 1966


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Computations of specific impulse and of flame temperatures were carried out by C. Z. Morgan on the basis of heats of formation estimated by J. N. Wilson. Empirical correlations of performance parameters with hydrocarbon properties were developed by Wilson and Morgan. Estimates of physical properties of specific hydrocarbons over a range of temperatures were made by C. V. Sternling and by D. C. Whitney by means of computer programs developed or adapted at these laboratories by Sternling and others. The discussion of heat transfer coefficients is based on calculations by P. A. Nelson. Economic estimates were made by W. M. Padgett, II. The section on estimation of hydrocarbon densities was written by A. A. Bondi, who estimated most of the unknown densities and provided valuable guidance concerning the estimation of other physical properties. Technical liaison and advice were provided by Mr. Paul Herr of Lewis Research Center, National Aeronautics and Space Administration.

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## ABSTRACT

Standard heats of formation and densities have been estimated or selected from the literature for over forty hydrocarbons whose heats of combustion per unit mass are higher than that of kerosene, RP-1. These hydrocarbons contain either multiple bonds or small strained carbon rings. Calculations of specific impulse (1000 psia/1 atm) for combustion with liquid oxygen have shown a potential increase in $I_{sp}$ (equilibrium expansion) of up to 18 seconds (6%) at an oxygen/fuel weight ratio, $(O/F)_w$, that is stoichiometric for combustion to carbon monoxide and water. These results and the calculated flame temperatures have been correlated with values of the hydrogen/carbon atom ratio, r, and the heat of formation, x, per gram-atom of carbon. The dependence of $I_{sp}$ on O/F has been calculated also for a number of representative hydrocarbons assuming both equilibrium and frozen expansion.

Available information on the thermal stabilities of these types of hydrocarbons has been assembled and reviewed. Physical properties have been estimated over a range of temperatures for seven selected hydrocarbons for comparision with those of RP-1. Heat transfer properties are discussed. Similar data are presented for a very dense hydrocarbon fuel.

Few of these hydrocarbons are articles of commerce; many of them are laboratory curiosities. Synthetic routes are discussed briefly. Approximate estimates have been made of the probable cost of large-scale manufacture for two hydrocarbons: 1,7 octadiyne and spiro(2,2)pentane. These estimates, excluding amortization of capital and with no provision for profit, range from \$0.53 to \$1.5 per pound, depending on scale and process options. The cost of experimental quantities would be higher by at least an order of magnitude.

In considering these fuels as possible higher-performance replacements for RP-1 in existing booster rocket engines, the major difficulty is posed by the fact that their hydrogen/carbon atom ratio in most cases is less than that of RP-1. This implies that the ratio $(O/F)_w$ under operating conditions will be lower than that used with RP-1. Thus, the mass-flow of fuel through the engine will have to be increased if a decrease in the mass-flow rate of propellant is to be avoided. Many of the fuels considered have densities lower than that of RP-1; this will tend to decrease their mass-flow rate through a given system with centrifugal pumping at constant power. Calculations are presented to show that if the mass-flow rate of propellant can be held constant, significant gains in payload can be achieved with the use of these energetic hydrocarbon fuels. It will be easiest to achieve these conditions with an energetic hydrocarbon whose density is relatively high and whose H/C ratio is not too low, such as dispirooctane or dispirodecane.

# THEORETICAL ANALYSIS OF THE PERFORMANCE AND PROPERTIES OF HIGH ENERGY HYDROCARBON BOOSTER FUELS

## SECTION I

## INTRODUCTORY SUMMARY

### A. Introduction

In the early 1950's the possible utility of energetic hydrocarbons as storable rocket fuels, hypergolic with nitric acid, was explored in work sponsored by several federal agencies. Such hydrocarbons have an abnormally high heat of combustion per unit mass as a result of the strain energy of unsaturation (nonaromatic double or triple carbon-carbon bonds) or of small ring structures containing three or four carbon atoms per ring. Among the hydrocarbons considered in this early work were derivatives of acetylene,[1),2)] unconjugated polyolefins,[2)] acetylenic olefins,[1),2)] derivatives of cyclopropane[2),3)] and some spiranes and dispiranes;[4)] a great many energetic hydrocarbons were synthesized and partially evaluated. With the development of hydrazines as energetic fuels hypergolic with nitric acid, interest in the synthesis of these hydrocarbons subsided. At about this time, however, a period of rapid development began in the chemistry of polycyclic small-ring hydrocarbons. During the past ten years many new hydrocarbons of this type have been synthesized, primarily by academic organic chemists. These hydrocarbons are also energetic. Most of them have been made only in small quantity, however, and their physical properties have been given only limited study; in many cases not even a density or refractive index is available in the literature. In addition to these energetic hydrocarbons, a potential source of a very dense, but not highly energetic liquid hydrocarbon has recently been developed.[5)] The work described in the present report was directed toward an evaluation of the potential utility of energetic or dense hydrocarbons in general as replacements for kerosene (RP-1) in combustion with liquid oxygen in existing rocket engines. It was thought that the increased payload attainable with special hydrocarbon fuels for special missions might justify their higher cost, especially if only minor modifications of existing large rockets were needed to use the novel fuels effectively. In order to explore this possibility, we have calculated performance parameters for a number of high energy hydrocarbons for combustion with liquid oxygen (LOX).

### B. Summary of Results

1) We have calculated specific impulse as a function of oxygen/fuel ratio (O/F) for over 40 known or hypothetical hydrocarbons for both equilibrium and frozen expansion from 1000 psia to one atmosphere; these results have been correlated with structural parameters such as heat of formation, density and chemical composition to provide formulas for interpolation or modest extrapolation. The calculations were based on experimental data where these were available; for many hydrocarbons, however, estimates had to be made of the heats of formation or densities. The methods of estimation used are described in an Appendix to this report.

---

1) See References at end of this section.

A number of hydrocarbons were found to provide theoretical advantages over RP-1 in specific impulse (gains of 2.5% to over 6%). A few hydrocarbons provide gains in propellant density (1% to 10%), but most of the fuels considered provide lower propellant densities than does RP-1. The performance parameters of some selected hydrocarbons are listed in the following Table 1 for comparison with RP-1. The comparison is made at an oxygen-to-fuel (O/F) ratio that is stoichiometric for combustion to CO plus $H_2O$; the operational O/F is likely to be close to this value. In general, the maximum specific impulse occurs at an O/F ratio that differs slightly from this stoichiometry; it is considered in detail in the body of the report. The parameters listed in the Table include specific impulse $I_{sp}$ (shifting equilibrium, stoichiometric), fuel density $\rho$, density impulse $\bar{\rho}\ I_{sp}$, where $\bar{\rho}$ is propellant density, and oxygen/fuel weight ratio $(O/F)_w$.

Several hydrocarbons that can provide even higher specific impulse are omitted from the Table. Cubane (314.8 sec) is very expensive to prepare. Tetrahedrane (320-327 sec) has never been made. Acetylene (324.9) and 1,4-pentadiyne (314.9 sec) present serious problems of handling and thermal stability.

The lighter high-energy hydrocarbons are low in density and in hydrogen/carbon ratio; these are characterized by low O/F stoichiometric volume ratios, low propellant densities, and low values for the density-impulse product. On the other hand, there are fuels such as 1,7-octadiyne that provide substantial advantages in both specific impulse and density-impulse. For most of these, however, the hydrogen/carbon ratio is low and this leads to stoichiometric O/F weight and especially volume ratios that are lower than those of RP-1. At another extreme, SHELLDYNE®, a proprietary high density hydrocarbon fuel, gives a slightly lower specific impulse than RP-1 but a much higher propellant density, density-impulse, and volumetric O/F ratio.

2) Performance parameters have been calculated for a few two-component blends of hydrocarbons that differ substantially from one another in individual properties. The density-impulse of such a blend is found to be very nearly a linear function of the weight-percent of one or its components in the blend. On this basis, a blend of 1,7-octadiyne with SHELLDYNE®, designed to match the volumetric O/F ratio of RP-1, was found to yield the following increments in performance parameters over RP-1: in specific impulse, 2.0%; in propellant density, 4.8%; in density-impulse, 7.0%.

On the basis of these results and considerations of preparative chemistry, approximate cost, and thermal stability, spiropentane and 1,7-octadiyne appear to be candidates for possible near-term application as high-energy hydrocarbon fuels, possibly in blends with SHELLDYNE® or quadricyclene as high-density blending agents for the adjustment of volumetric oxygen/fuel ratios. Other hydrocarbons of potential interest as high energy hydrocarbon fuels are 1,4-hexadiyne, 1,6-heptadiyne, bicyclo(1,1,0)butane, and bicyclo-(2,1,0)pentane. Two hydrocarbons that may be of greater long-range interest are dispiro(2,1,2,1)octane and dispiro(3,1,3,1)decane; synthetic routes for preparing these need further study. The potential advantage of these is that it may be easier to achieve with them the increased mass-flow of fuel required to maintain adequate mass-flow of propellant.

Table 1. THEORETICAL PERFORMANCE PARAMETERS OF SOME HIGH ENERGY HYDROCARBONS AS ROCKET FUELS FOR COMBUSTION WITH LOX AT STOICHIOMETRIC O/F

| Fuel | Formula | $I_{sp}$ a) sec | $\rho$ c) $\frac{\text{gm fuel}}{\text{ml}}$ | $\bar{\rho}\ I_{sp}$ $\frac{\text{gm sec}}{\text{ml}}$ | $(O/F)_w$ weight ratio |
|---|---|---|---|---|---|
| Allene b) | $C_3H_4$ | 314.1 | 0.660 | 288.5 | 1.997 |
| Bicyclobutane b) | $C_4H_6$ | 313.9 | 0.750 | 306.4 | 2.071 |
| Methylacetylene b) | $C_3H_4$ | 313.2 | 0.675 | 290.6 | 1.997 |
| 1,5 Hexadiyne | $C_6H_6$ | 311.4 | 0.794 | 308.2 | 1.844 |
| Ethylene b) | $C_2H_4$ | 311.3 | 0.5638 | 272.0 | 2.281 |
| Cyclopropylacetylene | $C_5H_6$ | 311.1 | 0.775 | 306.0 | 1.936 |
| Spiro(2,2)pentane | $C_5H_8$ | 310.2 | 0.7487 | 303.2 | 2.114 |
| 1,6-Heptadiyne | $C_7H_8$ | 309.1 | 0.8009 | 308.0 | 1.910 |
| Cyclopropane b) | $C_3H_6$ | 308.9 | 0.681 | 292.5 | 2.281 |
| Dimethylacetylene | $C_4H_6$ | 307.9 | 0.6856 | 289.0 | 2.071 |
| Dispiro(2,1,2,1)octane | $C_8H_{12}$ | 307.9 | 0.846 | 315.7 | 2.071 |
| Bicyclo(2,1,0)pentane | $C_5H_8$ | 307.9 | 0.7846 | 306.8 | 2.114 |
| 1,7-octadiyne | $C_8H_{10}$ | 307.5 | 0.808 | 308.2 | 1.959 |
| Spiro(3,2)hexane | $C_6H_{10}$ | 307.4 | 0.788 | 307.2 | 2.143 |
| Dicyclopropylacetylene | $C_8H_{10}$ | 307.3 | 0.870 | 317.5 | 1.959 |
| Cyclopropylcyclopropane | $C_6H_{10}$ | 306.4 | 0.785 | 305.7 | 2.143 |
| Cyclobutane b) | $C_4H_8$ | 306.3 | 0.702 | 293.8 | 2.281 |
| Methylenecyclobutane | $C_5H_8$ | 306.0 | 0.7349 | 296.8 | 2.114 |
| Dispiro(3,1,3,1)decane | $C_{10}H_{16}$ | 304. | 0.847 | 312. | 2.114 |
| RP-1 | $CH_{1.9}$ | 296.3 | 0.805 | 299.7 | 2.24-2.28 |
| SHELLDYNE® | $\sim C_{14}H_{16}$ | 295.0 | 1.09 | 331.6 | 1.910 |

a) Calculated for shifting equilibrium, expansion 1000 psia/1 atm.
b) For liquid fuel initially at boiling point. ($T_B$ below room temperature).
c) At 25°C for fuels boiling above 25°C; otherwise, at $T_B$.

4) Physical properties (heat capacity, density, thermal conductivity and viscosity) have been estimated by corresponding states correlation methods over the range 500-1200°F for nine hydrocarbons: 1,4-hexadiyne, 1,6-heptadiyne, 1,7-octadiyne, bicyclo(1,1,0)butane, bicyclo(2,1,0)pentane, tricyclo(3,1,0,$0^{2,4}$)hexane, spiropentane, SHELLDYNE® and RP-1. From these data the ratio of the heat transfer coefficient to that of RP-1 has been estimated over the same temperature range for film heat transfer to liquid in turbulent flow in a tube. Because of its high viscosity, the relative heat transfer coefficient of SHELLDYNE® is low; that of 1,7-octadiyne is close to unity; those of the other candidate hydrocarbons are well above unity.

5) Literature data concerning thermal stability of many of the candidate hydrocarbons have been assembled; most of these data, unfortunately, are based only on thermal decomposition of dilute vapors. It appears likely however, that most of the promising hydrocarbons will have adequate storage stability or can be adequately stabilized by means of additives. Some aspects of the chemistry of these materials are discussed.

6) Preliminary screening-type estimates have been made for the cost of production of 1,7-octadiyne and of spiropentane. The estimate for octadiyne was based on early small-scale process-development data; that for spiropentane was based on an extrapolation of known chemistry. The cost of large-scale continuous production of 1,7-octadiyne, without profit or amortization of capital, is estimated to lie in the range $0.53 to $0.80/lb, depending on scale and on process options; in the scale range 20-26 million lb/yr, the estimated capital costs ranged from $0.13 to $0.57 per annual pound of product. It is to be emphasized that these estimates are tentative and preliminary. The cost of specially manufactured test quantities is likely to be higher by a factor of ten or twenty. Spiropentane will be appreciably more expensive; it has a slightly higher specific impulse, higher thermal stability, lower fuel density and comparable O/F volumetric ratio at stoichiometric in comparison with the octadiyne.

## C. References for Section I


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2) J. Happel and C.J. Marsel, "Acetylenic Compounds for Rocket Fuels," New York University Report NYU-175.9, December 1, 1952, prepared under Contract No. Nonr-285(04) for ONR/Bu Aer.

3) V.A. Slabey, P.H. Wise and L.C. Gibbons, U.S. Nat. Advisory Comm. for Aeronautics Report No. 1112 (1953).

4) E.R. Buchman et al, California Institute of Technology, Final Report, Contract N6 onr-244/XI, October 1951.

5) Letter from F.G. Bollo, Products Application Department, Shell Oil Company, San Francisco, January 1965.

## SECTION II

## HYDROCARBON ROCKET FUELS, GENERAL CONSIDERATIONS

### A. Composition and Heat of Formation as Correlating Parameters

As a rocket fuel for combustion with liquid oxygen (LOX), the potential performance of a hydrocarbon depends on its composition, its heat of formation and its density. The molecular composition of a hydrocarbon can be represented in general as $C_nH_m$; we will represent its empirical composition as $CH_r$, where $r = m/n = H/C$ atom ratio. The value of r ranges from a maximum of 4.0 in methane, $CH_4$, to less than unity in the condensed poly-aromatics such as anthracene, $C_{14}H_{10}$ or $CH_{0.715}$; we shall use r as a correlating parameter.

The heat of formation of a hydrocarbon can be expressed in a variety of ways; in this report we have found it convenient to make correlations in terms of the heat of formation per gram atom of carbon, in kcal, for which we use the symbol x. Thus

$$x = \Delta H_f/n$$

where $\Delta H_f$ is the standard enthalpy of formation per gram mole. Methods for estimating x, in case it is not known experimentally, are discussed in Appendix 2.

When a hydrocarbon is burned with LOX in a rocket engine, the dominant products are carbon monoxide and water. The process can be approximately represented by the following stoichiometric equation:

$$CH_r(\ell) + [(2 + r)/4]O_2(\ell) = CO(g) + (r/2)H_2O(g). \qquad \text{II.1}$$

We shall refer to the weight ratio of oxygen to fuel in this equation as "stoichiometric". Hydrocarbon-fueled rocket engines usually operate slightly on the fuel-rich side of stoichiometric in order to maintain a protective film of carbon on the heat-exchange surfaces. Nevertheless, we have found it useful to compare hydrocarbons with respect to the specific impulse calculated for the stoichiometry of (1) in order to see systematic trends with composition and heat of formation.

When reaction II.1 operates to form products at 25°C, the heat evolved, q per gram of reactant mixture, can be written as

$$q = \frac{x + 24.9 + 28.1r}{28.01 + 9.008r} = \frac{0.888 + 0.0357x + 1.0035r}{1 + 0.322r} \qquad \text{II.2}$$

This equation is based on a heat of formation of liquid oxygen at 90°K, relative to the gas at 298°K, of -3.06 kcal/gm mole. The symbol x in the equation will be used throughout this report to refer to the heat of formation of the hydrocarbon in kcal per gram-formula-weight of $CH_r$ (i.e., kcal per

12.01 + 1.008r grams). The dependence of q on r results from the fact that the heat of formation of $H_2O$ is more strongly negative than that of CO.

At the same time the average molecular weight of the products decreases with increasing r in accordance with

$$\overline{M} = 28(1 + 0.3217r)/(1 + 0.500r) \qquad \text{II.3}$$

Thus, qualitatively, the specific impulse at "stoichiometric" can be expected to increase with x at constant r or with r at constant x. The results presented later show that this is indeed the case.

## B. Energetic Hydrocarbon Structures

For the saturated hydrocarbons that predominate in RP-1, the value of r is close to 2 and the value of x falls in the range -6 to -7 kcal/gm atom C. Higher (more positive) values of x can be attained by introducing chemical "unsaturation" in the form of double or triple carbon-carbon bonds, or by introducing structural "strain" in the form of three-carbon or four-carbon rings. In each case, however, an increase in x is achieved at the expense of a concommitant decrease in r, and the increase in specific impulse is less than would have been achieved if x had been increased at constant r. These effects are illustrated by Table 2a where the parameters x and r, and the calculated specific impulse at stoichiometric are compared for a number of hydrocarbons, all of which contain 4 carbon atoms but differ from one another in structure. The specific impulse listed was calculated for combustion of the liquid hydrocarbon, initially at 25 °C, with LOX at the stoichiometry of equation (1), followed by expansion from 1000 psia to 1 atm with shifting equilibrium. The results show that an increase in x at constant r results in an increase in $I_{sp}$, as expected (compare cyclobutane with butene-2). When the increase in x is accompanied by a decrease in r, however, the increase in $I_{sp}$ is smaller and may even be replaced by a decrease (compare cyclobutane with 1,3 butadiene). In general, however, a high value of x leads to a relatively high value of $I_{sp}$, even if r is relatively low. Parameters are given for comparison for two reference fuels, RP-1 and benzene.

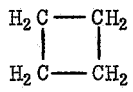
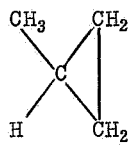
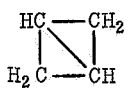
The outstanding contributors to high values of x in Table 2a are the triple bond, a pair of adjacent double bonds, and the bicyclobutyl group with two fused three-membered rings. Other energetic configurations that have been synthesized or can probably be synthesized are listed in Table 2b; for some of these polycyclic systems the value of x is not known experimentally and is difficult to estimate reliably. A quantum mechanical method for estimating the heats of formation of such molecules has recently been described by Baird and Dewar.[1)] In cases where it can be compared with experiment the error in x appears to be of the order of 10 to 30%.

The synthesis of most of the very highly strained hydrocarbons illustrated in Table 2b is difficult and involves many steps and expensive reagents. The very highly strained hydrocarbon, tetrahedrane, has been discussed for many years as a possible structure but has never been made; its estimated energy is so high that it would be thermodynamically unstable with respect to dissociation into two molecules of acetylene. There is therefore

1) See references at end of this section.

## Table 2a. COMPARISON OF SOME 4-CARBON HYDROCARBONS: STOICHIOMETRIC SPECIFIC IMPULSE ($I_S$), HEAT OF FORMATION PER GRAM-ATOM C (x) AND H/C ATOM RATIO (r)

**Estimated values of x are given in parentheses**

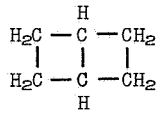
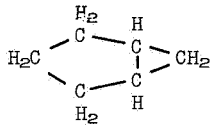
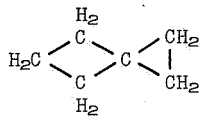
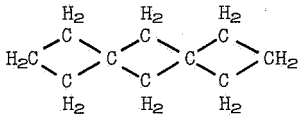
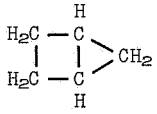
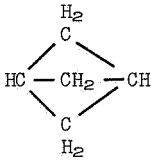
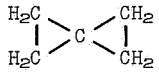
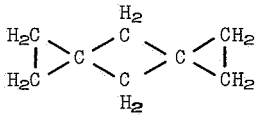
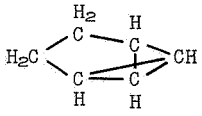
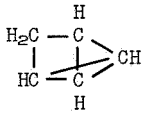
| Hydrocarbons | | | | | |
|---|---|---|---|---|---|
| Name | Structure | r | x, kcal/gm atom[a] | | $I_{sp}$, sec[b] stoichiometric |
| | | | gas | liquid | |
| n-butane | $H_3C-CH_2-CH_2-CH_3$ | 2.50 | -7.54 | -8.83 | 301.9 |
| butene-2 | $H_3C-CH=CH-CH_3$ | 2.00 | -0.42 | -1.72 | 303.8 |
| cyclobutane |  | 2.00 | 1.60 | 0.27 | 306.4 |
| methylcyclopropane |  | 2.00 | (1.6) | (0.3) | 306.4 |
| 1,3 butadiene | $H_2C=CH-CH=CH_2$ | 1.50 | 6.58 | 5.30 | 305.2 |
| 1,2 butadiene | $H_2C=C=CH-CH_3$ | 1.50 | 9.69 | 8.50 | 309.8 |
| butyne-2 (dimethylacetylene) | $H_3C-C\equiv C-CH_3$ | 1.50 | 8.74 | 7.16 | 307.9 |
| bicyclobutane |  | 1.50 | (13.0 ± 0.7) | (11.5 ± 0.7) | 313.9 |
| Reference Fuels | | | | | |
| RP-1 | ca $C_{12}H_{24}$ | 1.9 to 2.0 | | -5.8 to -7.0 | 296.3 |
| Benzene | $C_6H_6$ | 1.0 | | 1.96 | 288.6 |

a) At 25°C.
b) For combustion of liquid hydrocarbon at 25°C with LOX, expansion 1000 psia/1 atm, shifting equilibrium, theoretical.


Table 2b follows

## Table 2b. OTHER ENERGETIC HYDROCARBONS

Estimated values of x are given in parentheses to distinguish them from experimental values

| Name | Structure | x kcal/gm atom | r | Synthesized? |
|---|---|---|---|---|
| Bicyclo(2,2,0)hexane |  | - | 1.667 | Yes |
| Bicyclo(3,1,0)hexane |  | 0.183 | 1.667 | Yes |
| Spiro(3,2)hexane |  | (4.3-4.8) | 1.667 | Yes |
| Dispiro(3,1,3,1)decane |  | (3.0-3.6) | 1.600 | Yes |
| Bicyclo(2,1,0)pentane |  | 5.96 | 1.600 | Yes |
| Bicyclo(1,1,1)pentane |  | - | 1.600 | Yes |
| Spiro(2,2)pentane |  | 7.66 | 1.600 | Yes |
| Dispiro(2,1,2,1)octane |  | (6.3-7.2) | 1.500 | No |
| Tricyclo(3,1,0,$0^{2,6}$)hexane |  | - | 1.333 | Yes |
| Tricyclo(2,1,0,$0^{2,6}$)pentane |  | - | 1.200 | Yes |
| Cubane, $C_8 H_8$ | A cube of carbon atoms with a hydrogen atom attached to each corner. | 17.4 | 1.000 | Yes |
| Tetrahedrane, $C_4 H_4$ | A tetrahedron of carbon atoms with a hydrogen atom attached to each vertex. | (25-36) | 1.000 | No |

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some doubt that it can exist at room temperature. The almost equally exotic hydrocarbon, cubane, has been made, however, and is relatively stable. Its synthesis is very lengthy and expensive.

A very large number of possible energetic hydrocarbons can be visualized as combinations of the energetic groups illustrated in Tables 2a and 2b. Some simple examples of such combinations have been made, such as cyclopropyl acetylene and dicyclopropyl (cyclopropyl cyclopropane). Methods for estimating the heats of formation of such combinations are discussed in Appendix 2.

## C. Chemical Stability, General Considerations

Hydrocarbons that contain carbon-carbon double bonds or triple bonds are capable of combining with each other to form polymers. This process is usually accelerated by the presence of traces of oxygen, and may lead to the deposition of gummy deposits on heat-exchanger surfaces when the hydrocarbon is heated to moderately high temperatures in the regenerative heat exchanger section of a rocket engine. A number of "inhibitors" are known that at low concentrations are capable of minimizing the formation of such deposits. The most effective inhibitor for use with a given hydrocarbon under given conditions must usually be found by empirical trial. The strained hydrocarbons that contain 3-carbon or 4-carbon rings can rearrange at high temperatures to new structures containing double bonds; hence this class of energetic hydrocarbons is also likely to require the addition of inhibitors if they are to be used as rocket fuels. Some of the energetic hydrocarbons that contain small strained ring structures are relatively stable with respect to both thermal decomposition and reaction with oxygen. Examples are spiropentane, in which two 3-carbon rings are linked by a common carbon atom, and dispirodecane, in which a series of three 4-carbon rings is linked by shared carbon atoms. Energetic members of this class whose other properties are satisfactory are therefore attractive candidate rocket fuels; a search for more economical methods to make them may be justified.

Information available on the thermal stability of several classes of energetic hydrocarbons is summarized in Section VII.

## D. Properties of Standard Reference Fuel, RP-1

We shall compare the candidate hydrocarbons to a sample of the standard hydrocarbon fuel, RP-1, with the following arbitrarily assigned properties: Density $\rho$ at 25°C = 0.800 g/ml; r = 2.000; x = -7.056 kcal/g atom carbon. Actual samples of RP-1 can be expected to deviate slightly from these values. For example, some properties derived from those quoted by Shell Oil Company for its fuel UMF-A, which is intended to meet the specifications of RP-1, and those quoted by Pratt and Whitney Corporation[2)] for RP-1 are compared below.

SOME PROPERTIES VARIOUSLY QUOTED FOR RP-1

| | Shell | Pratt and Whitney |
|---|---|---|
| Atom Ratio H/C | 2.000 | 1.9063 |
| Liquid Density, $\rho$ g/ml at 25°C | 0.806 | 0.798 |
| Heat of Combustion, kcal/g | 10.35 | 10.28 |
| Heat of Formation, kcal/gm atom C | -6.68 | -5.94 |

The specifications quoted for RP-1 in MIL-F-25576 include a specific gravity at 60°F/60°F between 0.801 and 0.815; this corresponds to a density at 25°C between 0.798 and 0.812 g/ml. Similarly the specifications on composition call for 5.0% max vol % aromatics and 1.0% vol % olefins. If, as seems likely, most of the remainder is naphthenic, a value of r close to 1.90 seems not unreasonable. The net heat of combustion (minimum) is specified as 18,500 Btu/lb; this at r = 1.90 corresponds to a value of x of -5.72 kcal/g atom of carbon.

Since the properties arbitrarily assigned to our reference fuel are extreme for RP-1, we shall list also in our evaluation of candidate fuels performance figures for a sample of RP-1 with the properties $\rho$ (25°C) = 0.805, r = 1.90 and x = -5.80.

## E. Properties of Some Energetic Hydrocarbon Fuels

A number of properties are listed in Table 3 for two examples of the reference fuel RP-1, for a denser, higher-boiling kerosene RJ-1, and for a number of known or conceivable pure hydrocarbons. The latter are listed in the order of decreasing booster load index[a)] which is one of several possible measures of merit. The properties listed include carbon number n, H/C atom ratio r, boiling point, melting point, density, molar enthalpies of formation, $\Delta H_f$, for the vapor (g) and the liquid ($\ell$), molar enthalpies of vaporization, $\Delta H_v$ and the value of $x = \Delta H_f(\ell)/n$. Net heats of combustion to water vapor and $CO_2$ at 25°C are also given in Btu/lb and Btu/gal. Some of the values given in the Table are estimates; these are enclosed in parentheses.

Other properties such as viscosities, vapor pressures and heat-transfer coefficients are given for some selected candidate fuels in Section IV.

Heats of formation of a number of $C_4H_6$ hydrocarbons have recently been determined by Wiberg and Fenoglio.[3)] Their results are tabulated below; their value for bicyclobutane compares well with our estimate which was made before these data became available.

a) Defined as 100 $(2\Delta I/I_o + \Delta\bar{\rho}/\bar{\rho}_o)$, where $I_o$, $\bar{\rho}_o$ are respectively the specific impulse and propellant density for RP-1 at stoichiometric O/F, and $\Delta I$, $\Delta\bar{\rho}$ are increments from these. As discussed later, no single measure of this kind is adequate to evaluate a hydrocarbon as a potential replacement for RP-1.

## INDEX TO TABLE 3: THERMOCHEMICAL PROPERTIES OF HYDROCARBONS

| Name of Hydrocarbon | Key to Serial No. in Table |
|---|---|
| Acetylene | 21 |
| Allene | 30 |
| Bicyclo(1,1,0)butane | 11 |
| Bicyclo(2,2,1)heptadiene-2,5 | 20 |
| Bicyclo(3,1)hexane | 29 |
| Bicyclo(2,1,0)pentane | 22 |
| Cubane | 1 |
| Cyclopropylcyclopropane | 25 |
| Cyclobutene | 31 |
| 1,4-Cyclohexadiene | 32 |
| Cyclopentane | 41 |
| Cyclopropylacetylene | 14 |
| Dimethylacetylene | 40 |
| 1,3-Dimethylbicyclo(1,1,0)butane | 42 |
| Dicyclopropylacetylene | 7 |
| Dimethylcubane | 4 |
| Di(methylcyclopropyl)acetylene | 17 |
| 1,4-Dimethyltricyclo(3,1,0,$0^{2,4}$)hexane | 18 |
| Dispiro(3,1,3,1)decane | 16 |
| Dispiro(2,1,2,1)octane | 9 |
| trans-1,2-Divinylcyclobutane | 27 |
| Ethylene | 44 |
| 1,6-Heptadiyne | 15 |
| 1,5-Hexadiene(diallyl) | 43 |
| 1,5-Hexadiyne | 13 |

| Name of Hydrocarbon | Key to Serial No. in Table |
|---|---|
| Isopropenylacetylene | 46 |
| Methylacetylene | 28 |
| Methylcubane | 3 |
| 1-Methylcyclobutene | 38 |
| 1-Methyl-1,4-cyclohexadiene | 35 |
| Methylenecyclobutane | 33 |
| 1-Methyltricyclo(3,1,0,$0^{2,4}$)hexane | 12 |
| 1,7-Octadiyne | 19 |
| 1,3,7-Octatriene | 39 |
| 1,4-Pentadiyne | 8 |
| Quadricyclene | 10 |
| RP-1A | R-1 |
| RP-1B | R-2 |
| RJ-1 (Shell UMFC) | R-3 |
| SHELLDYNE | 6 |
| Spiro(3,3)heptane | 26 |
| Spiro(3,2)hexane | 23 |
| Spiro(4,3)octane | 37 |
| Spiro(2,2)pentane | 24 |
| Tetrahedrane | 2 |
| Tricyclo(3,1,0,$0^{2,4}$)hexane | 5 |



Table 3 follows

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## Table 3. PROPERTIES OF CANDIDATE HYDROCARBON FUELS: CnHrn

| Name | No. | n | r | $T_B$, °C | $T_M$, °C | ρ,[a] g/ml | $\Delta H_f(g)$[c] | $\Delta H_v$ | $\Delta H_f(l)$[c] | $\frac{\Delta H_f(l)}{n}$, x | $\Delta H_c$(net)[d] Btu/lb | $\Delta H_c$(net)[d] Btu/gal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RP-1A | R-1 | ~12 | 2.000 | >175 | <-40 | 0.80 | - | - | - | -7.056 | 18,600 | 124,000 |
| RP-1B | R-2 | ~12.5 | 1.900 | >175 | <-40 | 0.805 | - | - | - | -7.800 | 18,500 | 124,300 |
| RJ-1 (Shell UMFC) | R-3 | ~14 | 1.940 | >225 | <-50 | 0.8454 | - | - | - | -6.676 | 18,500 | 130,400 |
| Cubane | 1 | 8 | 1.000 | >100(S) | ~130 | (1.03) | 148.7 ± 1.0 | (10) | (139)[e] | 17.375 | 19,400 | 166,800 |
| Tetrahedrane | 2 | 4 | 1.000 | (4) | - | (0.81) | (111-106) | (6) | (105-100) | 26.250<br>25.000 | 20,600<br>20,500 | 139,400<br>138,300 |
| Methylcubane | 3 | 9 | 1.111 | (>125) | - | (0.986) | (142 ± 2) | (10.5) | (131.5) | 14.611 | 19,300 | 158,800 |
| Dimethylcubane | 4 | 10 | 1.200 | (>125) | - | (0.950) | ± | (11) | (125) | 12.500 | 19,200 | 152,400 |
| Tricyclo(3,1,0,$0^{2,4}$)hexane | 5 | 6 | 1.333 | (~85) | - | (0.865) | (67.6) | (8.1) | (59.5) | 9.917 | 19,200 | 138,600 |
| SHELLDYNE | 6 | ~14 | 1.143 | ~254 | <-20 | 1.09 | - | - | 49.65 | 3.546 | 17,900 | 162,500 |
| Dicyclopropylacetylene | 7 | 8 | 1.250 | (~135) | - | (0.870) | (88.0) | (10.3) | (77.7) | 9.713 | 19,000 | 137,800 |
| 1,4-Pentadiyne | 8 | 5 | 0.80 | 55.0 | - | (0.782) | (104.1) | (7.2) | (96.9) | 19.380 | 19,200 | 125,100 |
| Dispiro(2,1,2,1)octane | 9 | 8 | 1.500 | (115) | - | (0.846) | (65.7-59.0) | (8.5) | (57.2<br>50.5) | 7.150<br>6.313 | 19,200<br>19,100 | 135,800<br>135,000 |
| Quadricyclene | 10 | 7 | 1.143 | 109 | - | (0.935) | (60.5) | 9.0 | 51.5 | 7.357 | 18,400 | 143,400 |
| Bicyclo(1,1,0)butane | 11 | 4 | 1.500 | 8.3 | - | (0.750) | (52 ± 3) | 5.6 | (46 ± 3) | 11.500 | 19,800 | 124,000 |
| 1-Methyltricyclo(3,1,0,$0^{2,4}$)hexane | 12 | 7 | 1.429 | (115) | - | (0.840) | (60.3) | (8.4) | (51.9) | 7.414 | 19,100 | 133,900 |
| 1,5-Hexadiyne | 13 | 6 | 1.000 | 87 | -4 | 0.794 | (99.2) | (8.4) | (90.8) | 15.133 | 19,100 | 126,500 |
| Cyclopropylacetylene | 14 | 5 | 1.200 | 52 | - | 0.775 | (70.7) | (6.6) | (64.1) | 12.820 | 19,300 | 124,600 |
| 1,6-Heptadiyne | 15 | 7 | 1.143 | 112 | -84 | 0.8009 | (94.2) | (9.6) | (84.6) | 12.086 | 19,000 | 127,200 |
| Dispiro(3,1,3,1)decane | 16 | 10 | 1.600 | (162) | - | (0.847) | (47.0-41.0) | (10.9) | (36.1-30.1) | 3.610<br>3.010 | 19,000<br>18,900 | 134,400<br>133,800 |
| Di(methylcyclopropyl)acetylene | 17 | 10 | 1.400 | (>140) | - | (0.840) | (77) | (10.9) | (66) | 6.600 | 18,900 | 132,700 |
| 1,4-Dimethyltricyclo(3,1,0,$0^{2,4}$)hexane | 18 | 8 | 1.500 | (~100) | - | (0.830) | (53.0) | (8.7) | (44.3) | 5.538 | 19,000 | 131,800 |
| 1,7-Octadiyne | 19 | 8 | 1.250 | 139.0 | -22.0 | 0.808 | (89.3) | (10.4) | (78.9) | 9.863 | 19,000 | 123,100 |
| Bicyclo(2,2,1)heptadiene-2,5 | 20 | 7 | 1.143 | 89.5 | -19.9 | 0.903 | (56.4) | (8.4) | 48.0 | 6.857 | 18,300 | 138,000 |
| Acetylene | 21 | 2 | 1.000 | -84(S) | -80.8 | 0.620 | 53.16[b] | 3.98[b] | 49.18[b] | 24.590 | 20,400 | 105,500 |
| Bicyclo(2,1,0)pentane | 22 | 5 | 1.600 | 45.5 | - | 0.7846 | (36.7) | (6.9) | (29.8) | 5.960 | 19,300 | 126,500 |
| Spiro(3,2)hexane | 23 | 6 | 1.667 | (70) | - | (0.788) | (36.2-32.9) | (6.9 | (29.3-26.0) | 4.833<br>4.333 | 19,300<br>19,300 | 127,100<br>126,700 |
| Spiro(2,2)pentane | 24 | 5 | 1.600 | 38.8 | -107.0 | 0.7487 | 44.9 | 6.57 | 38.3 | 7.660 | 19,500 | 122,100 |
| Cyclopropylcyclopropane | 25 | 6 | 1.667 | 76.1 | - | 0.785 | (32.4) | (7.6) | (24.8) | 4.133 | 19,200 | 126,000 |
| Spiro(3,3)heptane | 26 | 7 | 1.714 | 94 | - | (0.797) | (28.1-24.5) | (8.3) | (19.8-16.2) | 2.829<br>2.314 | 19,200<br>19,100 | 127,600<br>127,100 |
| trans-1,2-Divinylcyclobutane | 27 | 8 | 1.500 | 111 | - | 0.774 | (46.5) | 9.0 | (37.5) | 4.688 | 18,900 | 122,200 |
| Methylacetylene | 28 | 3 | 1.333 | -23.2 | -102.7 | 0.675[b] | 43.72[b] | 5.32[b] | (38.4)[b] | 12.800 | 19,600 | 110,400 |
| Bicyclo(3,1,0)hexane | 29 | 6 | 1.667 | 81.2 | - | (0.815) | 9.07 | 8.0 | 1.1 | 0.183 | 18,700 | 127,300 |
| Allene | 30 | 3 | 1.333 | -34.5 | -136.3 | 0.660[b] | 44.6[b] | 4.17[b] | 40.4[b] | 13.466 | 19,700 | 108,400 |
| Cyclobutene | 31 | 4 | 1.500 | 2.0 | - | (0.733[b]) | (31.0)[b] | (5.5)[b] | (25.5)[b] | 6.375 | 19,100 | 117,100 |
| 1,4-Cyclohexadiene | 32 | 6 | 1.333 | 85.6 | - | 0.843 | (27.1) | (7.8) | (19.3) | 3.217 | 18,300 | 128,800 |
| Methylenecyclobutane | 33 | 5 | 1.600 | 41.5-42 | - | 0.7349 | (29.5) | (6.2) | (23.3) | 4.660 | 19,200 | 117,500 |
| Cyclopropane[b] | 34 | 3 | 2.000 | -32.8 | -127.4 | 0.681[b] | 11.9 | 4.80[b] | 6.4[b] | 2.133 | 19,800 | 112,300 |
| Cyclopropane (-79°C) | | | | | | 0.720(-79) | - | | (5.1)(-79) | 1.700 | 19,700 | 118,400 |
| 1-Methyl-1,4-cyclohexadiene | 35 | 7 | 1.429 | (115) | - | (0.841) | (18.6) | (8.7) | (9.9) | 1.414 | 18,300 | 128,400 |
| Cyclobutane | 36 | 4 | 2.000 | 12.51 | -90.73 | 0.702[b] | 6.50[b] | 5.78[b] | 0.72[b] | 0.180 | 19,500 | 114,300 |
| Spiro(4,3)octane | 37 | 8 | 1.750 | (126) | - | (0.830) | (-16.7) | (9.3) | (-26.0) | -3.250 | 18,500 | 128,000 |
| 1-Methylcyclobutene | 38 | 5 | 1.600 | 37.3 | - | 0.7183 | 28.5 | (6.4) | 22.1 | 4.420 | 19,100 | 114,700 |
| 1,3,7-Octatriene | 39 | 8 | 1.500 | 124 | - | 0.7560 | (34.9) | (9.4) | (25.5) | 3.188 | 18,700 | 118,000 |
| Dimethylacetylene | 40 | 4 | 1.500 | 26.99 | -32.26 | 0.6856 | 35.2 | 6.58 | 28.62 | 7.155 | 19,200 | 110,000 |
| Cyclopentane | 41 | 5 | 2.000 | 49.26 | -93.87 | 0.7405 | -18.46 | 6.818 | -25.28 | -5.060 | 18,800 | 116,400 |
| 1,3-Dimethylbicyclo(1,1,0)butane | 42 | 6 | 1.333 | - | - | (0.725) | (38.2) | (6.9) | (31.3) | 5.217 | 18,600 | 112,400 |
| 1,5-Hexadiene (diallyl) | 43 | 6 | 1.667 | 59.5 | -140.7 | 0.6878 | 20.1 | 7.1 | 13.0 | 2.167 | 19,000 | 109,000 |
| Ethylene | 44 | 2 | 2.000 | -103.71 | -169.15 | 0.5638[b] | 11.32[b] | 3.237[b] | 8.083[b] | 4.041 | 20,000 | 95,000 |
| 1,3-Butadiene | 45 | 4 | 1.500 | -4.41 | -108.92 | 0.650[b] | 25.8[b] | 5.61[b] | 20.2[b] | 5.050 | 19,000 | 102,900 |
| Isopropenylacetylene | 46 | 5 | 1.200 | 33.0 | -110.2 | 0.7016 | (37.4) | (6.4) | (31.0) | 6.020 | 18,300 | 107,400 |

a) Density of liquid in g/ml at 25°C for liquids boiling above 25°C, otherwise at the boiling point.
b) At the boiling point.
c) Heat of formation relative to elements at 25°C, and hydrocarbon at $T_B$ for liquids boiling below 25°C and at 25°C for others, in kcal/mole.
d) Heat of combustion (net) based on $O_2$ (g) at 25°C, and hydrocarbon at $T_B$ or 25°C whichever is lower.
e) Supercooled liquid or compound in solution.

| Compound | $\Delta H_f(g)$, 25°C kcal/gm mole | $\Delta H_f(g)$ (our estimate) |
|---|---|---|
| Cyclobutane | 37.5 ± 0.4 | |
| Methylenecyclopropane | 48.0 ± 0.4 | |
| Bicyclo(1,1,0)butane | 51.9 ± 0.2 | 52 ± 3 |
| 1-Methylcyclopropene | 58.2 ± 0.3 | |

## F. References for Section II


1) C. Baird and M.J.S. Dewar, J. Am. Chem. Soc. 89, 3966 (1967).

2) Pratt and Whitney Corp. Report No. NASA CR-54445, PWA FR-1443, issued September 1, 1965 under Contract NAS 3-4195.

3) K.B. Wiberg and R.A. Fenoglio, J. Am. Chem. Soc. 90, 3395 (1968).

## SECTION III

## PERFORMANCE CALCULATIONS AND CORRELATIONS FOR ENERGETIC HYDROCARBONS

### A. Specific Impulse Calculations

We have calculated specific impulse, I, at a variety of oxygen/fuel ratios for a number of hydrocarbons at both shifting equilibrium (E) and frozen equilibrium (F) expansions from a chamber pressure of 1000 psia to one atmosphere. These calculations were made by means of a NASA computer program[1)] that was supplied to us through the courtesy of Lewis Research Center. The general trends revealed by the calculations are described in this section. Detailed curves showing performance parameters as a function of O/F ratio for a variety of energetic hydrocarbons are presented in Appendix 1. Detailed performance parameters are shown for some selected candidate rocket fuels also in Section IV.

Specific impulse for expansion from 1000 psia to vacuum have also been calculated for most of these hydrocarbons but the results are not reproduced in this report; they are available on request.

### B. General Dependence of Specific Impulse on Heat of Formation x, Hydrogen/Carbon Ratio r, and Oxygen/Fuel Ratio, O/F

The general shape of the curves relating specific impulse, I(E) to O/F weight ratio is shown in Figure 1 for hydrocarbons with r = 1.00, 1.50 and 2.00. For r = 1.00, the curve shown is for acetylene, with x = 24.59 kcal/gm atom C. For other hydrocarbons with r = 1.0 but lower values of x, the curve will have the same general shape but its maximum I(E) will be lower and will occur at a higher value of O/F. The locus of these maxima is shown by the approximately straight line which slopes down and to the right. The arrow on the figure indicates the stoichiometric O/F ratio; it will be noted that for hydrocarbons with r = 1.0 and high values of x, the maximum specific impulse occurs on the oxygen-lean side of stoichiometric, whereas for those with low values of x, such as benzene [I(E) max = 293.3 sec], the maximum impulse occurs at $(O/F)_W$ = 2.228, on the oxygen-rich side of stoichiometric.

For hydrocarbons with H/C = 1.50, a similar behavior occurs but the curves are shifted to a higher O/F ratio. The curve shown is for bicyclo (1,1,0) butane, with x = 11.5 kcal/gm atom C. For this hydrocarbon as shown by the arrow on the figure, maximum I(E) occurs very close to stoichiometric O/F; other hydrocarbons with r = 1.5 but lower values of x develop their maximum impulse on the oxygen-rich side of stoichiometric. For r = 2.0, the curve shown is for a fictitious hydrocarbon with a value of x somewhat higher than that of cyclopropane (x = 2.13 kcal/gm atom). For all known hydrocarbons with r = 2.0, maximum impulse is developed at O/F ratios on the oxygen-rich side of stoichiometric.

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1) See references at end of this section.

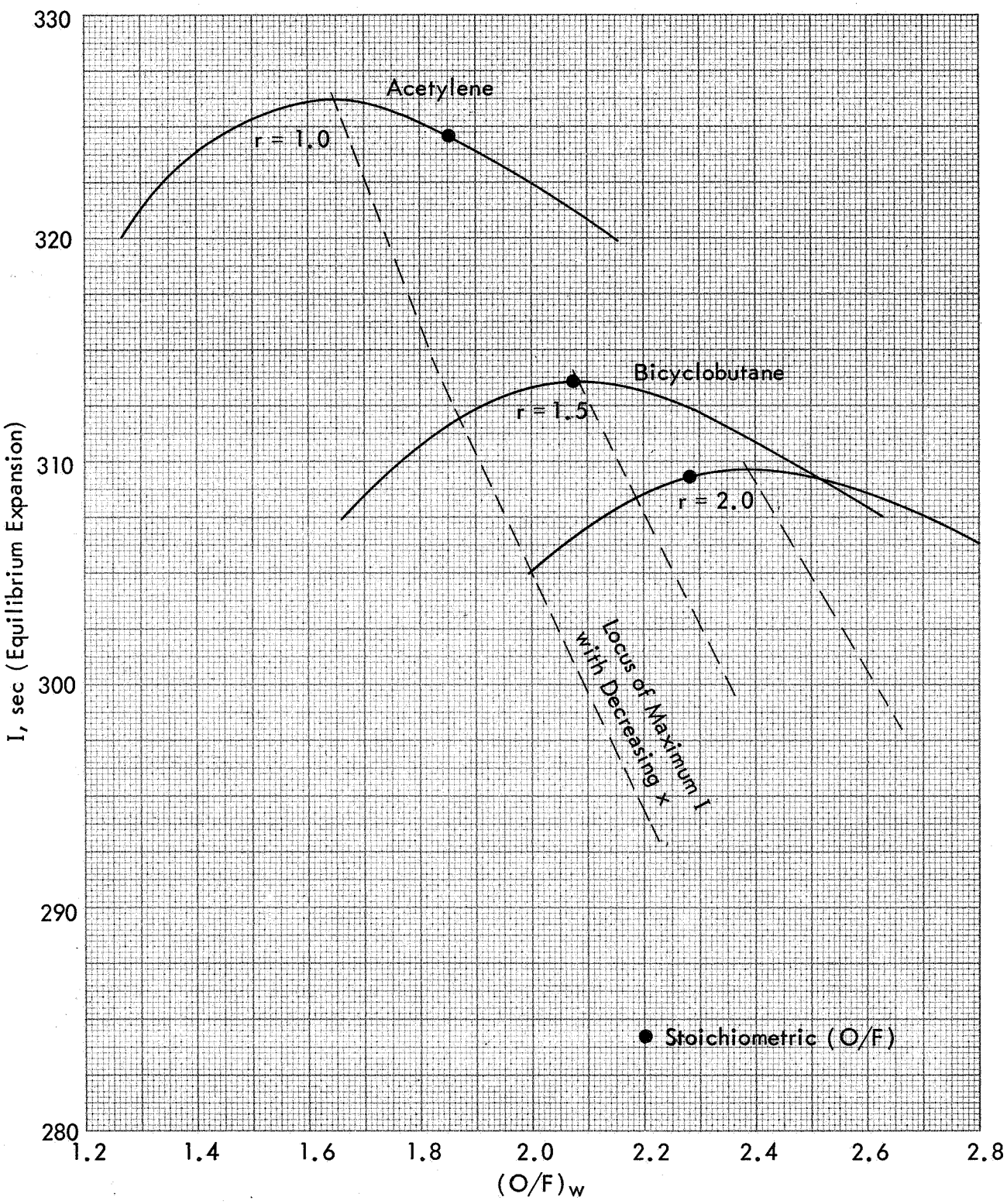


Figure 1. SPECIFIC IMPULSE vs (O/F)w WITH LOX FOR HYDROCARBONS AT VARIOUS VALUES OF ATOM RATIO H/C = r

1000 psia/atm

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## C. Propellant Density and Specific Impulse at Stoichiometric O/F

Calculated performance parameters at the stoichiometric O/F ratio are given in Table 4 for 47 energetic hydrocarbons and for 3 reference kerosene fuels. The pure hydrocarbons are listed in order of decreasing values of density-impulse, $\bar{\rho}$ I(E) at equilibrium expansion. Properties listed in Table 4 include fuel density $\rho$, heat of formation x per gram-atom carbon, H/C ratio r, propellant density $\bar{\rho}$, specific impulse (shifting) I(E) (1000 psia/atm), density-impulse $\bar{\rho}$ I(E), specific impulse (frozen) I(F), $\bar{\rho}$ I(F), and oxygen/fuel ratio O/F by weight and by volume. Among the energetic hydrocarbons for which reasonably straightforward synthetic routes are available, and for which the stoichiometric propellant densities exceed 0.97 (RP-1 = 1.01), those showing the highest values of I(E) (lb f· sec/lb) are 1,5 hexadiyne, 311.4; cyclopropyl acetylene, 311.1; spiropentane, 310.2; 1,6 heptadiyne, 309.1; 1,7 octadiyne, 307.5; cyclopropyl cyclopropane, 306.4 (RP-1 = 296.3).

Similar data are listed in Table 4a for the O/F ratio giving maximum impulse.

Correlations between the stoichiometric specific impulse and specific heat of formation x at constant H/C ratio r are shown in Figure 2 for shifting equilibrium expansion and in Figure 3 for frozen equilibrium. These correlations can be described empirically by the following equations:

$$I(E)\ (\text{stoich}) = 251.10 + 2.8905\,x - 0.0149\,x^2 + r\,(39.932 - 1.0777\,x) + r^2\,(-6.217 + 0.1452\,x + 0.0015\,x^2)\ \text{sec} \qquad \text{III.1}$$

$$I(F)\ (\text{stoich}) = 245.95 + 1.9025\,x - 0.0077\,x^2 + r\,(30.989 - 0.6862\,x) + r^2\,(-4.584 + 0.0969\,x + 0.0004\,x^2)\ \text{sec} \qquad \text{III.2}$$

where I(E) is specific impulse calculated for shifting equilibrium during expansion whereas I(F) is for frozen equilibrium. These expressions were developed from a regression analysis of specific impulse calculations for 46 hydrocarbons ranging in H/C atom ratio r from 0.80 to 2.0 and in x from -7 to +24 kcal/gm atom. The correlations can be expected to be less accurate outside this range. Within the range quoted, the maximum deviation in I(E) between equation III.1 and direct calculation was -0.28 sec; the average absolute deviation was 0.053 sec and the root mean square deviation was 0.104 sec. The corresponding magnitudes for expression III.2 are -0.16, 0.048 and 0.073 sec, respectively.

Partial differentiation of these equations with respect to x yields

$$\partial I(E)/\partial x\ (\text{stoich}) = 2.8905 - 0.0298x - 1.077r + r^2\,(0.1452 + 0.0030x) \qquad \text{III.3}$$

$$\partial I(F)/\partial x\ (\text{stoich}) = 1.9025 - 0.0154x - 0.6862r + r^2\,(0.0969 + 0.0008x) \qquad \text{III.4}$$

## INDEX TO TABLE 4: PROPERTIES OF HYDROCARBONS AT STOICHIOMETRIC O/F

| Name of Hydrocarbon | Key to Serial No. in Table | Name of Hydrocarbon | Key to Serial No. in Table |
|---|---|---|---|
| Acetylene | 43 | 1,6-Heptadiyne | 18 |
| Allene | 41 | 1,5-Hexadiyne | 16 |
| Bicyclo(1,1,0)butane | 22 | 1,6-Hexadiene(diallyl) | 42 |
| Bicyclo(2,2,1,)heptadiene-2,5 | 10 | 1,7-Octadiyne | 15 |
| 1,4-Cyclohexadiene | 26 | 1,3,5-Octatriene | 33 |
| Bicyclo(2,1,0)pentane | 21 | Isopropenylacetylene | 44 |
| 1,3-Butadiene | 45 | Methylacetylene | 38 |
| Cubane | 1 | Methylcubane | 2 |
| Cyclobutane | 34 | 1-Methylcyclobutene | 35 |
| Cyclobutene | 32 | Methylenecyclobutane | 31 |
| 1,4-Cyclohexadiene | 25 | 1-Methyl-1,4-cyclohexadiene | 27 |
| Cyclopentane | 36 | 1-Methyltricyclo(3,1,0,$0^{2,4}$)hexane | 11 |
| Cyclopropane | 37 | 1-4-Pentadiyne | 17 |
| Cyclopropylacetylene | 23 | Quadricyclene | 6 |
| Cyclopropylcyclopropane | 24 | RP-1A | R-1 |
| Dicyclopropylacetylene | 8 | RP-1B | R-2 |
| 1,3-Dimethylbicyclo(1,1,0)butane | 39 | RJ-1 (Shell UMFC) | R-3 |
| Dimethylcubane | 3 | SHELLDYNE | 4 |
| Di(methylcyclopropyl)acetylene | 13 | Spiro(3,3)heptane | 20 |
| 1,4-Dimethyltricyclo(3,1,0,$0^{2,4}$)hexane | 14 | Spiro(3,2)hexane | 19 |
| Dispiro(3,1,3,1)decane | 12 | Spiro(4,3)octane | 27 |
| Dispiro(2,1,2,1)octane | 9 | Spiro(2,2)pentane | 29 |
| trans-1,2-Divinylcyclobutane | 30 | Tetrahedrane | 5 |
| Ethylene | 46 | Tricyclo(3,1,0,$0^{2,4}$)hexane | 7 |



Tables 4 and 4a follow

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Table 4. ESTIMATED THRUST PERFORMANCE OF CANDIDATE HYDROCARBON FUELS, CnHrn, AT STOICHIOMETRIC O/F; FUELS LISTED ON DECREASING RANK OF $\bar{\rho}I$ (E)

| Name | No. | $\rho$ | $\frac{\Delta H_f(1)}{n}$, x | r | $\bar{\rho}$, g/ml | I(E), sec | $\bar{\rho}I(E)$ | I(F), sec | $\bar{\rho}I(F)$ | O/F Wt | O/F Vol |
|---|---|---|---|---|---|---|---|---|---|---|---|
| RP-1A | R-1 | 0.800 | -7.056 | 2.000 | 1.011 | 296.4 | 299.5 | 284.8 | 287.8 | 2.281 | 1.597 |
| RP-1B | R-2 | 0.805 | -5.800 | 1.900 | 1.012 | 296.3 | 299.7 | 284.6 | 287.9 | 2.240 | 1.579 |
| RJ-1 (Shell UMFC) | R-3 | 0.8454 | -6.676 | 1.940 | 1.031 | 295.8 | 305.0 | 284.3 | 293.2 | 2.257 | 1.670 |
| Cubane | 1 | (1.03) | 17.375 | 1.000 | 1.100 | 314.8 | 346.3 | 295.0 | 324.5 | 1.844 | 1.662 |
| Methylcubane | 2 | 0.986 | 14.611 | 1.111 | 1.083 | 312.4 | 338.3 | 293.6 | 318.0 | 1.895 | 1.636 |
| Dimethylcubane | 3 | 0.950 | 12.500 | 1.200 | 1.069 | 310.7 | 332.0 | 292.6 | 312.8 | 1.936 | 1.610 |
| SHELLDYNE | 4 | 1.09 | 3.546 | 1.143 | 1.124 | 295.0 | 331.6 | 281.7 | 316.6 | 1.910 | 1.822 |
| Tetrahedrane | 5 | 0.81 | 26.250 | 1.000 | 0.998 | 327.0 | 326.4 | 303.8 | 303.3 | 1.844 | 1.307 |
| | | | 25.000 | | | 325.4 | 324.9 | 302.6 | 302.1 | | |
| Quadricyclene | 6 | 0.935 | 7.357 | 1.143 | 1.062 | 301.5 | 320.0 | 286.2 | 303.8 | 1.910 | 1.563 |
| Tricyclo(3,1,0,$0^{2,4}$)hexane | 7 | 0.865 | 9.917 | 1.333 | 1.032 | 309.1 | 319.0 | 291.9 | 301.3 | 1.997 | 1.512 |
| Dicyclopropylacetylene | 8 | 0.870 | 9.713 | 1.250 | 1.033 | 307.3 | 317.5 | 290.5 | 300.1 | 1.959 | 1.492 |
| Dispiro(2,1,2,1)octane | 9 | 0.846 | 7.150 | 1.500 | 1.026 | 307.9 | 315.7 | 291.6 | 299.0 | 2.071 | 1.533 |
| | | | 6.313 | | | 306.7 | 314.5 | 290.7 | 298.1 | | |
| Bicyclo(2,2,1)heptadiene-2,5 | | 0.903 | 6.857 | 1.143 | 1.047 | 300.7 | 314.8 | 285.6 | 299.0 | 1.910 | 1.510 |
| 1-Methyltricyclo(3,1,0,$0^{2,4}$)hexane | 11 | 0.840 | 7.414 | 1.429 | 1.022 | 307.0 | 313.6 | 290.8 | 297.0 | 2.039 | 1.499 |
| Dispiro(3,1,3,1)decane | 12 | 0.847 | 3.610 | 1.600 | 1.027 | 304.5 | 312.8 | 289.5 | 297.4 | 2.114 | 1.567 |
| | | | 3.010 | | | 303.6 | 311.9 | 288.9 | 296.8 | | |
| Di(methylcyclopropyl)acetylene | 13 | 0.840 | 6.600 | 1.400 | 1.021 | 305.3 | 311.7 | 289.5 | 295.6 | 2.027 | 1.490 |
| 1,4-Dimethyltricyclo(3,1,0,$0^{2,4}$)hexane | 14 | 0.830 | 5.538 | 1.500 | 1.018 | 305.5 | 310.9 | 290.0 | 295.0 | 2.071 | 1.504 |
| 1,7-Octadiyne | 15 | 0.808 | 9.863 | 1.250 | 1.002 | 307.5 | 308.2 | 290.6 | 291.3 | 1.959 | 1.386 |
| 1,5-Hexadiyne | 16 | 0.794 | 15.133 | 1.000 | 0.990 | 311.4 | 308.2 | 292.6 | 289.6 | 1.844 | 1.281 |
| 1,4-Pentadiyne | 17 | 0.782 | 19.380 | 0.800 | 0.978 | 314.9 | 308.1 | 294.5 | 288.1 | 1.748 | 1.196 |
| 1,6-Heptadiyne | 18 | 0.8009 | 12.086 | 1.143 | 0.997 | 309.1 | 308.0 | 291.4 | 290.3 | 1.910 | 1.339 |
| Spiro(3,2)hexane | 19 | 0.788 | 4.833 | 1.667 | 0.999 | 307.4 | 307.2 | 291.7 | 291.5 | 2.143 | 1.478 |
| | | | 4.333 | | | 306.7 | 306.5 | 291.2 | 291.0 | | |
| Spiro(3,3)heptane | 20 | 0.797 | 2.829 | 1.714 | 1.005 | 305.4 | 306.8 | 290.4 | 291.8 | 2.163 | 1.509 |
| | | | 2.314 | | | 304.6 | 306.1 | 289.9 | 291.3 | | |
| Bicyclo(2,1,0)pentane | | 0.785 | 5.960 | 1.600 | 0.997 | 307.9 | 306.8 | 291.8 | 290.8 | 2.114 | 1.452 |
| Bicyclo(1,1,0)butane | | 0.750 | 11.500 | 1.500 | 0.976 | 313.9 | 306.4 | 295.8 | 288.7 | 2.071 | 1.359 |
| Cyclopropylacetylene | 23 | 0.775 | 12.820 | 1.200 | 0.984 | 311.1 | 306.0 | 293.0 | 288.2 | 1.936 | 1.314 |
| Cyclopropylcyclopropane | 24 | 0.785 | 4.133 | 1.667 | 0.998 | 306.4 | 305.7 | 291.0 | 290.4 | 2.143 | 1.472 |
| 1,4-Cyclohexadiene | 25 | 0.843 | 3.217 | 1.333 | 1.021 | 298.7 | 305.1 | 284.8 | 290.9 | 1.997 | 1.473 |
| Bicyclo(3,1,0)hexane | 26 | 0.815 | 0.183 | 1.667 | 1.013 | 300.7 | 304.6 | 287.1 | 290.8 | 2.143 | 1.528 |
| 1-Methyl-1,4-cyclohexadiene | 27 | 0.841 | 1.414 | 1.429 | 1.022 | 297.8 | 304.3 | 284.4 | 290.7 | 2.039 | 1.501 |
| Spiro(4,3)octane | 28 | 0.830 | -3.250 | 1.750 | 1.022 | 297.1 | 303.5 | 284.8 | 291.0 | 2.178 | 1.582 |
| Spiro(2,2)pentane | 29 | 0.7487 | 7.660 | 1.600 | 0.977 | 310.2 | 303.2 | 293.5 | 286.8 | 2.114 | 1.385 |
| trans-1,2-Divinylcyclobutane | 30 | 0.774 | 4.688 | 1.500 | 0.989 | 304.3 | 301.0 | 289.1 | 285.9 | 2.071 | 1.403 |
| Methylenecyclobutane | 31 | 0.735 | 4.660 | 1.600 | 0.970 | 306.0 | 296.8 | 290.6 | 281.8 | 2.114 | 1.360 |
| Cyclobutene | 32 | 0.733 | 6.375 | 1.500 | 0.967 | 306.8 | 296.5 | 290.8 | 281.1 | 2.071 | 1.328 |
| 1,3,7-Octatriene | 33 | 0.756 | 3.188 | 1.500 | 0.979 | 302.0 | 295.8 | 287.5 | 281.6 | 2.071 | 1.370 |
| Cyclobutane | 34 | 0.702 | 0.180 | 2.000 | 0.959 | 306.3 | 293.8 | 291.8 | 279.8 | 2.281 | 1.402 |
| 1-Methylcyclobutene | 35 | 0.719 | 4.420 | 1.600 | 0.961 | 305.7 | 293.6 | 290.3 | 278.9 | 2.114 | 1.330 |
| Cyclopentane | 36 | 0.741 | -5.060 | 2.000 | 0.980 | 299.2 | 293.3 | 286.8 | 281.2 | 2.281 | 1.479 |
| Cyclopropane[b] | 37 | 0.681 | 2.133 | 2.000 | 0.947 | 308.9 | 292.5 | 293.5 | 277.9 | 2.281 | 1.360 |
| Cyclopropane (-79°C) | | 0.720 | 1.700 | | 0.969 | 308.3 | 298.8 | 293.1 | 284.1 | | 1.438 |
| Methylacetylene | 38 | 0.675 | 12.800 | 1.333 | 0.928 | 313.2 | 290.6 | 294.8 | 273.6 | 1.997 | 1.180 |
| 1,3-Dimethylbicyclo(1,1,0)butane | 39 | 0.725 | 5.217 | 1.333 | 0.958 | 301.9 | 289.3 | 287.0 | 275.0 | 1.997 | 1.267 |
| Dimethylacetylene | 40 | 0.6858 | 7.155 | 1.500 | 0.939 | 307.9 | 289.0 | 291.6 | 273.7 | 2.071 | 1.243 |
| Allene | | 0.660 | 13.466 | 1.333 | 0.918 | 314.1 | 288.5 | 295.5 | 271.4 | 1.997 | 1.154 |
| 1,5-Hexadiene (diallyl) | 42 | 0.6878 | 2.167 | 1.667 | 0.944 | 303.6 | 286.6 | 289.1 | 272.9 | 2.143 | 1.290 |
| Acetylene | | 0.620 | 24.590 | 1.000 | 0.881 | 324.9 | 286.3 | 302.2 | 266.4 | 1.844 | 1.000 |
| Isopropenylacetylene | 44 | 0.7016 | 6.020 | 1.200 | 0.941 | 300.5 | 282.8 | 285.6 | 268.8 | 1.936 | 1.189 |
| 1,3-Butadiene | 45 | 0.6500 | 5.050 | 1.500 | 0.916 | 304.8 | 279.3 | 289.5 | 265.3 | 2.071 | 1.178 |
| Ethylene | 46 | 0.5688 | 4.042 | 2.000 | 0.873 | 311.3 | 272.0 | 295.2 | 258.0 | 2.281 | 1.136 |

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# Table 4a. ESTIMATED THRUST PERFORMANCE OF CANDIDATE HYDROCARBON FUELS AT MAXIMUM IMPULSE, ORDERED BY $\bar{\rho}\ I_{max}(E)$

| Name | No. in Table 2 | H/C Atom Ratio, r | ΔHf/n kcal/g atom C, x | Equilibrium Expansion (E) | | | | | Frozen Expansion (F) | | | | | O/F wt, Stoichiometric |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $I_{max}$ a) | $\bar{\rho}$ | $\bar{\rho}\ I_{max}$ | O/F wt b) | O/F Vol | $I_{max}$ c) | $\bar{\rho}$ | $\bar{\rho}\ I_{max}$ | O/F wt d) | O/F Vol | |
| RP-1A | R-1 | 2.000 | -7.056 | 299.3 | 1.022 | 305.9 | 2.630 | 1.842 | 284.9 | 1.105 | 287.8 | 2.276 | 1.594 | 2.281 |
| RP-1B | R-2 | 1.900 | -5.800 | 299.2 | 1.023 | 305.9 | 2.577 | 1.816 | 284.6 | 1.012 | 287.9 | 2.239 | 1.578 | 2.240 |
| RJ-1 (Shell UMFC) | R-3 | 1.940 | -6.676 | 298.8 | 1.041 | 311.1 | 2.609 | 1.930 | 284.3 | 1.031 | 293.2 | 2.262 | 1.674 | 2.257 |
| Cubane | 1 | 1.000 | 17.375 | 314.8 | 1.100 | 364.4 | 1.848 | 1.666 | 297.3 | 1.096 | 325.8 | 1.563 | 1.409 | 1.844 |
| Methyl Cubane | 3 | 1.111 | 14.611 | 312.4 | 1.084 | 338.7 | 1.939 | 1.673 | 295.4 | 1.078 | 318.4 | 1.649 | 1.423 | 1.895 |
| SHELLDYNE | 6 | 1.143 | 3.546 | 297.9 | 1.126 | 335.3 | 2.211 | 2.109 | 281.8 | 1.124 | 316.7 | 1.909 | 1.822 | 1.910 |
| Dimethylcubane | 4 | 1.200 | 12.500 | 310.8 | 1.070 | 332.7 | 2.007 | 1.669 | 294.0 | 1.063 | 312.6 | 1.714 | 1.425 | 1.936 |
| Tetrahedrane | 2 | 1.000 | 26.250 | 328.9 | 0.989 | 325.4 | 1.652 | 1.172 | 310.7 | 0.974 | 302.5 | 1.365 | 0.968 | 1.844 |
| | | | 25.000 | 326.8 | 0.991 | 323.8 | 1.679 | 1.190 | 308.8 | 0.975 | 301.1 | 1.393 | 0.988 | |
| Quadricyclene | 10 | 1.143 | 7.357 | 302.9 | 1.067 | 323.1 | 2.117 | 1.732 | 286.4 | 1.059 | 303.4 | 1.821 | 1.490 | 1.910 |
| Tricyclo(3,1,0,$0^{2,4}$)hexane | 5 | 1.333 | 9.917 | 309.4 | 1.035 | 320.2 | 2.093 | 1.584 | 293.0 | 1.025 | 300.3 | 1.798 | 1.361 | 1.997 |
| Dicyclopropylacetylene | 7 | 1.250 | 9.713 | 307.8 | 1.037 | 319.2 | 2.081 | 1.585 | 291.3 | 1.027 | 299.2 | 1.788 | 1.361 | 1.959 |
| Bicyclo(2,2,1)heptadiene-2,5 | 20 | 1.143 | 6.857 | 302.2 | 1.053 | 318.3 | 2.129 | 1.682 | 285.8 | 1.045 | 298.6 | 1.833 | 1.449 | 1.910 |
| Dispiro(2,1,2,1)octane | 9 | 1.500 | 7.150 | 308.3 | 1.029 | 317.3 | 2.186 | 1.619 | 292.4 | 1.019 | 297.9 | 1.890 | 1.399 | 2.071 |
| | | | 6.313 | 307.3 | 1.030 | 316.4 | 2.205 | 1.633 | 291.4 | 1.020 | 297.1 | 1.909 | 1.414 | |
| Dispiro(3,1,3,1)decane | 16 | 1.600 | 3.610 | 305.4 | 1.033 | 315.5 | 2.286 | 1.695 | 289.9 | 1.023 | 296.6 | 1.987 | 1.473 | 2.114 |
| | | | 3.010 | 304.7 | 1.033 | 314.9 | 2.300 | 1.705 | 289.2 | 1.024 | 296.0 | 2.001 | 1.483 | |
| 1-Methyltricyclo(3,1,0,$0^{2,4}$)hexane | 12 | 1.429 | 7.414 | 307.6 | 1.026 | 315.5 | 2.167 | 1.594 | 291.5 | 1.015 | 295.9 | 1.872 | 1.377 | 2.039 |
| Di(methylcyclopropyl)acetylene | 17 | 1.400 | 6.600 | 306.1 | 1.026 | 314.1 | 2.181 | 1.604 | 290.0 | 1.016 | 294.6 | 1.886 | 1.387 | 2.027 |
| 1,4-Dimethyltricyclo(3,1,0,$0^{2,4}$)hexane | 18 | 1.500 | 5.538 | 306.3 | 1.023 | 313.3 | 2.223 | 1.615 | 290.8 | 1.012 | 294.0 | 1.927 | 1.400 | 2.071 |
| 1,7-Octadiyne | 19 | 1.250 | 9.863 | 308.0 | 1.007 | 310.2 | 2.078 | 1.469 | 291.5 | 0.995 | 289.9 | 1.959 | 1.386 | 1.959 |
| 1,4-Cyclohexadiene | 32 | 1.333 | 3.217 | 300.7 | 1.030 | 309.7 | 2.251 | 1.661 | 284.9 | 1.020 | 290.5 | 1.953 | 1.441 | 1.997 |
| Spiro(3,3)heptane | 26 | 1.714 | 2.829 | 306.2 | 1.011 | 309.5 | 2.323 | 1.620 | 290.8 | 0.999 | 290.6 | 2.021 | 1.410 | 2.163 |
| | | | 2.314 | 305.6 | 1.011 | 309.0 | 2.335 | 1.629 | 290.3 | 1.000 | 290.2 | 2.033 | 1.418 | |
| 1,6-Heptadiyne | 15 | 1.143 | 12.086 | 309.4 | 1.001 | 309.5 | 2.004 | 1.405 | 292.5 | 0.987 | 288.8 | 1.713 | 1.201 | 1.910 |
| 1-Methyl 1,4-cyclohexadiene | 35 | 1.429 | 1.414 | 300.1 | 1.031 | 309.4 | 2.312 | 1.702 | 284.5 | 1.021 | 290.4 | 2.011 | 1.480 | 2.039 |
| Spiro(3,2)hexane | 23 | 1.667 | 4.833 | 307.9 | 1.004 | 309.2 | 2.268 | 1.564 | 292.4 | 0.992 | 290.1 | 1.969 | 1.358 | 2.143 |
| | | 1.667 | 4.333 | 307.3 | 1.005 | 308.7 | 2.279 | 1.572 | 291.8 | 0.993 | 289.6 | 1.980 | 1.366 | |
| 1,5-Hexadiyne | 13 | 1.000 | 15.133 | 311.5 | 0.992 | 309.1 | 1.900 | 1.321 | 294.2 | 0.978 | 287.8 | 1.614 | 1.122 | 1.844 |
| Spiro(4,3)octane | 37 | 1.750 | -3.250 | 299.7 | 1.031 | 309.0 | 2.483 | 1.804 | 284.8 | 1.210 | 290.8 | 2.165 | 1.573 | 2.178 |
| Bicyclo(3,1,0)hexane | 29 | 1.667 | 0.183 | 302.4 | 1.021 | 308.8 | 2.381 | 1.698 | 287.2 | 1.011 | 290.2 | 2.075 | 1.481 | 2.143 |
| Bicyclo(2,1,0)pentane | 22 | 1.600 | 5.960 | 308.3 | 1.001 | 308.7 | 2.230 | 1.532 | 292.6 | 0.989 | 289.3 | 1.933 | 1.327 | 2.114 |
| Cyclopropylcyclopropane | 25 | 1.667 | 4.133 | 307.1 | 1.003 | 308.1 | 2.284 | 1.567 | 291.6 | 0.991 | 289.0 | 1.985 | 1.364 | 2.143 |
| 1,4-Pentadiyne | 8 | 0.800 | 19.380 | 314.9 | 0.978 | 308.1 | 1.745 | 1.194 | 296.9 | 0.963 | 285.9 | 1.473 | 1.009 | 1.748 |
| Cyclopropylacetylene | 14 | 1.200 | 12.820 | 311.3 | 0.987 | 307.1 | 2.000 | 1.356 | 294.5 | 0.972 | 286.3 | 1.707 | 1.158 | 1.936 |
| Bicyclo(1,1,0)butane | 11 | 1.500 | 11.500 | 313.9 | 0.977 | 306.7 | 2.089 | 1.372 | 297.7 | 0.962 | 286.4 | 1.789 | 1.175 | 2.071 |
| Spiro(2,2)pentane | 24 | 1.600 | 7.660 | 310.4 | 0.981 | 304.5 | 2.192 | 1.436 | 294.6 | 0.967 | 284.8 | 1.894 | 1.241 | 2.114 |
| trans-1,2-Divinylcyclobutane | 27 | 1.500 | 4.688 | 305.2 | 0.996 | 304.1 | 2.244 | 1.520 | 289.5 | 0.984 | 284.7 | 1.947 | 1.319 | 2.071 |
| 1,3,7-Octatriene | 39 | 1.500 | 3.188 | 303.4 | 0.988 | 299.9 | 2.280 | 1.508 | 287.7 | 0.975 | 280.6 | 1.981 | 1.311 | 2.071 |
| Methylene cyclobutane | 33 | 1.600 | 4.660 | 306.7 | 0.976 | 299.5 | 2.261 | 1.454 | 291.1 | 0.962 | 280.1 | 1.963 | 1.263 | 2.114 |
| Cyclopentane | 41 | 2.000 | -5.060 | 301.4 | 0.992 | 299.0 | 2.573 | 1.668 | 286.9 | 0.978 | 280.6 | 2.233 | 1.447 | 2.281 |
| Cyclobutene | 31 | 1.500 | 6.375 | 307.3 | 0.973 | 299.0 | 2.204 | 1.414 | 291.5 | 0.958 | 279.3 | 1.908 | 1.224 | 2.071 |
| Cyclobutane | 36 | 2.000 | 0.180 | 307.2 | 0.966 | 296.7 | 2.434 | 1.495 | 292.3 | 0.951 | 278.0 | 2.116 | 1.300 | 2.281 |
| 1-Methyl cyclobutene | 38 | 1.600 | 4.420 | 306.4 | 0.968 | 296.6 | 1.968 | 1.238 | 290.8 | 0.953 | 277.2 | 2.266 | 1.426 | 2.114 |
| Cyclopropane (bp) | 34 | 2.000 | 2.133 | 309.4 | 0.952 | 294.5 | 2.385 | 1.421 | 294.4 | 0.936 | 275.6 | 2.071 | 1.235 | 2.281 |
| Cyclopropane (-79°C) | | | 1.700 | 308.9 | 0.974 | 300.9 | 2.395 | 1.510 | 294.0 | 0.960 | 282.1 | 2.081 | 1.312 | |
| 1,3-Dimethylbicyclo(1,1,0)butane | 42 | 1.333 | 5.217 | 303.3 | 0.968 | 293.7 | 2.203 | 1.398 | 287.2 | 0.954 | 273.9 | 1.907 | 1.210 | 1.997 |
| Dimethyl acetylene | 40 | 1.500 | 7.155 | 308.3 | 0.945 | 291.3 | 2.186 | 1.312 | 292.4 | 0.928 | 271.4 | 1.890 | 1.134 | 2.071 |
| Methylacetylene | 28 | 1.333 | 12.800 | 313.2 | 0.930 | 291.3 | 2.028 | 1.198 | 296.7 | 0.911 | 270.4 | 1.732 | 1.023 | 1.997 |
| 1,5-Hexadiene (diallyl) | 43 | 1.667 | 2.167 | 304.7 | 0.953 | 290.5 | 2.331 | 1.404 | 289.3 | 0.938 | 271.4 | 2.030 | 1.222 | 2.143 |
| Allene | 30 | 1.333 | 13.466 | 314.2 | 0.920 | 288.8 | 2.014 | 1.163 | 297.5 | 0.900 | 267.8 | 1.717 | 0.992 | 1.997 |
| Isopropenylacetylene | 46 | 1.200 | 6.020 | 302.1 | 0.953 | 287.9 | 2.160 | 1.326 | 285.8 | 0.937 | 267.8 | 1.863 | 1.144 | 1.936 |
| Acetylene | 21 | 1.000 | 24.590 | 326.2 | 0.870 | 283.7 | 1.688 | 0.916 | 308.1 | 0.846 | 260.6 | 1.402 | 0.761 | 1.844 |
| 1,3-Butadiene | 45 | 1.500 | 5.050 | 305.7 | 0.926 | 283.0 | 2.235 | 1.272 | 289.9 | 0.908 | 263.3 | 1.938 | 1.103 | 2.071 |
| Ethylene | 44 | 2.000 | 4.042 | 311.5 | 0.877 | 273.4 | 2.339 | 1.164 | 296.5 | 0.857 | 254.1 | 2.028 | 1.010 | 2.281 |

a) $I_{max}(E) = 269.54 + 1.296x + 0.0173x^2 + r(23.84 - 0.0126x^2) - r^2(2.56 + 0.046x - 0.0029x^2)$.
b) O/F wt (at $I_{max}(E)$) $= 2.1210 - 0.03347x + r(0.1584 + 0.00969x + 0.00009x^2) + r^2(0.000086 - 0.00286x + 0.0000149x^2)$.
c) $I_{max}(F) = 252.25 + 1.253x + 0.0140x^2 + r(25.17 - 0.95x - 0.0072x^2) - r^2(2.61 - 0.0012x^2)$.
d) O/F wt (at $I_{max}(F)$) $= 1.6955 - 0.02372x + 0.000016x^2 + r(0.3223 + 0.00005248x^2) + r^2(0.05509 - 0.000291x + 0.000043x^2)$.

These expressions are useful for estimating the effect of a revised value of x (from a better estimate of the heat of formation) on the estimated value of I.

Similarly, the oxygen/fuel weight ratio $(O/F)_W$, the volume ratio $(O/F)_V$, and the propellant density $\bar{\rho}$ can be expressed at this stoichiometry on the basis of equation II.1 and the density of LOX taken as 1.1425 gm/ml:

$$(O/F)_W = \frac{1.333 + 0.6667\ r}{1.000 + 0.0840\ r} \qquad \text{III.5}$$

$$(O/F)_V = \frac{(1.1670 + 0.5835\ r)\rho}{1.000 + 0.0840\ r} \qquad \text{III.6}$$

where $\rho$ is the density of the hydrocarbon. The propellant density $\bar{\rho}$ is

$$\bar{\rho}\ (\text{stoich}) = \frac{2.332\ \rho + 0.7500\ r\ \rho}{1 + 0.0840\ r + 1.166\ \rho + 0.5831\ r\rho} \qquad \text{III.7}$$

D. Flame Temperatures at Stoichiometric O/F Ratio

Calculated combustion-chamber flame temperatures are plotted against specific heat of formation x at constant r in Figure 4. Similar plots are shown for throat temperatures in Figure 5 (shifting equilibrium) and in Figure 6 (frozen equilibrium). Exit temperatures are shown in Figure 7 (shifting equilibrium) and in Figure 8 (frozen equilibrium). The data are shown only for r = 1.0, 1.5 and 2.0; temperatures for intermediate values of r can be estimated by interpolation.

E. Dependence of Maximum Specific Impulse on Fuel Parameters

As indicated in Figure 1, the maximum specific impulse, $I_{max}$, is generated for most hydrocarbon fuels at an oxygen/fuel ratio that differs from the stoichiometric one. Values of $I_{max}$ are shown in Table 5. We have found that correlations similar to those shown in Figures 2 and 3 can be developed to describe the dependence of $I_{max}$ on x and r. These correlations have been fitted to the following equations

$$I_{max}(E) = 269.54 + 1.296x + 0.0173x^2 + r(23.84 - 0.0126x^2) + r^2(-2.56 - 0.046x + 0.0029x^2) \qquad \text{III.8}$$

$$(O/F)w[\text{at } I_{max}(E)] = 2.121 - 0.03347x + r(0.1584 + 0.00969x + 0.00009x^2) + r^2(0.000086 - 0.00286x + 0.0000149x^2) \qquad \text{III.9}$$

$$I_{max}(F) = 252.25 + 1.253x + 0.0140x^2 + r(25.17 - 0.095x - 0.0072x^2) + r^2(-2.61 + 0.0012x^2) \qquad \text{III.10}$$

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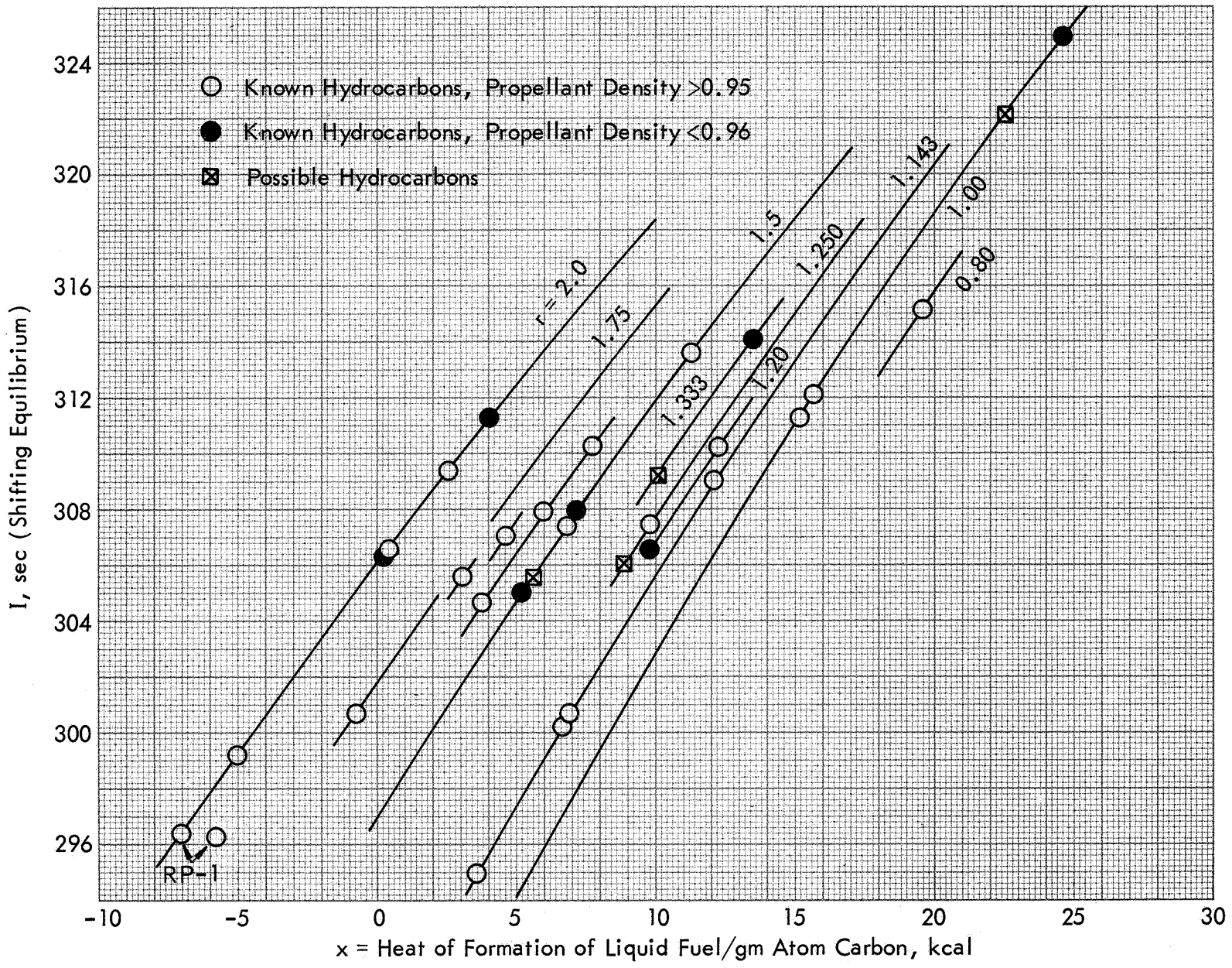


Figure 2. SPECIFIC IMPULSE vs x AT VARIOUS VALUES OF ATOM RATIO H/C = r
Stoichiometric, 1000 psia/atm

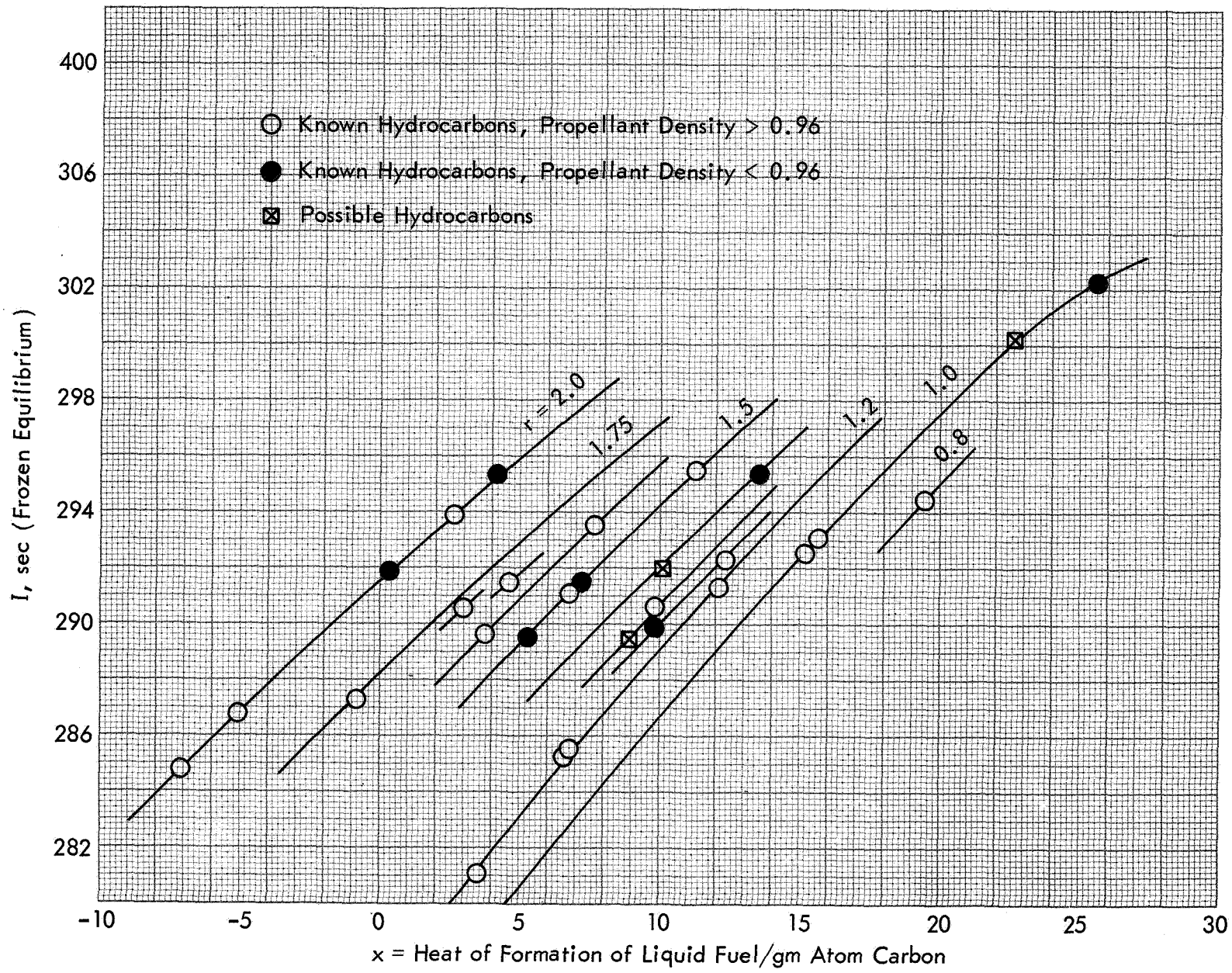


Figure 3. SPECIFIC IMPULSE vs x AT VARIOUS VALUES OF ATOM RATIO H/C = r
Stoichiometric

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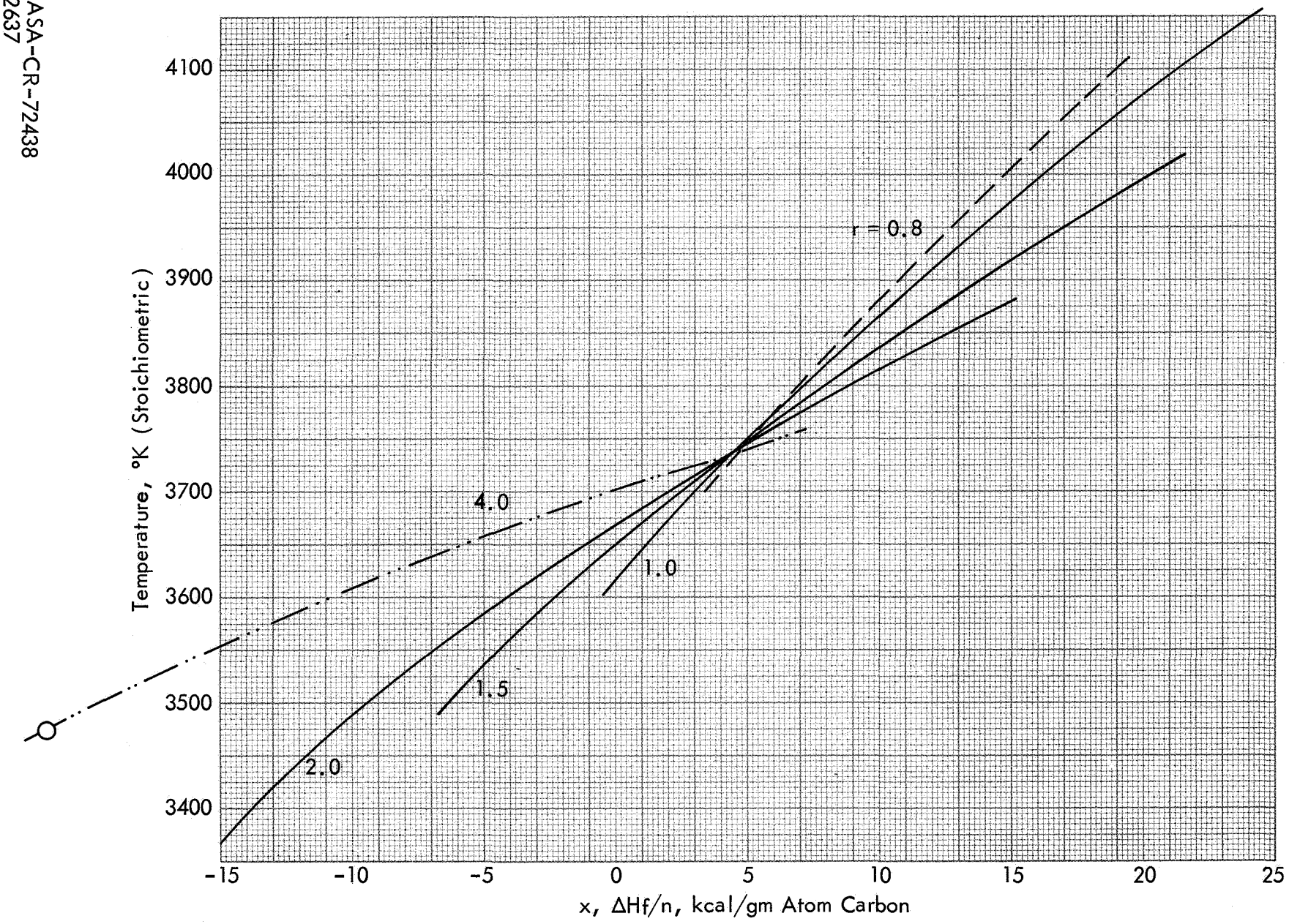


Figure 4. CHAMBER TEMPERATURE AS f(r,x) (STOICHIOMETRIC)
1000 psia/atm

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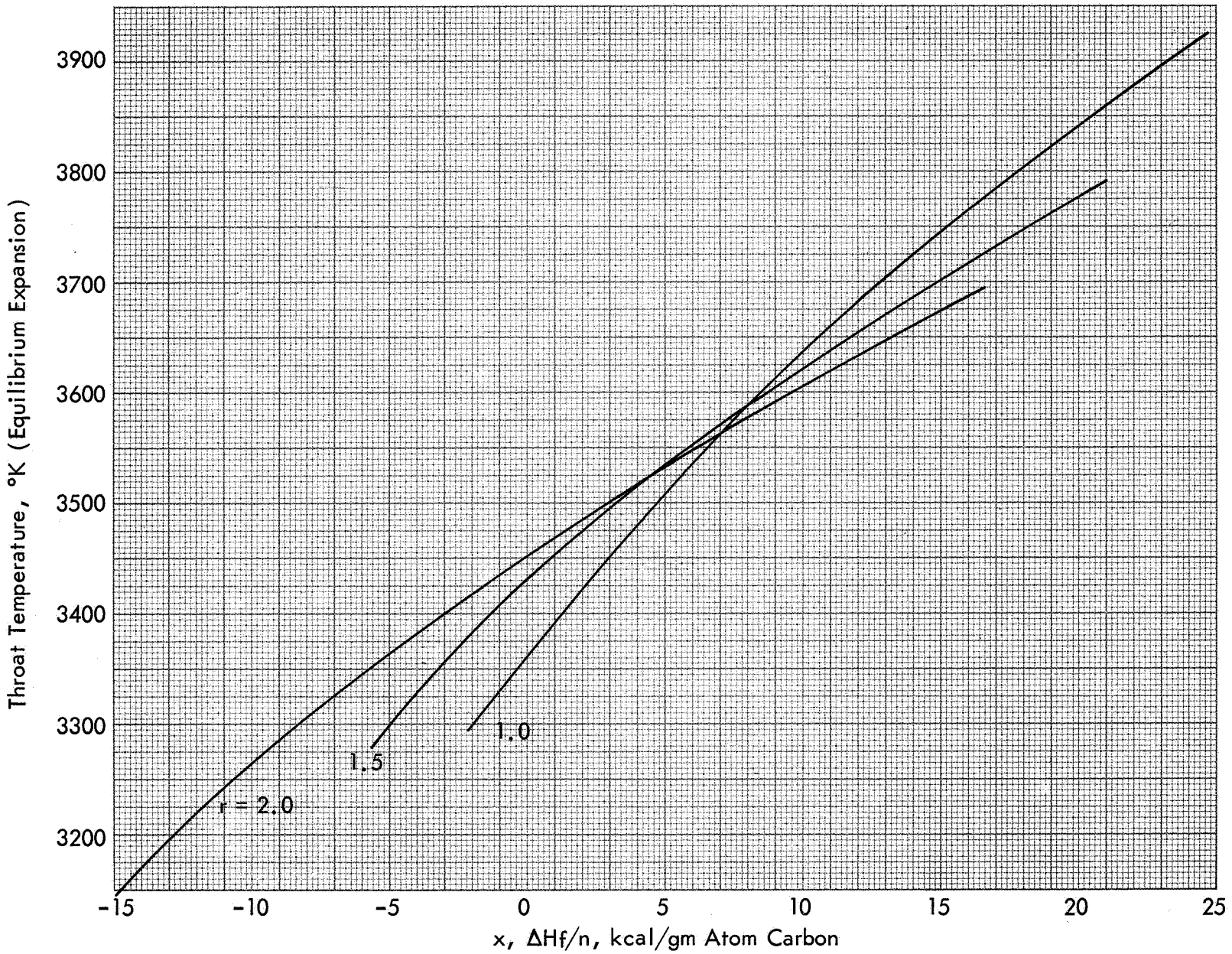


Figure 5. THROAT TEMPERATURE (STOICHIOMETRIC, EQUILIBRIUM EXPANSION) vs x FOR VARIOUS r
1000 psia/atm

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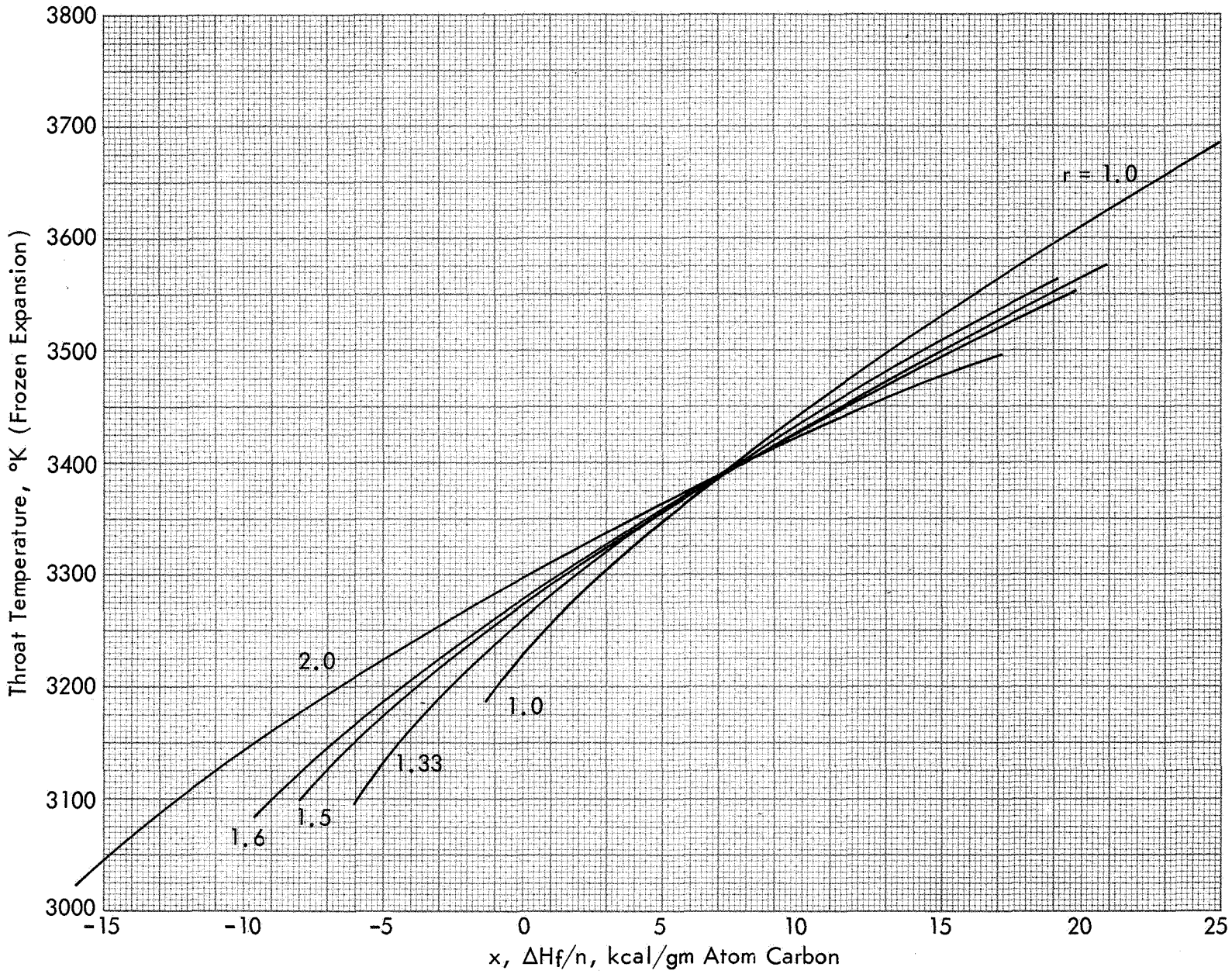


Figure 6. THROAT TEMPERATURE (STOICHIOMETRIC, FROZEN EQUILIBRIUM) vs x FOR VARIOUS r

1000 psia/atm

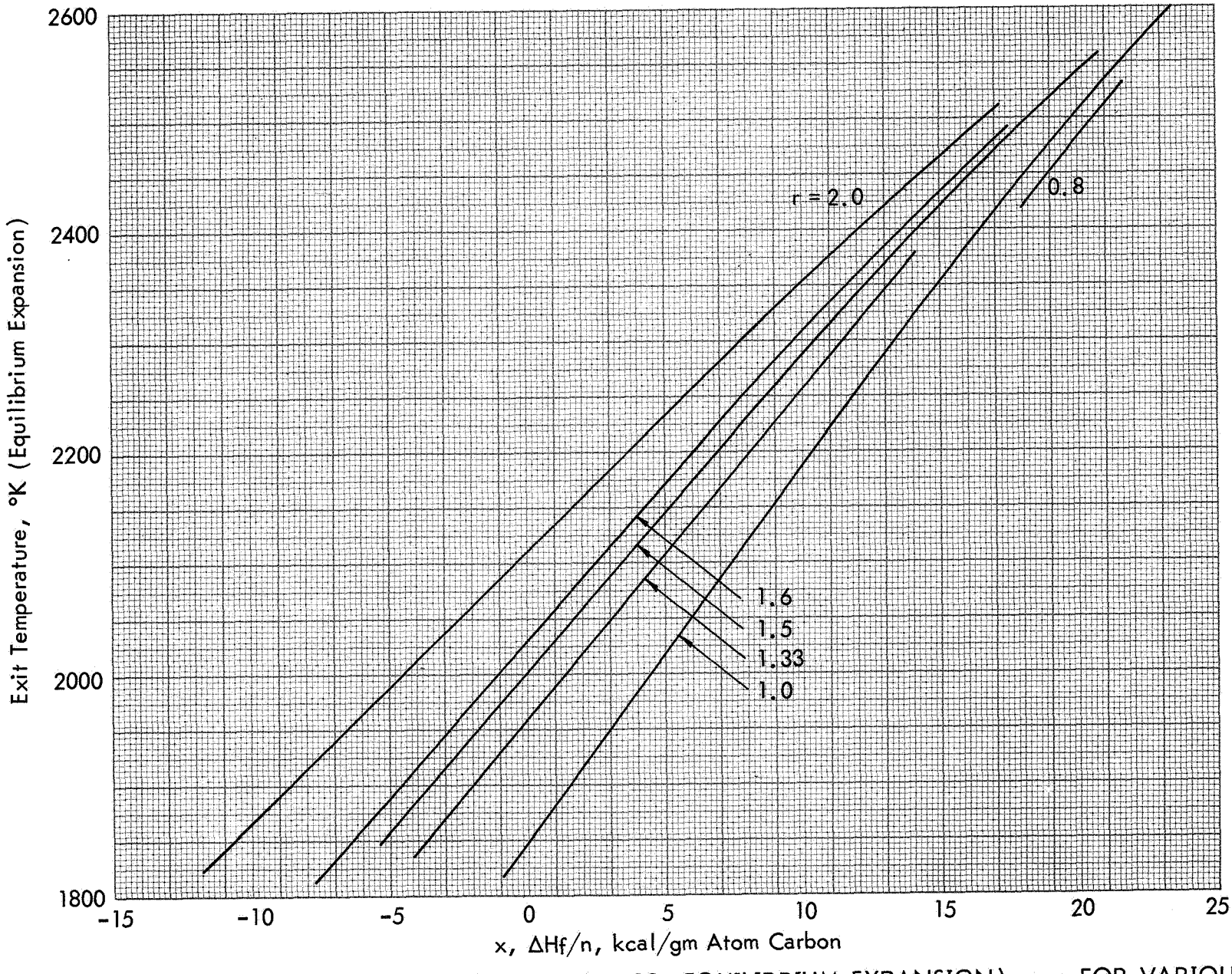


Figure 7. EXIT TEMPERATURE (STOICHIOMETRIC, EQUILIBRIUM EXPANSION) vs x FOR VARIOUS r

1000 psia/atm

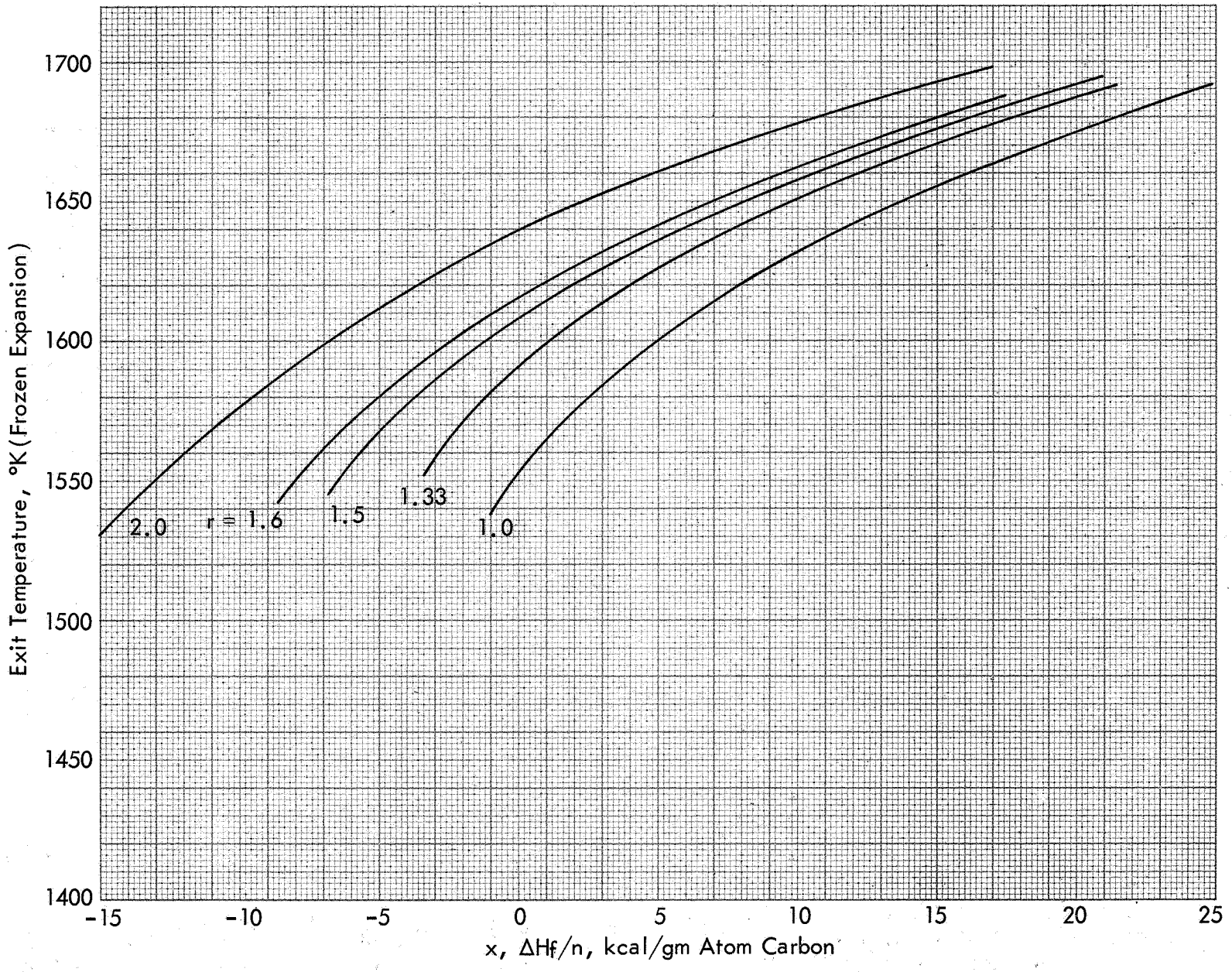


Figure 8. EXIT TEMPERATURE (STOICHIOMETRIC, FROZEN EQUILIBRIUM) vs x FOR VARIOUS r

1000 psia/atm

$$(O/F)_w[\text{at } I_{max}(F)] = 1.6955 - 0.02372x + 0.000016x^2 + r(0.3223 + 0.0000525x^2) + r^2(0.0551 - 0.000291x + 0.000043x^2) \quad 111.11$$

## F. Specific Impulse of Some Energetic Hydrocarbons With LOX

For the convenience of the reader, the more energetic hydrocarbons are listed in order of stoichiometric specific impulse (equilibrium expansion) in Table 5. Values of maximum specific impulse are also given. Many of the lighter hydrocarbons with a high specific impulse have too low a density to yield a high density impulse. Examples are acetylene, allene, methyl acetylene and ethylene. More significantly, these low fuel densities in combination with the relatively low H/C ratio result in low values for the oxygen/fuel volume ratio at the stoichiometric O/F weight ratio. The range of these effects is illustrated in Figure 9, where relative specific impulse at stoichiometric (ratio of I(E) to that of RP-1) is plotted against the volumetric O/F ratio. In Figure 10 the density-impulse product, $\bar{\rho}$ I(E), relative to that of RP-1 is plotted in the same way. The low O/F ratio of some of the low-density energetic fuels will increase the difficulty of adapting these fuels to an existing rocket engine; in addition, as discussed later, the low density of the fuel will tend to decrease the mass-flow rate of fuel that can be delivered to the engine by a power-limited centrifugal pump. This in turn will tend to raise the O/F weight ratio above the design value for RP-1.

### 1. Basis for Data in Tables 2 Through 5

In appraising the performance data presented above, one should bear in mind that many of the values used for the density and the heat of formation of the liquid hydrocarbons are estimates. In some cases two estimates are given, of which the second is a rough guess at a lower limit to the heat of formation on the basis of an estimate of the uncertainties involved. The methods used to estimate the heats of formation and the density are described in Appendix 2. Also listed in Appendix 2 are the references to the sources of experimental data used in constructing Tables 2 through 5.

## G. Performance of Hydrocarbon Blends

It may be desirable for a variety of reasons to use a mixture of two or more hydrocarbons rather than a single hydrocarbon as a fuel. For example, the use of a mixture may permit a compromise on fuel cost or an adjustment of the physical properties of the fuel. In addition, it may be desired to operate at close to the "stoichiometric" ratio of oxygen to fuel and yet to adjust the volumetric ratio of oxygen to fuel to a value close to that already chosen for RP-1. In this connection it is interesting to note that the value of $(O/F)_V$ at "stoichiometric" is higher for SHELLDYNE than for RP-1 but is lower for such high-impulse fuels as bicyclobutane, bicyclopentane and spiropentane. The condition that must be met to match a required value of $(O/F)_V$ with a mixture of two fuels at constant stoichometry is

$$(O/F) = x_1(O/F)_1 + (1 - x_1)(O/F)_2$$

Table 5. SPECIFIC IMPULSE VALUES FOR SOME ENERGETIC HYDROCARBONS

| Hydrocarbon | Formula | Calculated $I_{sp}$ With LOX,[a] sec | |
|---|---|---|---|
| | | Stoichiometric | Maximum |
| Tetrahedrane | $C_4H_4$ | 327-320 | 329-322 |
| Acetylene[b] | $C_2H_2$ | 324.9 | 326.2 |
| 1,4-Pentadiyne | $C_6H_6$ | 314.9 | 314.9 |
| Cubane | $C_8H_8$ | 314.8 | 314.8 |
| Allene[b] | $C_3H_4$ | 314.1 | 314.2 |
| Bicyclobutane[b] | $C_4H_6$ | 313.9 | 313.9 |
| Methylacetylene[b] | $C_3H_4$ | 313.2 | 313.2 |
| Methylcubane | $C_9H_{10}$ | 312.4 | 312.4 |
| 1,5-Hexadiyne | $C_6H_6$ | 311.4 | 311.5 |
| Ethylene[b] | $C_2H_4$ | 311.3 | 311.5 |
| Cyclopropylacetylene | $C_5H_6$ | 311.1 | 311.3 |
| Dimethylcubane | $C_{10}H_{12}$ | 310.7 | 310.8 |
| Spiro(2,2)pentane | $C_5H_8$ | 310.2 | 310.4 |
| Tricyclo(3,1,0,$0^{2,4}$)hexane | $C_6H_8$ | 309.1 | 309.4 |
| 1,6-Heptadiyne | $C_7H_8$ | 309.1 | 309.4 |
| Cyclopropane[b] | $C_3H_6$ | 308.9 | 309.4 |
| Dimethylacetylene | $C_4H_6$ | 307.9 | 308.3 |
| Dispiro(2,1,2,1)octane | $C_8H_{12}$ | 307.9 | 308.3 |
| Bicyclo(2,1,0)pentane | $C_5H_8$ | 307.9 | 308.3 |
| 1,7-Octadiyne | $C_8H_{10}$ | 307.5 | 308.0 |
| Spiro(3,2)hexane | $C_6H_{10}$ | 307.4 | 307.9 |
| Dicyclopropylacetylene | $C_8H_{10}$ | 307.3 | 307.8 |
| 1-Methyltricyclo(3,1,0,$0^{2,4}$)-hexane | $C_7H_{10}$ | 307.0 | 307.6 |
| Cyclobutene[b] | $C_4H_6$ | 306.8 | 307.3 |
| Cyclopropylcyclopropane | $C_6H_{10}$ | 306.4 | 307.1 |
| Cyclobutane[b] | $C_4H_8$ | 306.3 | 307.2 |
| Methylenecyclobutane | $C_5H_8$ | 306.0 | 306.7 |
| RP-1 | | 296.3 | 299.7 |

a) Calculated for Shifting Equilibrium, expansion 1000 psia/atm.
b) For liquid fuel at boiling point.

## KEY TO FIGURES 9 AND 10

1. Spiro(4,3)octane
2. Quadricyclene
3. Dispiro(3,1,3,1)decane
4. Dispiro(2,1,2,1)octane
5. Tricyclo(3,1,0,$0^{2,4}$)hexane
6. Dicyclopropylacetylene
7. Spiro(3,2)hexane
8. Cyclopropylcyclopropane
9. Bicyclo(2,1,0)pentane
10. 1,7 Octadiyne
11. Spiro(2,2)pentane
12. Bicyclo(1,1,0)butane
13. Cyclopropylacetylene
14. Isopropenylacetylene
15. Methylacetylene
16. Allene

S SHELLDYNE

 Figures 9 and 10 follow

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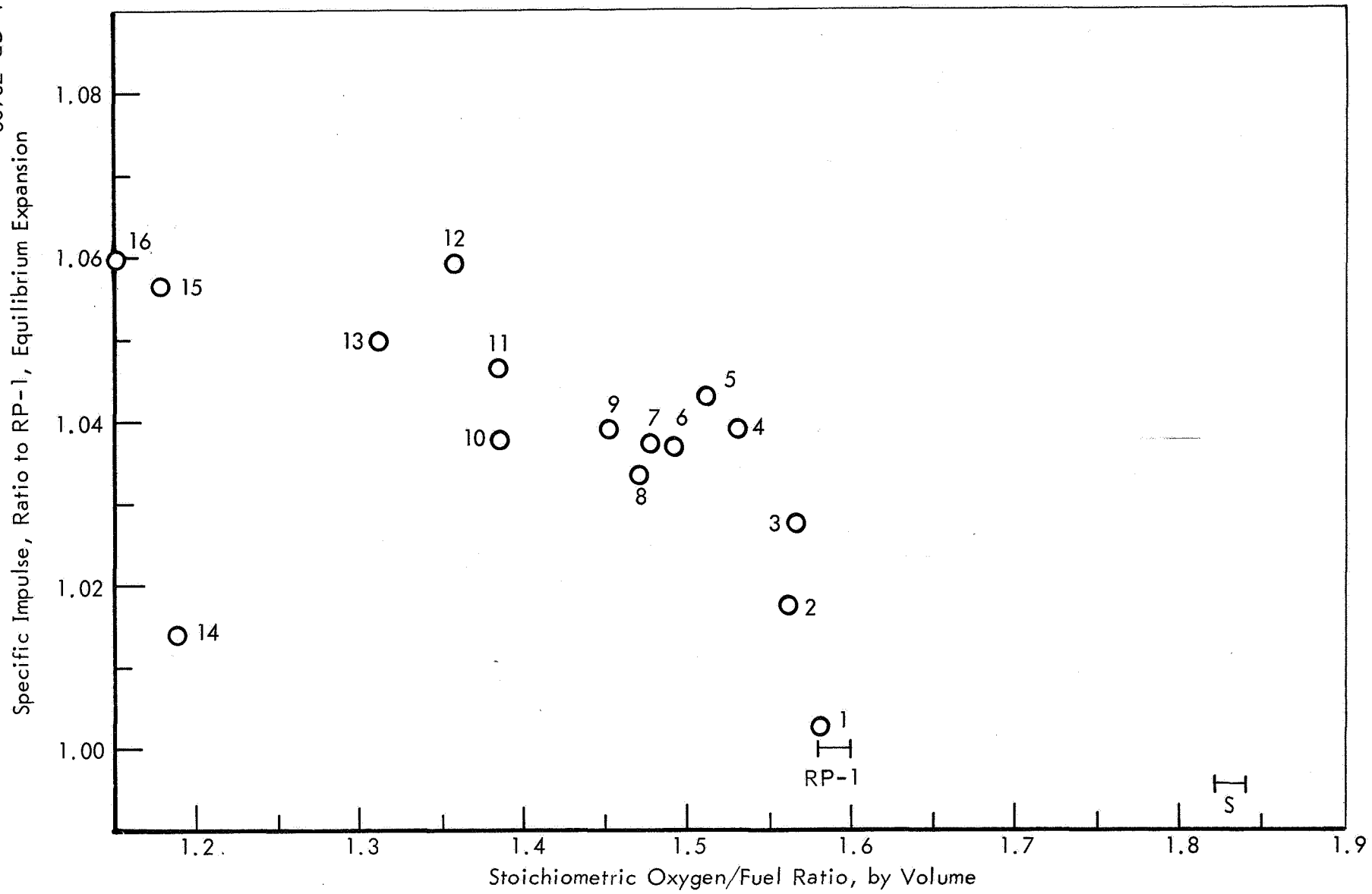


Figure 9. RATIO OF STOICHIOMETRIC SPECIFIC IMPULSE, I(E), TO THAT OF RP-1 vs STOICHIOMETRIC OXYGEN/FUEL VOLUME RATIO

1000 psia/atm

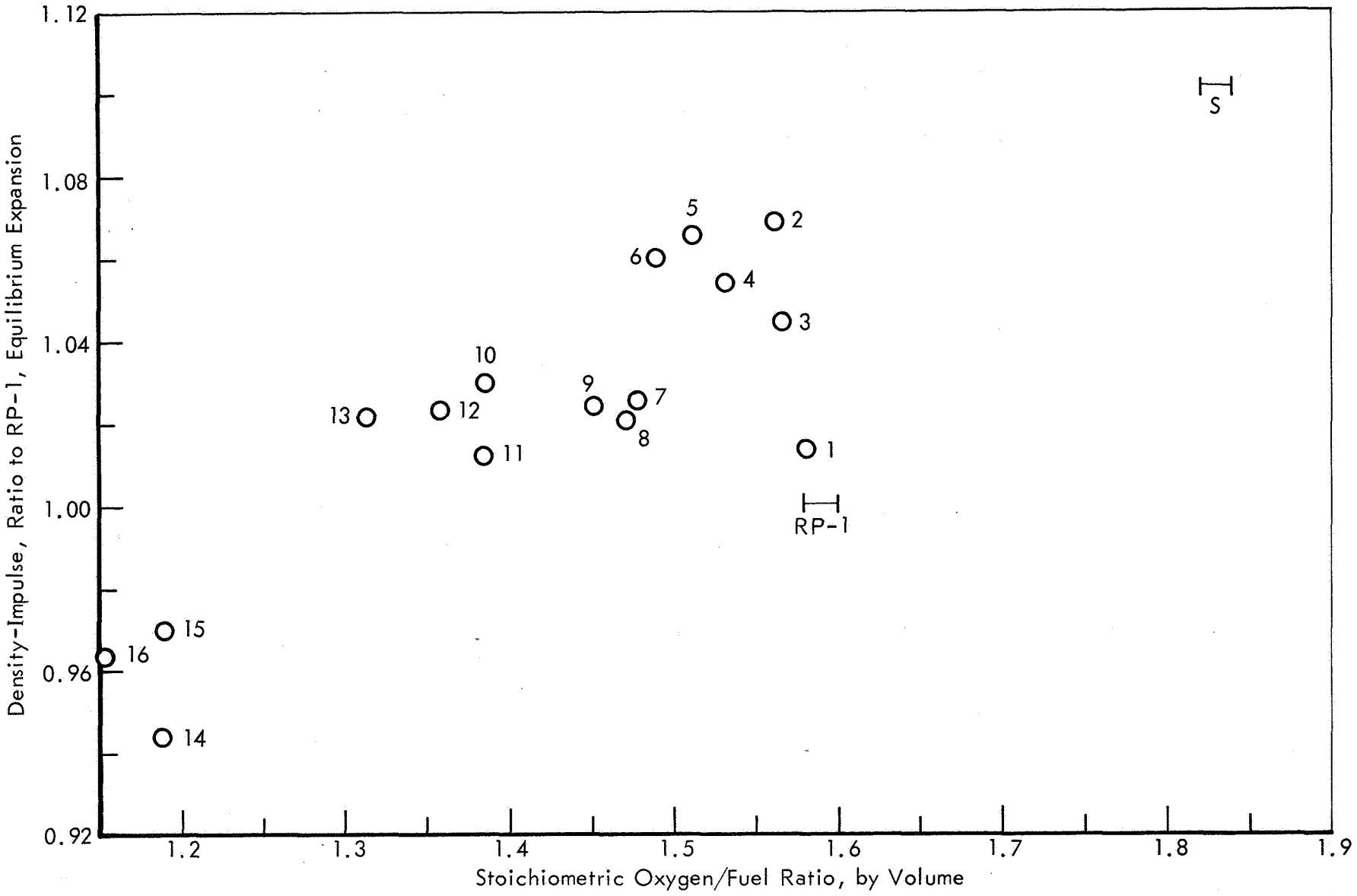


Figure 10. RATIO OF STOICHIOMETRIC DENSITY-IMPULSE, $\bar{\rho}\, I(E)$, TO THAT OF RP-1 vs STOICHIOMETRIC OXYGEN/FUEL VOLUME RATIO
1000 psia/atm

where $x_1$ is the volume fraction of fuel 1 in the blend and $(O/F)_1$ is its oxygen/fuel ratio at the desired stoichiometry. Thus to match $(O/F)_V = 1.58$ as for RP-1 at "stoichiometric" with blends of SHELLDYNE (1.822) and bicyclopentane (1.452) or spiropentane (1.385) would require volume fractions of 0.65 bicyclopentane or 0.55 spiropentane in the blended fuel, on the basis of assuming no change in volume on mixing.

For the reasons given above, we have calculated the performance of some blends of SHELLDYNE with the low-density high-impulse fuels bicyclobutane or bicyclopentane. The calculations were made with the assumption, which is certainly not precise, that the fuels mix without change in volume. For "stoichiometric" conditions, the calculations were made by means of equations III. 1-7; for maximum impulse conditions they were made by means of equations III. 8-11.

The results are given in Table 6; some of them are displayed in Figures 11 and 12. As shown in Figure 11, the blending law for specific impulse displays a slight positive deviation from linearity whereas that for density-impulse (Figure 12) shows a slight negative deviation. A merit index of the form $I^n \bar{\rho}$, with n greater than unity, would therefore be expected to exhibit a still more nearly linear blending behavior. As we shall see in the next section, however, a single merit index of this kind is not adequate to assess the merit of an unusual hydrocarbon fuel as a replacement for RP-1; the density of the fuel itself and the oxygen/fuel ratio for combustion must also be taken into account.

## H. References for Section III


1) NASA Technical Note D-1454(1962) and D-1737(1963) by S. Gordon and F.J. Zeleznik, Lewis Research Center: "A General IBM 707 or 7090 Computer Program for Chemical Equilibrium Compositions, Rocket Performance and Chapman-Jougouet Detonations."





Table 6 and Figures 11 and 12 follow

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# Table 6. PROPELLANT PERFORMANCE PARAMETERS FOR HYDROCARBON MIXTURES

| SHELLDYNE, %w | At Stoichiometric Oxygen/Fuel | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ρ | r | x | Btu/lb | Btu/gal | O/F wt | O/F Vol | $\bar{\rho}$ | I (E) | $\bar{\rho}$I (E) | I (F) | $\bar{\rho}$I (F) | BLI (E), % | BLI (F), % | MI (E), % | MI (F), % |
| 100 | 1.0900 | 1.143 | 3.546 | 17,860 | 162,500 | 1.910 | 1.822 | 1.1240 | 295.0 | 331.6 | 281.7 | 316.6 | 10.3 | 9.0 | 10.7 | 10.0 |
| 90 | 1.049 | 1.187 | 3.780 | 18,010 | 157,700 | 1.931 | 1.773 | 1.1088 | 296.4 | 328.7 | 282.8 | 313.6 | 9.8 | 8.3 | 9.7 | 8.9 |
| 80 | 1.011 | 1.232 | 4.016 | 18,150 | 153,200 | 1.951 | 1.727 | 1.0944 | 297.8 | 325.9 | 283.9 | 310.7 | 9.3 | 7.6 | 8.8 | 7.9 |
| 70 | 0.976 | 1.277 | 4.253 | 18,300 | 149,000 | 1.971 | 1.684 | 1.0805 | 299.2 | 323.3 | 285.0 | 307.9 | 8.8 | 7.0 | 7.9 | 7.0 |
| 60 | 0.943 | 1.322 | 4.492 | 18,450 | 145,200 | 1.992 | 1.644 | 1.0671 | 300.5 | 320.7 | 286.0 | 305.2 | 8.4 | 6.4 | 7.1 | 6.3 |
| 50 | 0.912 | 1.368 | 4.732 | 18,590 | 141,600 | 2.012 | 1.606 | 1.0542 | 301.8 | 318.2 | 287.0 | 302.6 | 8.0 | 5.9 | 6.2 | 5.1 |
| 40 | 0.884 | 1.413 | 4.975 | 18,740 | 138,200 | 2.032 | 1.572 | 1.0418 | 303.1 | 315.8 | 288.0 | 300.1 | 7.6 | 5.3 | 5.4 | 4.3 |
| 30 | 0.857 | 1.460 | 5.200 | 18,890 | 135,000 | 2.053 | 1.539 | 1.0299 | 304.3 | 313.4 | 289.0 | 297.7 | 7.3 | 4.9 | 4.6 | 3.4 |
| 20 | 0.831 | 1.5060 | 5.464 | 19,030 | 132,000 | 2.073 | 1.508 | 1.0184 | 305.5 | 311.1 | 290.0 | 295.3 | 6.9 | 4.4 | 3.9 | 2.6 |
| 10 | 0.807 | 1.553 | 5.711 | 19,180 | 129,200 | 2.0936 | 1.479 | 1.0073 | 306.7 | 308.9 | 290.9 | 293.0 | 6.6 | 4.0 | 3.1 | 1.8 |
| Bicyclo(2,1,0)pentane 0 | 0.7846 | 1.600 | 5.960 | 19,320 | 126,500 | 2.114 | 1.452 | 0.9965 | 307.9 | 306.8 | 291.8 | 290.8 | 6.4 | 3.5 | 2.4 | 1.0 |

| SHELLDYNE, %w | At Maximum Impulse | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Equilibrium Expansion | | | | | Frozen Expansion | | | | |
| | O/F wt | O/F Vol | $\bar{\rho}$ | $I_{max}$ (E) | $\bar{\rho}_x$I | O/F wt | O/F Vol | $\bar{\rho}$ | $I_{max}$ (F) | $\bar{\rho}_x$I (F) |
| 100 | 2.183 | 2.083 | 1.126 | 298.0 | 335.4 | 1.928 | 1.839 | 1.124 | 281.8 | 316.7 |
| 90 | 2.189 | 2.010 | 1.112 | 299.2 | 332.7 | 1.930 | 1.772 | 1.109 | 282.6 | 313.4 |
| 80 | 2.194 | 1.942 | 1.098 | 300.5 | 329.9 | 1.931 | 1.709 | 1.094 | 283.5 | 310.1 |
| 70 | 2.198 | 1.878 | 1.085 | 301.8 | 327.5 | 1.932 | 1.651 | 1.080 | 284.5 | 307.3 |
| 60 | 2.203 | 1.819 | 1.072 | 303.0 | 324.8 | 1.933 | 1.596 | 1.066 | 285.7 | 304.6 |
| 50 | 2.208= | 1.763 | 1.059 | 304.0 | 321.9 | 1.935 | 1.545 | 1.052 | 287.0 | 301.9 |
| 40 | 2.212 | 1.711 | 1.047 | 305.0 | 319.3 | 1.935 | 1.497 | 1.039 | 288.3 | 299.5 |
| 30 | 2.217 | 1.662 | 1.035 | 305.8 | 316.5 | 1.936 | 1.452 | 1.026 | 289.5 | 297.0 |
| 20 | 2.221 | 1.616 | 1.024 | 306.7 | 314.1 | 1.937 | 1.409 | 1.013 | 290.7 | 294.5 |
| 10 | 2.225 | 1.572 | 1.012 | 307.5 | 311.2 | 1.937 | 1.369 | 1.001 | 291.8 | 292.1 |
| Bicyclo(2,1,0)pentane 0 | 2.230 | 1.531 | 1.001 | 308.3 | 308.6 | 1.938 | 1.331 | 0.989 | 292.6 | 289.4 |

| SHELLDYNE, %w | At Stoichiometric Oxygen/Fuel | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ρ | r | x | Btu/lb | Btu/gal | O/F wt | O/F Vol | $\bar{\rho}$ | I (E) | $\bar{\rho}$I (E) | I (F) | $\bar{\rho}$I (F) | BLI (E), % | BLI (F), % | MI (E), % | MI (F), % |
| 100 | 1.090 | 1.143 | 3.546 | 17,860 | 162,500 | 1.910 | 1.822 | 1.124 | 295.0 | 331.6 | 281.7 | 316.6 | 10.3 | 9.0 | 10.7 | 10.0 |
| 90 | 1.043 | 1.178 | 4.323 | 18,060 | 157,100 | 1.926 | 1.758 | 1.106 | 297.2 | 328.7 | 283.3 | 313.4 | 10.0 | 8.4 | 9.8 | 8.9 |
| 80 | 0.999 | 1.213 | 5.103 | 18,250 | 152,200 | 1.942 | 1.699 | 1.090 | 299.2 | 326.0 | 284.8 | 310.3 | 9.7 | 7.8 | 8.8 | 7.8 |
| 70 | 0.960 | 1.248 | 5.888 | 18,450 | 147,700 | 1.958 | 1.645 | 1.074 | 301.3 | 323.3 | 286.3 | 307.3 | 9.5 | 7.2 | 7.9 | 6.8 |
| 60 | 0.923 | 1.283 | 6.677 | 18,650 | 143,600 | 1.974 | 1.595 | 1.058 | 303.2 | 320.7 | 287.8 | 304.4 | 9.3 | 6.7 | 7.1 | 5.7 |
| 50 | 0.889 | 1.319 | 7.470 | 18,840 | 139,700 | 1.990 | 1.548 | 1.043 | 305.1 | 318.2 | 289.1 | 301.6 | 9.1 | 6.3 | 6.2 | 4.8 |
| 40 | 0.857 | 1.355 | 8.267 | 19,040 | 136,100 | 2.006 | 1.505 | 1.029 | 307.0 | 315.7 | 290.6 | 298.8 | 8.9 | 5.8 | 5.4 | 3.8 |
| 30 | 0.827 | 1.391 | 9.069 | 19,230 | 132,800 | 2.022 | 1.465 | 1.015 | 308.8 | 313.3 | 291.9 | 296.1 | 8.8 | 5.4 | 4.6 | 2.9 |
| 20 | 0.800 | 1.427 | 9.875 | 19,430 | 129,700 | 2.039 | 1.427 | 1.001 | 310.6 | 311.0 | 293.2 | 293.6 | 8.7 | 5.0 | 3.8 | 2.0 |
| 10 | 0.774 | 1.463 | 10.685 | 19,620 | 126,800 | 2.055 | 1.392 | 0.989 | 312.3 | 308.7 | 294.5 | 291.1 | 8.5 | 4.6 | 3.1 | 1.1 |
| Bicyclo(1,1,0)butane 0 | 0.750 | 1.500 | 11.500 | 19,820 | 124,000 | 2.071 | 1.359 | 0.976 | 313.9 | 306.4 | 295.8 | 288.7 | 8.41 | 4.3 | 2.3 | 0.3 |

| SHELLDYNE, %w | At Maximum Impulse | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Equilibrium Expansion | | | | | Frozen Expansion | | | | |
| | O/F wt | O/F Vol | $\bar{\rho}$ | $I_{max}$ (E) | $\bar{\rho}_x$I | O/F wt | O/F Vol | $\bar{\rho}$ | $I_{max}$ (F) | $\bar{\rho}_x$I |
| 100 | 2.183 | 2.083 | 1.126 | 298.0 | 335.4 | 1.928 | 1.839 | 1.124 | 281.8 | 316.7 |
| 90 | 2.173 | 1.984 | 1.109 | 299.6 | 332.3 | 1.915 | 1.748 | 1.106 | 283.3 | 313.3 |
| 80 | 2.163 | 1.892 | 1.093 | 301.2 | 329.2 | 1.902 | 1.664 | 1.089 | 284.8 | 310.1 |
| 70 | 2.153 | 1.808 | 1.077 | 303.0 | 326.3 | 1.889 | 1.587 | 1.072 | 286.4 | 307.0 |
| 60 | 2.142 | 1.730 | 1.062 | 304.8 | 323.7 | 1.876 | 1.515 | 1.055 | 288.0 | 303.8 |
| 50 | 2.131 | 1.658 | 1.047 | 306.6 | 321.0 | 1.862 | 1.449 | 1.039 | 289.8 | 301.1 |
| 40 | 2.121 | 1.591 | 1.032 | 308.3 | 318.2 | 1.849 | 1.387 | 1.023 | 291.4 | 298.1 |
| 30 | 2.110 | 1.528 | 1.018 | 309.8 | 315.4 | 1.835 | 1.329 | 1.007 | 292.9 | 295.0 |
| 20 | 2.099 | 1.469 | 1.004 | 311.3 | 312.5 | 1.821 | 1.275 | 0.992 | 294.4 | 292.0 |
| 10 | 2.087 | 1.414 | 0.990 | 312.7 | 309.6 | 1.807 | 1.224 | 0.977 | 295.8 | 289.0 |
| Bicyclo(1,1,0)butane 0 | 2.076 | 1.363 | 0.976 | 314.0 | 306.6 | 1.793 | 1.177 | 0.962 | 297.1 | 285.9 |

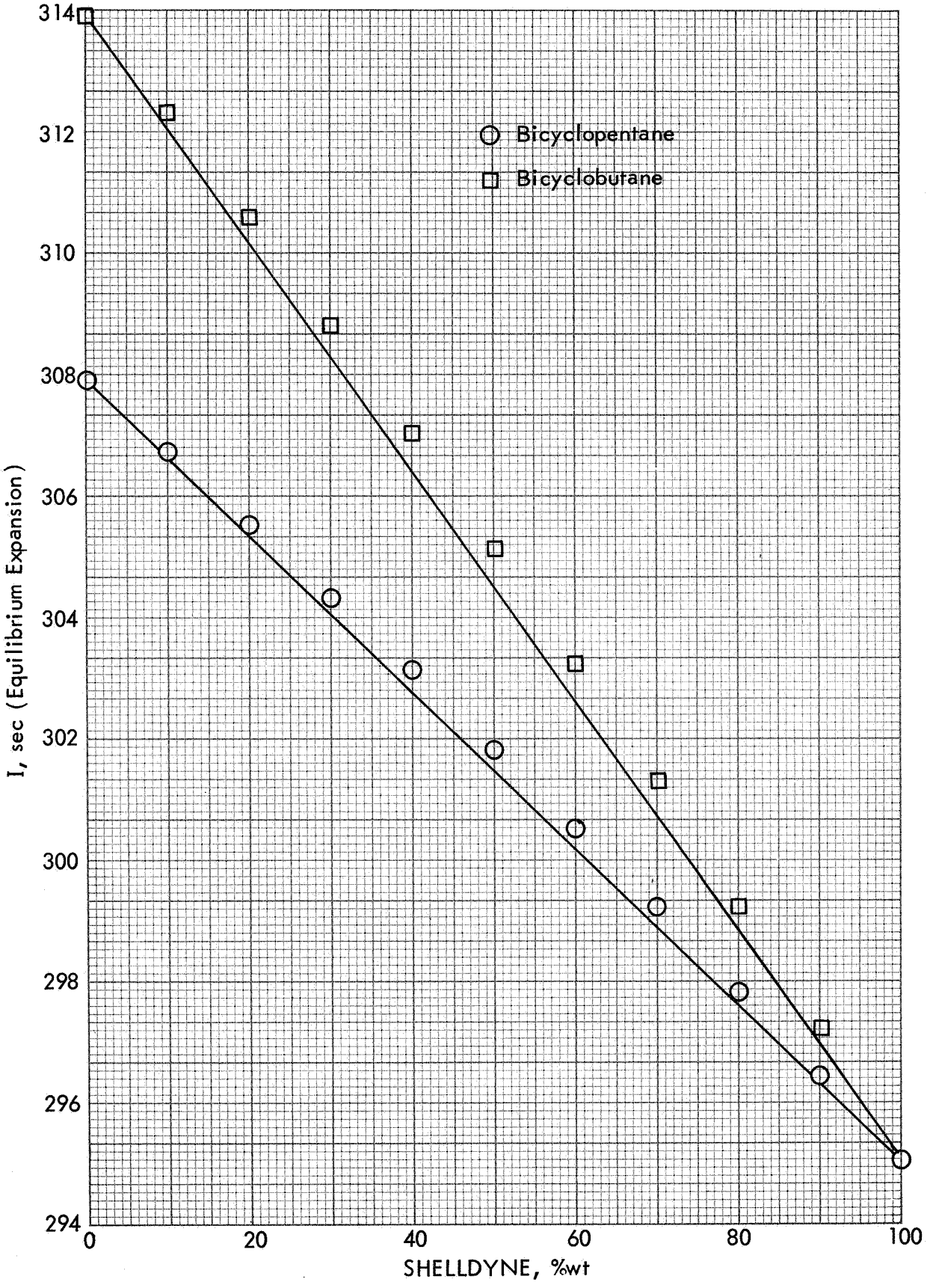


Figure 11. SPECIFIC IMPULSE OF BLENDS OF SHELLDYNE
1000 psia/atm

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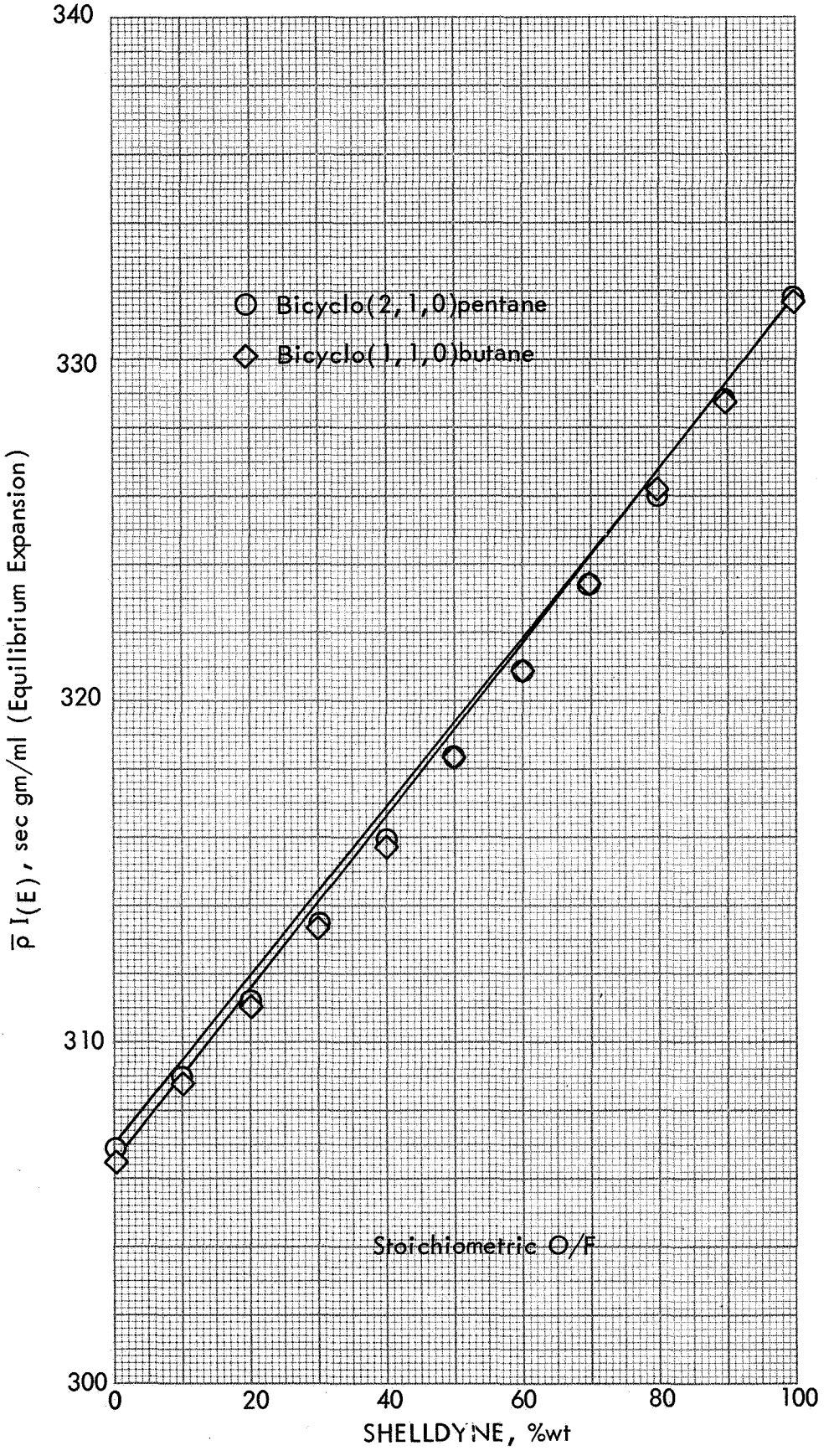


Figure 12. DENSITY-IMPULSE OF MIXTURES OF SHELLDYNE AND BICYCLOBUTANE OR BICYCLOPENTANE

1000 psia/atm

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## SECTION IV

## PERFORMANCE PROPERTIES OF SOME CANDIDATE ROCKET FUELS

### A. Specific Impulse Curves for Some Candidate Fuels

Specific impulse I(E) for equilibrium expansion, 1000 psia/1 atm, is shown in Figure 13 as a function of oxygen/fuel weight ratio, $(O/F)_W$, for the energetic fuels bicyclobutane, bicyclo(2,1,0)pentane, spiropentane, 1,5-hexadiyne and 1,7-octadiyne in comparison with the standard fuel RP-1 and the dense fuel SHELLDYNE. Also shown by means of an arrow on each curve is the O/F ratio for "stoichiometric" combustion. Similar plots against the volumetric ratio, $(O/F)_V$, are shown in Figure 14. Curves of this kind for all the hydrocarbons considered are collected in Appendix 1, including both frozen and equilibrium expansion calculations.

### B. Problems in the Application of Specialized Hydrocarbon Fuels to Existing Booster Rockets: Effects of H/C Ratio and of Density

A major problem in the utilization of a new hydrocarbon fuel in an existing booster rocket engine is that the design of the engine is tailored to the properties of the standard kerosene fuel, RP-1. A new fuel, with different density, vapor pressure and viscosity from RP-1 will behave differently in the pumps, flow channels and heat-exchanger sections of the engine. In addition, if it differs in composition from RP-1, as in general it will, it will have to be burned at a different oxygen/fuel ratio from that used with RP-1. A detailed consideration of the influence of the physical properties of the fuel on its pumping and flow behavior is beyond the scope of this report. Some qualitative considerations of the general trends to be expected are offered below.

The major basic problem in the use of high-energy hydrocarbons in existing rocket engines is posed by the fact that, with the exception of cyclopropane, cyclobutane and the mono-olefins, all of these hydrocarbons have a lower hydrogen/carbon atom ratio r than does RP-1. When this is the case, the stoichiometric oxygen/fuel weight ratio will be lower than it is for RP-1, in accordance with the equation

$$(O/F)_W \text{ (stoich)} = \frac{1.333 + 0.667r}{1 + 0.0840r} \qquad \text{IV.1}$$

This means that if the pumping rate of fuel in pounds/sec is held constant, the pumping rate of oxygen will have to be decreased. As a consequence, the mass-flow rate of propellant will decrease and this will result in a decreased thrust that will partially or may even completely eliminate the advantage of higher specific impulse. This effect can be compensated, of course, by increasing the mass-flow of fuel, but the possibility for doing this by minor alterations of the plumbing is limited; a more substantial increase in the mass-flow of fuel would require a more powerful or a supplementary fuel pump.

 Figures 13 and 14 follow

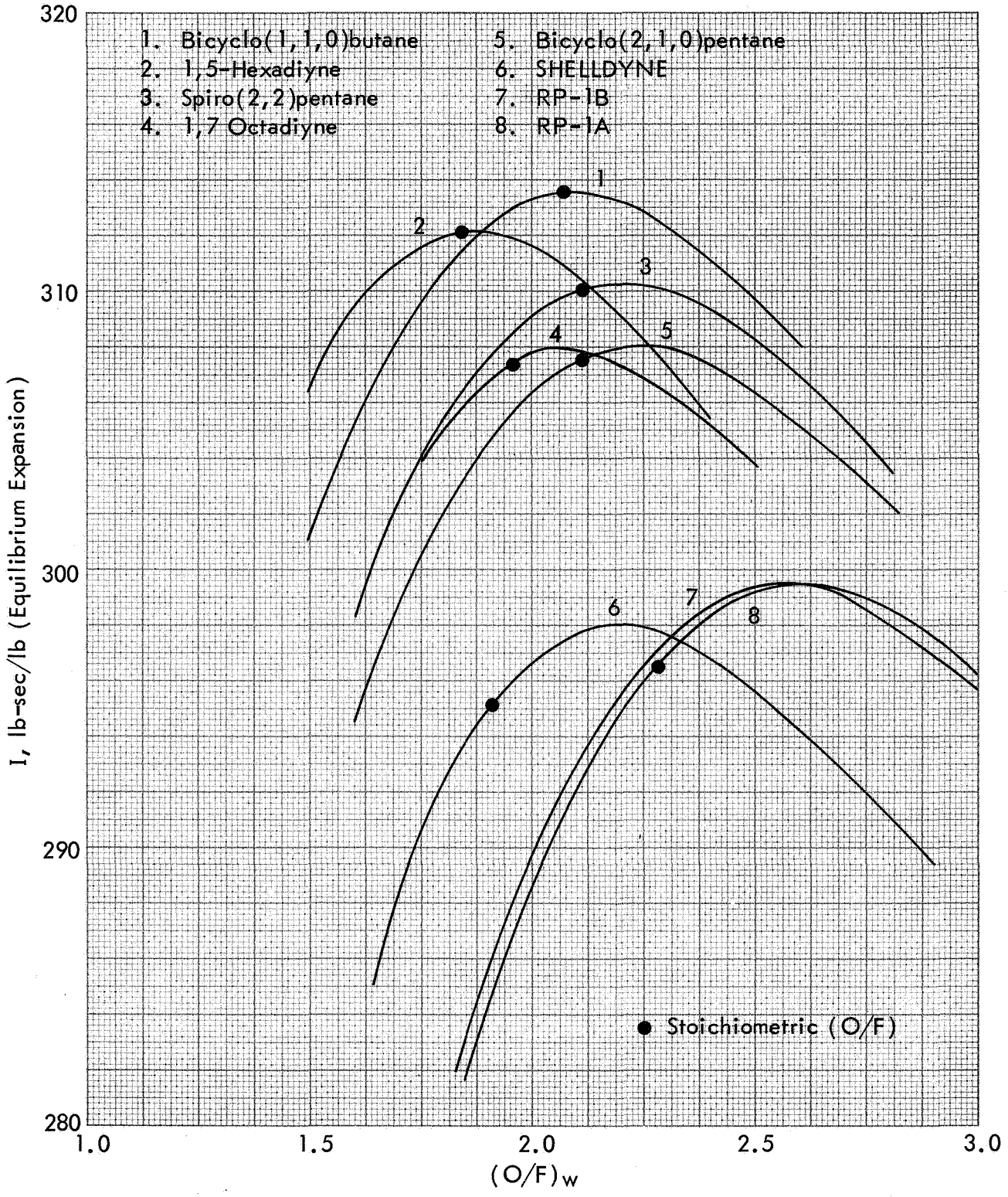


Figure 13. SPECIFIC IMPULSE vs $(O/F)_W$ FOR SOME CANDIDATE FUELS
1000 psia/atm

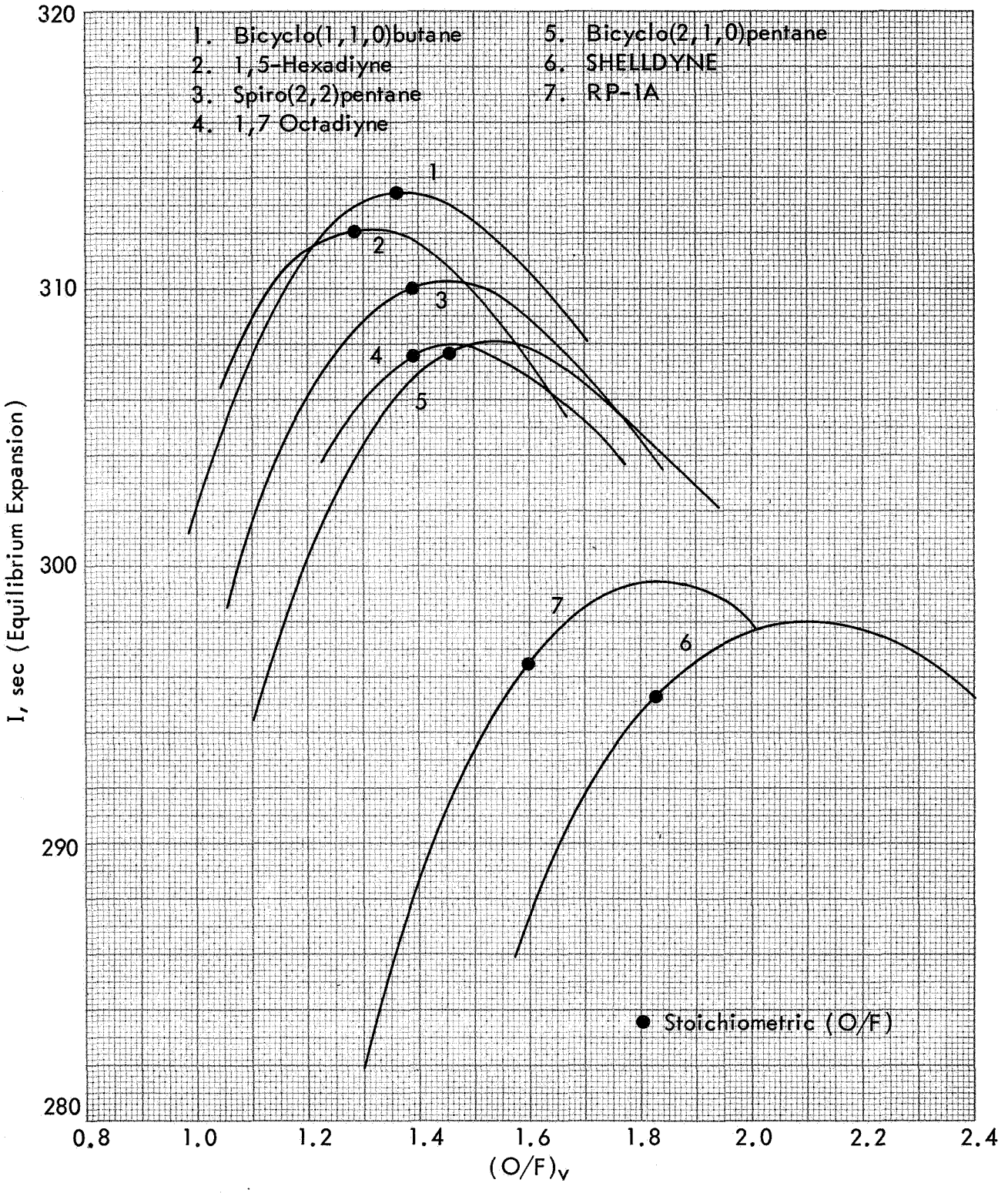


Figure 14. SPECIFIC IMPULSE vs $(O/F)_V$ FOR SOME CANDIDATE FUELS
1000 psia/atm

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The magnitude of these effects of the H/C ratio is illustrated in Table 7a, relative to an RP-1 with H/C equal to 1.90.

Table 7a. EFFECT OF H/C RATIO ON STOICHIOMETRIC OXYGEN/FUEL RATIO AND ON MASS-FLOW RATES

| H/C Ratio, r | 1.00 | 1.25 | 1.50 | 1.60 | 1.75 | 1.90 | 2.00 |
|---|---|---|---|---|---|---|---|
| $(O/F)_W$ | 1.845 | 1.961 | 2.072 | 2.117 | 2.180 | 2.242 | 2.283 |
| Relative $\dot{m}$ at constant $\dot{F}$ a) | 0.8775 | 0.9133 | 0.9337 | 0.9614 | 0.9809 | 1.000 | 1.0126 |
| Relative $\dot{m}$ at constant $\dot{O}$ b) | 1.066 | 1.0442 | 1.0253 | 1.0183 | 1.0087 | 1.000 | 0.9945 |
| Relative $\dot{F}$ at constant $\dot{O}$ c) | 1.215 | 1.143 | 1.0821 | 1.0592 | 1.0285 | 1.000 | 0.9821 |
| Relative $\dot{F}$ at constant $\dot{m}$ d) | 1.140 | 1.095 | 1.0554 | 1.040 | 1.0195 | 1.000 | 0.9875 |

a) Relative mass-flow of propellant at constant mass-flow of fuel.
b) Relative mass-flow of propellant at constant mass-flow of oxygen.
c) Relative mass-flow of fuel at constant mass-flow of oxygen.
d) Relative mass-flow of fuel at constant mass-flow of propellant.

It will be observed that if the H/C ratio does not fall below 1.5, only a relatively modest increase in the mass-flow of fuel is required to maintain constant mass-flow of propellant.

The problem discussed above will be aggravated if the fuel not only has a lower H/C ratio than does RP-1 but also has a lower density. This is so because the mass-flow of fuel in the highly turbulent flow regimes of a rocket engine will be determined primarily by the density of the fuel and will not be very sensitive to the viscosity.

If the hardware, power available for pumping fuel and pump efficiency are held constant, the mass-flow rate of fuel can be expected to vary approximately as $\rho_e^{2/3}$, where $\rho_e$ is the effective density of the fuel. The effective density will be a suitably weighted average over the path of the fuel from pump to nozzle, taking account of the variations in pressure and temperature along that path. Thus, if no changes are made in hardware, the oxygen/fuel weight ratio, $(O/F)_W$, will be changed from that used with the reference fuel (density $\rho_o$) in the ratio $(\rho_o/\rho_e)^{2/3}$. For most of the high-energy fuels, the density $\rho$ is less than that of RP-1; thus the $(O/F)_W$ ratio delivered by the unaltered engine will tend to be higher with the specialty fuel than with the standard RP-1. On the other hand, as we have just seen, the stoichiometric O/F mass ratio for most of these fuels is less than that of RP-1.

The magnitude of these effects is illustrated in Table 7b where we have compared the stoichiometric $(O/F)_W$ for various candidate fuels with the quantity $2.24\ (0.803/\rho)^{2/3}$. This comparison is based on an assumed value of 2.24 for the stoichiometric O/F ratio and 0.803 for the density of RP-1; slightly different values would characterize an RP-1 for which H/C were closer to 2.0. The densities $\rho$ of the fuels have not been corrected for the effects of temperature and pressure in the engine, since the calculation is

in any case an approximate one. The figures in the last column of the table show that in order to achieve a stoichiometric O/F ratio, the "natural" flow rate of fuel will require an enhancement that ranges from 4% for dispirodecane to 25% for 1,5-hexadiyne. Only for the dense fuel SHELLDYNE, which delivers a relatively low specific impulse, is there an indication that the flow of fuel might require throttling; this might be provided automatically by the relatively high viscosity of this fuel.

One possible measure to increase the mass flow of fuel is to increase its density by blending with a dense component such as the hydrogenated such as SHELLDYNE-H.

Table 7b. COMPARISON OF STOICHIOMETRIC OXYGEN/FUEL MASS RATIOS WITH THOSE ESTIMATED FOR DENSITY-LIMITED MASS-FLOW OF FUEL

| Fuel | Density $\rho$ gm/ml | O/F Mass Ratios | | Ratio | $\left(\frac{\rho}{\rho_o}\right)^{2/3}$ |
|---|---|---|---|---|---|
| | | Stoichiometric | $1.94/\rho^{2/3}$ | | |
| Bicyclo(1,1,0)butane | 0.750 | 2.071 | 2.35 | 1.14 | 0.956 |
| Bicyclo(2,1,0)pentane | 0.785 | 2.114 | 2.28 | 1.08 | 0.985 |
| Spiro(2,2)pentane | 0.749 | 2.114 | 2.35 | 1.12 | 0.955 |
| 1,5-Hexadiyne | 0.794 | 1.844 | 2.27 | 1.23 | 0.993 |
| 1,7-Octadiyne | 0.808 | 1.959 | 2.23 | 1.14 | 1.004 |
| SHELLDYNE-H | 1.09 | 1.977 | 1.83 | 0.927 | 1.227 |
| Dispiro(3,1,3,1)decane | 0.847 | 2.114 | 2.17 | 1.03 | 1.036 |
| Dispiro(2,1,2,1)octane | 0.846 | 2.071 | 2.17 | 1.05 | 1.036 |
| RP-1 | 0.803 | 2.24 | 2.24 | 1.00 | 1.000 |

Though the use of such a blend would decrease the specific impulse attainable from the propellant, this loss in performance would be compensated, at least partially, by an increase in the attainable mass-flow of propellant.

## C. Effects of Fuel on Thrust and Payload

We shall assume that to provide adequate stability during lift-off, the thrust generated by a booster must exceed the weight to be lifted by at least 20%. Thus we define the maximum mass M that can be lifted by $\dot{m}I = 1.20\ M$, where $\dot{m}$ is the mass-flow rate of the propellant. The mass M consists of the burnout mass $M_o$, plus the initial mass $V_o\bar{\rho}$ of propellant, where $V_o$ is the initial volume of propellant. Thus the maximum burnout mass that can be achieved under these conditions is

$$M_o = \dot{m}I/1.20 - V_o\bar{\rho} \qquad \text{IV.2}$$

When the fuel is changed, all of the parameters in this equation, $\dot{m}$, I, $V_o$ and $\bar{\rho}$ may change also.

In order to make our examples more specific, we will choose as our base case stoichiometric operation with RP-1, with I at its calculated equilibrium expansion value of 296.3 sec. We take $\dot{m}_o$ = 5000 lb/sec, and a

burnout time of 150 sec. Thus $V_o\bar{\rho} = 7.5 \times 10^5$ lb and the propellant tankage $V_o = 7.4 \times 10^5$ lb ml/gm. Then the maximum burnout mass $M_o$ is $4.85 \times 10^5$ lb.

For comparison of the potential performance of the special fuels with that of RP-1 we have based our calculations on the calculated specific impulse I(E) for equilibrium expansion at the stoichiometric O/F ratio; this choice is based on the concept that the hydrodynamic inefficiencies and the departures from equilibrium during expansion are likely to be similar for all of these hydrocarbons, so that relative values based on calculated values of I(E) should not be too greatly in error. We have not only compared the relative values of the burnout mass $M_o$ that can be accelerated under the lift-off requirements described above, but have also compared idealized values of the velocity $v_b$ attained at burnout of the booster. These idealized values of $v_b$ were calculated for vertical flight through a frictionless atmosphere at a constant pressure and constant mass-flow $\dot{m}$ of propellant; no allowance was made for change of specific impulse with altitude. Under these conditions the equation for $v_b$ is well known to be

$$v_b/g = I \ln_e (1 + V_o\bar{\rho}/M_o) - V_o\bar{\rho}/\dot{m} \qquad \text{IV.3}$$

We first compare relative performance at the same mass-flow rate of propellant for all fuels. As discussed above, this requires that the mass-flow of fuel is greater for a hydrogen-deficient fuel than for RP-1. Assuming that this can be achieved, the results are presented in Table 8. The first two columns show the stoichiometric propellant densities and calculated values of I(E). The third column shows the factor by which the mass-flow of fuel must be increased to achieve constant $\dot{m}$ while maintaining the stoichiometric O/F ratio. The fourth column shows the ratio $(\rho/\rho_o)^{2/3}$, where $\rho_o$ is the density of RP-1; this factor is a measure of the tendency of the mass-flow of the fuel to fall below that of RP-1 at constant pumping power and flow geometry. The fifth column shows the ratio of the entries in the preceding two columns; it presents an approximate measure of the difficulty of achieving constant mass-flow of propellant.

The sixth column shows the relative maximum burnout masses that can be lifted by the various fuels under the restrictions of the assumed criterion for guidance stability; the seventh column shows the corresponding idealized velocity $v_b$ achieved at burnout. For the eighth column we have assumed that a constant $v_b$ is required; this can be achieved by decreasing the burnout $M_o$. The column shows the relative values of $M_o$ calculated under this constraint.

Of the fuels considered in Table 8, the easiest to adapt in terms of fuel flow to a rocket engine designed to burn RP-1 are dispirodecane, which has been synthesized, and dispirooctane, which has not. The latter is estimated to provide a potential increase in $M_o$ of 7.5% at maximum lift and 6% at constant burnout velocity. The highest potential performance is provided by bicyclobutane, with an increase in $M_o$ of 20% at maximum lift and nearly 8% at constant burnout velocity. This hydrocarbon is difficult to prepare, however, and also, because of its low density and relatively low boiling point, may be less easily adapted to an existing engine. Of the

Table 8. RELATIVE PERFORMANCE OF SOME ENERGETIC HYDROCARBON FUELS AT CONSTANT MASS-FLOW RATE OF PROPELLANT

| Fuel | $\bar{\rho}$, g/ml | I(E) sec | Rel $\dot{F}$ a) | $(\rho/\rho_o)^{2/3}$ | $F(\rho_o/\rho)^{2/3}$ | Max Lift | | Rel $v_b$ = 1 Rel $M_o$ d) |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Rel $M_o$ b) | Rel $v_b$ c) | |
| Bicyclo(1,1,0)butane | 0.976 | 313.9 | 1.055 | 0.956 | 1.103 | 1.203 | 0.870 | 1.079 |
| Bicyclo(2,1,0)pentane | 0.997 | 307.9 | 1.040 | 0.985 | 1.055 | 1.117 | 0.934 | 1.052 |
| Spiro(2,2)pentane | 0.977 | 310.2 | 1.040 | 0.955 | 1.090 | 1.170 | 0.883 | 1.059 |
| 1,5-Hexadiyne | 0.990 | 311.4 | 1.140 | 0.993 | 1.149 | 1.162 | 0.899 | 1.070 |
| 1,7-Octadiyne | 1.002 | 307.5 | 1.095 | 1.004 | 1.090 | 1.108 | 0.941 | 1.053 |
| Dispiro(3,1,3,1)octane | 1.026 | 307.9 | 1.055 | 1.036 | 1.019 | 1.075 | 0.987 | 1.062 |
| Dispiro(2,1,2,1)decane | 1.027 | 304 | 1.040 | 1.036 | 1.005 | 1.045 | 0.995 | 1.042 |
| RP-1 | 1.012 | 296.3 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| SHELLDYNE | 1.124 | 295.0 | 1.12 | 1.227 | 0.915 | 0.817 | 1.285 | ----- |

a) Relative mass-flow of fuel required to maintain constant mass-flow of propellant at stoichiometric O/F.
b) Relative burnout mass under conditions of maximum lift-off weight.
c) Relative (idealized) burnout velocity under conditions of maximum lift-off weight.
d) Relative burnout mass if (idealized) burnout velocity is held constant.

energetic hydrocarbon whose chemistry of preparation is well enough known to provide a basis for the development of a production process, spiropentane and 1,7-octadiyne present intermediate gains in $M_o$ and intermediate problems of adaptability.

Many other modes of operation can of course be considered. One possibility is to leave the fuel-pumping system unchanged, and to compensate for the lower mass-flow of fuel by throttling the mass-flow of oxygen to achieve a stoichiometric O/F ratio. We have made calculations for this case also, assuming that the mass-flow of fuel was proportional to the 2/3 power of its density. In this case, with the propellant tankage full and partitioned in accordance with the stoichiometric O/F ratio, we found a very small increase in $M_o$ was predicted for dispirooctane but a decrease for all other fuels. Another alternative was to leave the fuel and oxygen tankage unchanged from present design and to fill the fuel tank completely but only part-fill the oxygen tank in order to maintain the O/F ratio. This procedure results in a decrease of the total mass of propellant available for acceleration. With this option, increases in $M_o$ were predicted to be 6% for bicyclobutane, 5% for bicyclopentane, 7% for spiropentane, 5% for dispirooctane, 2% for dispirodecane and zero or negative for the other fuels of Table 8. These gains in $M_o$ were accompanied in most cases by decreases in the burnout velocity $v_b$: 12% for bicyclobutane, 7% for bicyclopentane, 13% for spiropentane, and 2% for dispirooctane; a gain of 1% was calculated for dispirodecane. We conclude that if increased payload is to be achieved by the use of these energetic hydrocarbons, means must be found for enhancing the mass-flow of fuel through the engine.

## SECTION V

## PHYSICAL PROPERTIES OF SOME CANDIDATE FUELS

### A. Methods of Estimation

Some physical properties that are relevant to considerations of fluid flow and heat transfer have been estimated or assembled from the literature for six energetic hydrocarbons, SHELLDYNE and the reference fuel RP-1. For RP-1, values for the thermal conductivity and specific heat were taken in part from a report by Pratt and Whitney[a)] and in part from computer estimates as described later. Representative densities and viscosities at several temperatures were taken from various sources for RP-1 and extrapolated to cover the indicated temperature range. The heat capacity of spiropentane up to 560°R was taken from the results of a study of the thermodynamic properties of that substance by D. W. Scott et al[2)] and was extrapolated to higher temperatures. For the terminal diacetylenes, use was made of various literature data as follows:

Density and refractive index data for several diynes have been measured by Henne and Greenlee[3)] and by Hayman and Weiss;[4)] these values are shown in Table 9 together with our own estimates of the most likely values on the basis of correlations between molecular volume and the number of $CH_2$ groups in this series of compounds. The refractive indices given by Hayman and Weiss may be too low by 0.0003 since the value they report for benzene is low by that amount and a similar difference occurs between their value for the nonadiyne and that given by Henne and Greenlee. The latter authors purified their samples very carefully; their data for the heptadiyne are preferred for that reason.

Table 9a. SOME PROPERTIES OF THE LINEAR TERMINAL DIACETYLENES

Our estimates in parentheses.

| Compound | $T_B$, °C | $\rho$ (20°C), g/ml | Ref | $\rho$ (25°C), g/ml | $n_P$, 20°C | R, cc/mole | $V_M^{20}$, cc/mole |
|---|---|---|---|---|---|---|---|
| 1,4-Pentadiyne | 55 | (0.787) | (c) | (0.782) | | | |
| 1,5-Hexadiyne | 88 | 0.8000 | (a) | (0.795) | 1.4378 | 17.546 | 97.64 |
| | | (0.799) | (c) | (0.794) | (1.4381) | (17.60) | (97.8) |
| 1,6-Heptadiyne | 111.5 | 0.8051 | (b) | | 1.4423 | 20.723 | 114.43 |
| | | 0.8046 | (a) | | 1.4410 | | |
| | | 0.8051 | (c) | (0.800) | | | |
| 1,7-Octadiyne | 139 | 0.8123 | (a) | (0.808) | 1.4462 | | 130.69 |
| | | | (c) | | (1.4465) | 23.853 | |
| 1,8-Nonadiyne | 162.0 | 0.8158 | (b) | (0.813) | 1.4490 | 27.010 | 147.3 |
| | | 0.8158 | (a) | | 1.4487 | | |

a) H. J. H. Hayman and S. Weiss, J. Chem. Phys. 42, 3701 (1965).
b) A. Henne and K. W. Greenlee, J. Am. Chem. Soc. 67, 484 (1945).
c) Value chosen for this work.

a) See references at end of this section.

Kinematic viscosities for 1,6-heptadiyne over the temperature range -69 to 22°F have been reported by Happel and Marsel.[5] In order to extrapolate these data to other members of the series we obtained a laboratory sample of 1,7-octadiyne from Farchan Research Laboratories. The sample as received was a water-white liquid with a slightly unpleasant odor; its density as measured here at 25.0°C was 0.8211 g/ml and kinematic viscosities at 25°C and 50°C, respectively, were 1.323 and 0.898 centistokes. The high density suggested that the sample was impure; a rough distillation through a vigreux column yielded 4 fractions plus a low-boiling fraction (ca 6%) and a high-boiling bottoms fraction (ca 12%). No attempt was made to exclude oxygen during the distillation. The boiling liquid was observed to develop a yellow color which deepened to orange as the bottoms became concentrated. It is likely that some polymerization occurred during the distillation. The volatile fractions were water-white and had the odor of the original samples. Densities of the fractions collected were measured with the following results.

Fraction 1 (24%): $T_B$ 135.5-136.5°C; ρ (25°) 0.813 g/ml

Fraction 2 (23%): $T_B$ 136.5-137.0; ρ (25°) 0.814

Fraction 3 (20%): $T_B$ 137.0-137.5; ρ (25°) 0.817

Fraction 4 (14%): $T_B$ 137.5-139; ρ (25°) 0.822

The thermal expansion coefficient of fraction 2 was found to be approximately 1.1(3) x $10^{-3}$ between 25° and 35°C. This value was used, with literature densities at 20°C, to obtain the density at 25°C in Table 6; the estimates of ρ (25°) for the other diynes were made by an empirical correlation between boiling point and fractional change in density using this datum and data for monoacetylenes cited in the reports of API Project 44.

It is clear that our sample of the octadiyne contained an impurity with a higher density and a slightly lower volatility than that of the pure material. In view of the limited scope of this contract, the nature of this impurity was not investigated further; from its properties and the probable method of preparation, it is very probably 6-bromohexyne-1. The viscosities given for the terminal diynes in this section are based on the information assembled above together with empirical regularities observed in homologous series of other linear hydrocarbons. It is not likely that the viscosity of the octadiyne was changed grossly by the small amount of impurity present.

The properties given for SHELLDYNE are based on proprietary information. The remaining properties given in this section are estimates made on the basis of molecular structure and boiling point; the estimates were made by means of a computer program developed locally in which the correlations are based on the law of corresponding states and a local modification of a computer program developed by the American Institute of Chemical Engineers. These estimates were in some cases by comparison with experimental data for homologous series of hydrocarbons with related structures. The resulting data are of limited reliability, especially for dynamic properties such as thermal conductivity and viscosity.

## B. Data

Estimated values in engineering units for the viscosity at saturation pressure and for the density, specific heat and thermal conductivity at 1000 psia are shown in the following figures for the liquids as a function of temperature. Bicyclobutane and bicyclopentane are compared with RP-1 in Figure 15; similar comparisons are made for the terminal diacetylenes in Figure 16 and for spiropentane and SHELLDYNE in Figure 17.

Numerical values are given in Tables 10 to 16 for the molecular weight, freezing and boiling points, critical constants (estimates) and estimated values for the viscosity, heat of vaporization, vapor pressure and surface tension over a range of temperatures at saturation pressures. It should be re-emphasized that these values are estimates; if a serious interest develops in their accurate knowledge, they will need to be determined experimentally.

It would have been desirable to make estimates also for dispiro-octane and dispirodecane, but interest in these compounds developed too late in the course of this work.

### Table 9b. SOME ESTIMATED PROPERTIES OF LIQUID RP-1

Liquid at Saturation Pressure

| | | | |
|---|---|---|---|
| Molecular Weight: | 170 | Critical Temp, °F: | 622 (760)[a] |
| Freezing Point, °F: | -52 | | |
| Boiling Point, °F: | 417 | Critical Pressure, psia: | 301 (315)[a] |
| | | Critical Volume, $ft^3/lb$: | 0.0620 (0.060)[a] |

| Temp, °F | Viscosity, lb(mass)/ft hr | Heat of Vaporization Btu/lb | Vapor Pressure, psia | Surface Tension, poundal/ft |
|---|---|---|---|---|
| 0 | 15 | 163.3 | 0.00 | 0.092 |
| 40 | 7.4 | 159.2 | 0.002 | 0.085 |
| 80 | 4.1(5) | 155.0 | 0.007 | 0.078 |
| 160 | 2.00 | 145.8 | 0.080 | 0.064 |
| 240 | 1.20 | 135.7 | 0.562 | 0.051 |
| 320 | 0.80 | 124.1 | 2.83 | 0.038 |
| 400 | 0.56 | 110 | 11.2 | 0.026 |
| 440 | 0.47 | 102 | 20.9 | 0.020 |
| 480 | 0.39 | 93 | 37.6 | 0.015 |
| 560 | 0.28 | 68 | 117 | 0.006 |

a) Alternative literature data or estimates.



Figures 15 through 17 follow

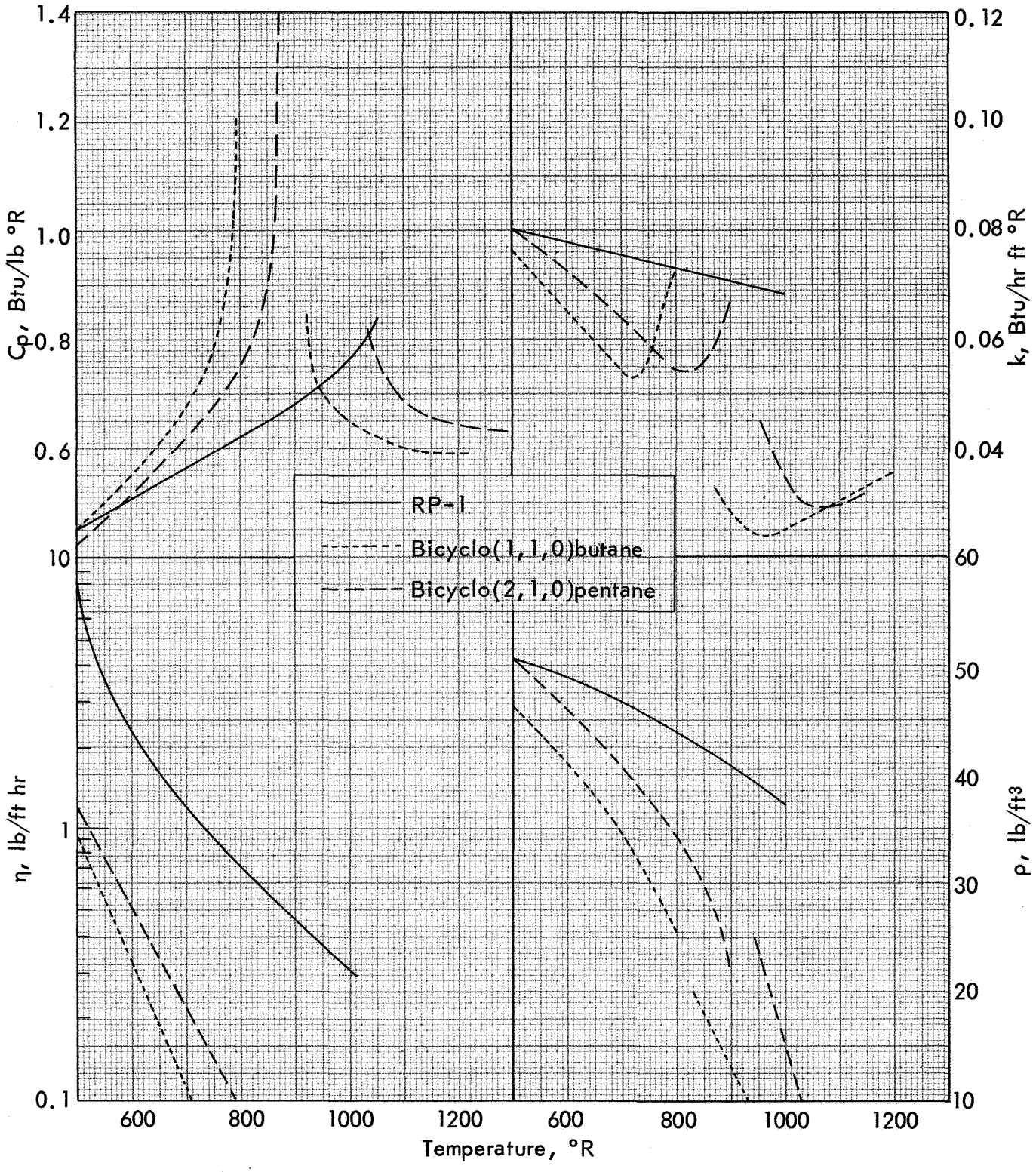


Figure 15. SOME ESTIMATED PROPERTIES OF RP-1 AND POLYCYCLANES

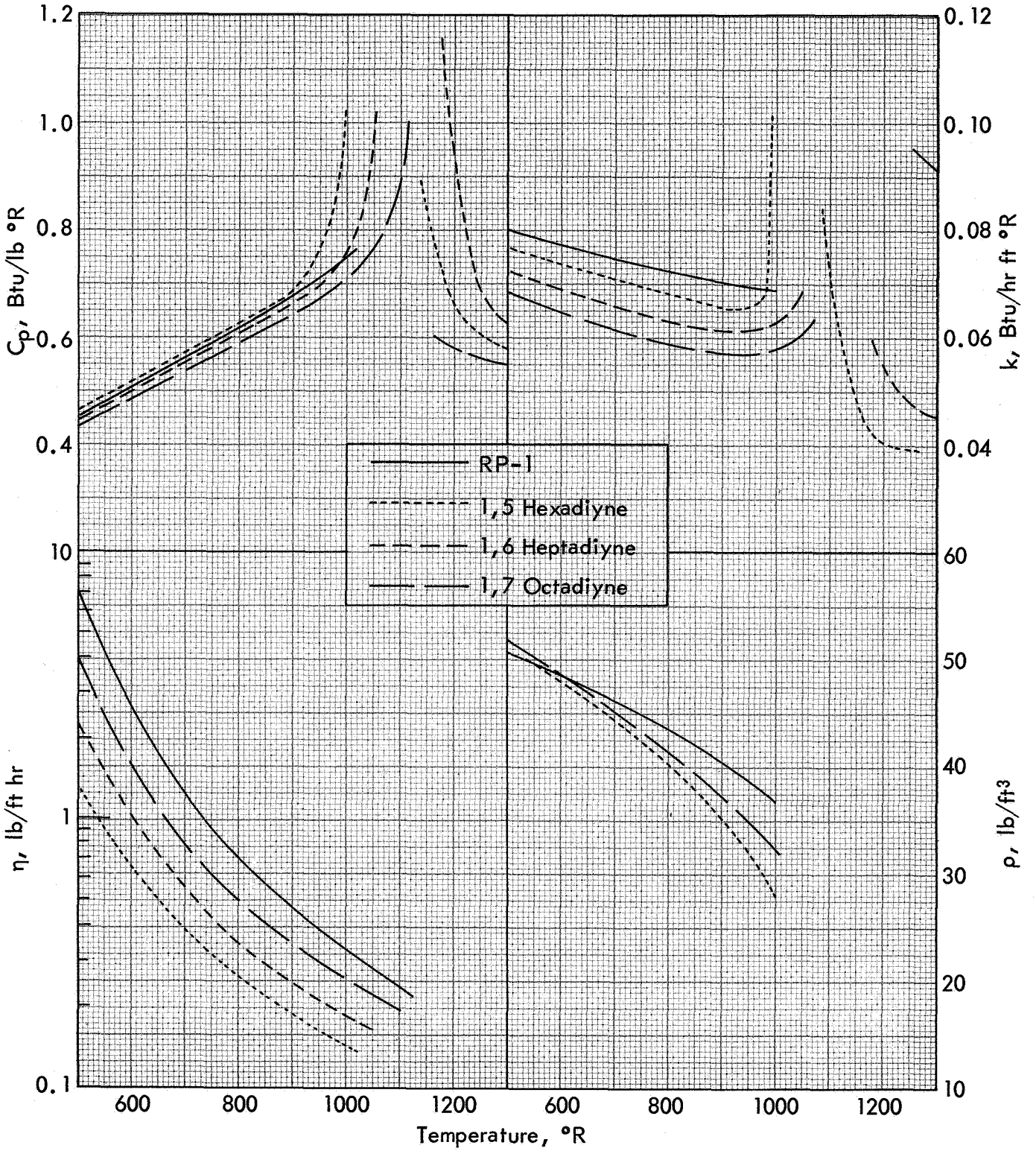


Figure 16. SOME ESTIMATED PROPERTIES OF RP-1 AND TERMINAL DIYNES

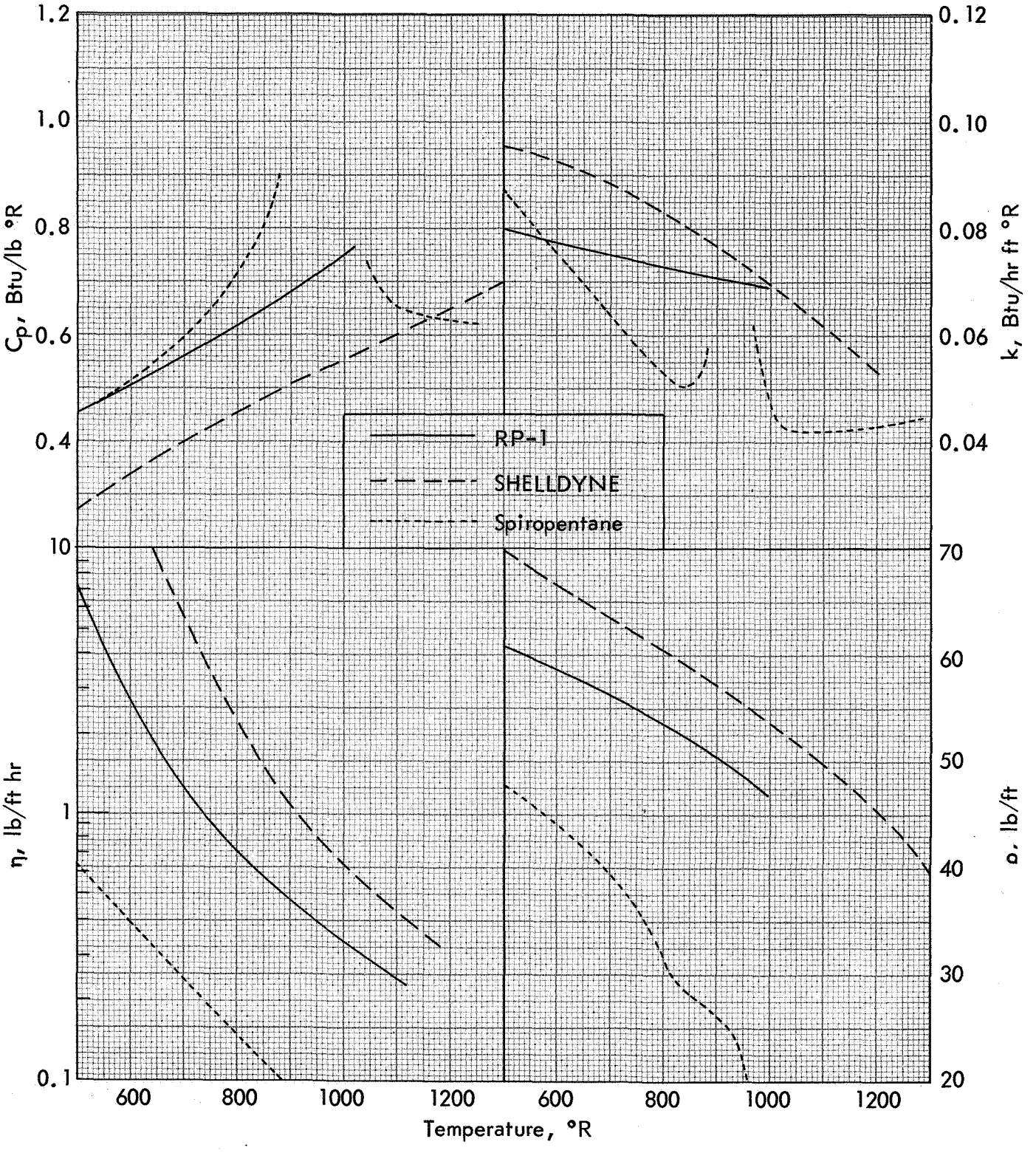


Figure 17. SOME ESTIMATED PROPERTIES OF RP-1, SHELLDYNE AND SPIROPENTANE

Table 10. SOME ESTIMATED PROPERTIES OF LIQUID "SHELLDYNE", $C_{14}H_{16}$

Liquid at Saturation Pressure

| | |
|---|---|
| Molecular Weight: | 184.3 |
| Freezing Point, °F: | <-5 |
| Boiling Point, °F: | 488 |
| Critical Temp, °F: | 802 |
| Critical Pressure, psia: | 330 |
| Critical Volume, $ft^3/lb$: | 0.0561 |
| Acentric Factor: | 0.835 |

| Temp, °F | Viscosity, lb(mass)/ft hr | Heat of Vaporization, Btu/lb | Vapor Pressure, psia | Surface Tension, poundal/ft |
|---|---|---|---|---|
| 40 | 123 | 139.1 | 0.000 | 0.087 |
| 80 | 143.9 | 136.7 | 0.000 | 0.083 |
| 160 | 12.2 | 131.8 | 0.014 | 0.073 |
| 240 | 5.60 | 126.5 | 0.153 | 0.064 |
| 320 | 2.61 | 120.9 | 0.920 | 0.056 |
| 400 | 1.41 | 114.7 | 3.72 | 0.047 |
| 440 | 1.07 | 111.5 | 6.68 | 0.043 |
| 480 | 0.844 | 108.0 | 11.3 | 0.039 |
| 560 | 0.573 | 100.6 | 27.8 | 0.031 |
| 640 | 0.424 | 92.0 | 58.8 | 0.023 |
| 720 | 0.318 | 82.0 | 110.6 | 0.016 |

Table 11. SOME ESTIMATED PROPERTIES OF LIQUID 1,5-HEXADIYNE, $C_6H_6$

Liquid at Saturation Pressure

| | |
|---|---|
| Molecular Weight: | 78.11 |
| Freezing Point, °F: | 24.8 |
| Boiling Point, °F: | 189 |
| Critical Temp, °F: | 570 |
| Critical Pressure, psia: | 580 |
| Critical Volume, $ft^3/lb$: | 0.0603 |
| Acentric Factor: | 0.173 |

| Temp, °F | Viscosity, lb(mass)/ft hr | Heat of Vaporization, Btu/lb | Vapor Pressure, psia | Surface Tension, poundal/ft |
|---|---|---|---|---|
| 40 | 1.33 | 201 | 0.62 | 0.064 |
| 80 | 0.94 | 195 | 1.78 | 0.059 |
| 160 | 0.55 | 182 | 9.15 | 0.047 |
| 240 | 0.36 | 168 | 30.9 | 0.036 |
| 320 | 0.26 | 151 | 79.2 | 0.026 |
| 400 | 0.20 | 130 | 169 | 0.016 |
| 440 | 0.18 | 118 | 235 | 0.011 |
| 520 | 0.14 | 81 | 422 | 0.004 |
| 560 | 0.12 | 42 | 550 | 0.0004 |

Table 12. SOME ESTIMATED PROPERTIES OF LIQUID 1,6-HEPTADIYNE, $C_7H_8$

Liquid at Saturation Pressure

| | |
|---|---|
| Molecular Weight: | 92.14 |
| Freezing Point, °F: | -119 |
| Boiling Point, °F: | 234 |
| Critical Temp, °F: | 620 |
| Critical Pressure, psia: | 510 |
| Critical Volume, $ft^3/lb$: | 0.0607 |
| Acentric Factor: | 0.178 |

| Temp, °F | Viscosity, lb(mas)/ft hr | Heat of Vaporization, Btu/lb | Vapor Pressure, psia | Surface Tension, poundal/ft |
|---|---|---|---|---|
| 0 | 3.86 | 194 | 0.06 | 0.070 |
| 40 | 2.32 | 189 | 0.24 | 0.064 |
| 80 | 1.54 | 184 | 0.73 | 0.059 |
| 160 | 0.85 | 173 | 4.33 | 0.048 |
| 240 | 0.53 | 161 | 16.1 | 0.038 |
| 320 | 0.37 | 147 | 44.4 | 0.029 |
| 400 | 0.27 | 131 | 99.8 | 0.020 |
| 440 | 0.24 | 121 | 141 | 0.015 |
| 520 | 0.19 | 97 | 261 | 0.008 |
| 600 | 0.16 | 53 | 446 | 0.0011 |

Table 13. SOME ESTIMATED PROPERTIES OF LIQUID 1,7-OCTADIYNE, $C_8H_{10}$

Liquid at Saturation Pressure

| | |
|---|---|
| Molecular Weight: | 106.17 |
| Freezing Point, °F: | -7.6 |
| Boiling Point, °F: | 282 |
| Critical Temp, °F: | 682 |
| Critical Pressure, psia: | 450 |
| Critical Volume, $ft^3/lb$: | 0.0610 |
| Acentric Factor: | 0.185 |

| Temp, °F | Viscosity, lb(mass)/ft hr | Heat of Vaporization, Btu/lb | Vapor Pressure, psia | Surface Tension, poundal/ft |
|---|---|---|---|---|
| 0 | 7.7 | 184 | 0.045 | 0.070 |
| 40 | 4.0 | 180 | 0.156 | 0.065 |
| 80 | 2.5 | 175 | 0.445 | 0.060 |
| 160 | 1.28 | 166 | 2.36 | 0.051 |
| 240 | 0.77 | 156 | 8.41 | 0.041 |
| 320 | 0.54 | 144 | 23.0 | 0.032 |
| 400 | 0.39 | 131 | 52.6 | 0.024 |
| 440 | 0.34 | 124 | 75.5 | 0.020 |
| 520 | 0.27 | 106 | 145 | 0.012 |
| 600 | 0.22 | 82 | 258 | 0.005 |
| 640 | 0.20 | 64 | 340 | 0.002 |

Table 14. SOME ESTIMATED PROPERTIES OF LIQUID BICYCLOBUTANE, $C_4H_6$

Liquid at Saturation Pressure

| | |
|---|---|
| Molecular Weight: | 54.09 |
| Freezing Point, °F: | - |
| Boiling Point, °F: | 46.9 |
| Critical Temp, °F: | 358 |
| Critical Pressure, psia: | 670 |
| Critical Volume, $ft^3/lb$: | 0.0654 |
| Acentric Factor: | 0.155 |

| Temp, °F | Viscosity, lb(mass)/ft hr | Heat of Vaporization, Btu/lb | Vapor Pressure, psia | Surface Tension, poundal/ft |
|---|---|---|---|---|
| 40 | 0.96 | 193 | 12.7 | 0.044 |
| 80 | 0.61 | 183 | 27.5 | 0.037 |
| 120 | 0.41 | 172 | 52.8 | 0.030 |
| 160 | 0.26 | 161 | 92.4 | 0.024 |
| 200 | 0.17 | 148 | 150 | 0.018 |
| 240 | 0.12 | 132 | 232 | 0.013 |
| 280 | 0.08 | 113 | 343 | 0.008 |
| 320 | 0.05 | 86 | 489 | 0.003 |

Table 15. SOME ESTIMATED PROPERTIES OF BICYCLOPENTANE, $C_5H_8$

Liquid at Saturation Pressure

| | |
|---|---|
| Molecular Weight: | 68.1 |
| Freezing Point, °F: | - |
| Boiling Point, °F: | 114 |
| Critical Temp, °F: | 446 |
| Critical Pressure, psia: | 615 |
| Critical Volume, $ft^3/lb$: | 0.0623 |
| Acentric Factor: | 0.205 |

| Temp, °F | Viscosity, lb(mass)/ft hr | Heat of Vaporization, Btu/lb | Vapor Pressure, psia | Surface Tension, poundal/ft |
|---|---|---|---|---|
| 40 | 1.30 | 188 | 3.01 | 0.053 |
| 80 | 0.87 | 181 | 7.56 | 0.046 |
| 120 | 0.62 | 173 | 16.4 | 0.040 |
| 160 | 0.46 | 165 | 31.8 | 0.034 |
| 200 | 0.33 | 156 | 56 | 0.029 |
| 240 | 0.22 | 145 | 93 | 0.023 |
| 280 | 0.16 | 134 | 145 | 0.018 |
| 320 | 0.11 | 121 | 216 | 0.013 |
| 360 | 0.08 | 104 | 310 | 0.008 |
| 400 | 0.05 | 82 | 430 | 0.004 |
| 440 | 0.025 | 38 | 590 | 0.0003 |

Table 16. SOME ESTIMATED PROPERTIES OF SPIROPENTANE, $C_5H_8$

Liquid at Saturation Pressure

| | |
|---|---|
| Molecular Weight: | 68.12 |
| Freezing Point, °F: | -160.7 |
| Boiling Point, °F: | 102.2 |
| Critical Temp, °F; | 381 |
| Critical Pressure, psia: | 660 |
| Critical Volume, $ft^3/lb$: | 0.0586 |
| Acentric Factor | 0.129 |

| Temp, °F | Viscosity, lb(mass)/ft hr | Heat of Vaporization, Btu/lb | Vapor Pressure, psia | Surface Tension, poundal/ft |
|---|---|---|---|---|
| -40 | 0.94 | 198 | 0.184 | 0.055 |
| 0 | 0.76 | 190 | 0.884 | 0.049 |
| 40 | 0.63 | 182 | 3.14 | 0.043 |
| 80 | 0.52 | 174 | 8.92 | 0.037 |
| 120 | 0.43 | 165 | 21.2 | 0.031 |
| 160 | 0.35 | 155 | 44.3 | 0.025 |
| 240 | 0.24 | 130 | 144 | 0.014(5) |
| 320 | 0.16 | 95 | 361 | 0.005(2) |
| 360 | 0.13 | 63 | 539 | 0.001(4) |

Table 17. SOME PROPERTIES OF "SHELLDYNE" H (HYDROGENATED "SHELLDYNE")

| | |
|---|---|
| Freezing Point, °F | ca-65(a) |
| Boiling Range, °F | 509-526 |
| Density, 25°C, gm/ml | 1.07 |
| Kinematic Viscosity, CS | |
| 212°F | 3.19 |
| 68°F | 26.2 |
| Heat of Combustion, BTU/lb | 18,000 |

## C. References for Section V


1) Pratt and Whitney Corporation Report NASA-CR-54445, PWA FR-1443, Contract NAS3-4195, issued September 1, 1965.

2) D. W. Scott et al, J. Am. Chem. Soc. 72, 4664 (1950).

3) A. Henne and K. W. Greenlee, J. Am. Chem. Soc. 67, 484 (1945).

4) H. J. H. Hayman and S. Weiss, J. Chem. Phys. 42, 3701 (1965).

5) J. Happel and C. J. Marsel, "Acetylenic Compounds for Rocket Fuels", New York University Report NYU-175.9, Contract Nour-285(04), December 1, 1952.


# SECTION VI

## REGENERATIVE HEAT-EXCHANGE PROPERTIES OF SOME HYDROCARBON FUELS

An adequate evaluation of the properties of the candidate hydrocarbon fuels as regenerative coolants would require reliable values for the viscosities, thermal conductivities, specific heats, densities and vapor pressures over the temperature range existing in the regenerator, and a detailed analysis of the fluid flows and temperature gradients in the system. Since such an analysis is beyond the scope of the present work we have limited ourselves to the consideration of heat transfer coefficients for a turbulent flow situation in which the liquid enters a tube of constant cross-section at 40°F with an initial linear velocity v. The correlation used to obtain heat transfer coefficients was a Rocketdyne modification[1] of the Dittus-Boelter equation

$$Nu = 0.005\ Re^{0.95}\ Pr^{0.4}$$

1) See references at end of Section.

where Nu, the Nusselt number, is $hD/k$; Re, the Reynolds number, is $D\rho v/\eta$, and Pr, the Prandtl number, is $\eta C_p/k$; h is the heat transfer coefficient, D is the tube diameter, k is the thermal conductivity, $\rho$ is the density, v is the linear velocity, $\eta$ is the viscosity and $C_p$ is the heat capacity.

Since the mass velocity is constant along the pipe at the steady state, this leads to

$$h = 0.005\ D^{-0.05}\ (v\rho)_o^{0.95}\ k^{0.6}\ C_p^{0.4}\ \eta^{-0.55}\ \text{Btu/hr ft}^2\ \text{R}, \qquad \text{VI.2}$$

where $(v\rho)_o$ is the mass velocity per unit area at the entrance temperature.

If we make the approximate assumption that the mass-flow rate is proportional to $\rho_o$ 2/3, where $\rho_o$ is the density of the fuel at the entrance to the pipe, then the ratio $h/h_r$, where $h_r$ is the heat transfer coefficient of the reference fuel, RP-1, is given by

$$h/h_r = (\rho/\rho_r)_o^{0.63}\ (k/k_r)^{0.6}\ (\eta_r/\eta)^{0.55}\ (C_p/C_{pr})^{0.4} \qquad \text{VI.3}$$

where the ratio of densities is taken at the entrance temperature and the other ratios are taken at the temperature at which h is to be evaluated. The ratio $h/h_r$ has been calculated by means of this expression and the physical property data from the previous section; the results are shown in Figure 18. The breaks shown in the curves for the lower-boiling hydrocarbons occur in the vicinity of the critical temperature (at an assumed pressure of 1000 psia). The shapes of the curves in these regions should be regarded as only schematic.

The dominant term in the expression of $h/h_r$ is the viscosity term, $(\eta/\eta_r)^{0.55}$; the other terms introduce factors that do not depart very far from unity at temperatures below the critical temperature of the fuel. The dominant effect of the viscosity accounts for the relatively high heat transfer coefficients of bicyclobutane, bicyclopentane, and 1,5-hexadiyne and the relatively low coefficients for SHELLDYNE. It should be borne in mind that uncertainties in the estimation of the viscosity introduce corresponding uncertainties in the predicted heat transfer coefficients; nevertheless, the curves shown in Figure 18 appear to fall in a reasonable order and are believed to provide at least a rough approximation to the truth. The curves would not be changed greatly if they were calculated on the basis of constant mass-flow rate; this would require the use of a factor $(\rho/\rho_r)^{0.95}$ in place of $(\rho/\rho_r)^{0.63}$, but in most cases the indicated ratio is not very far from unity.

A possible limitation on the use of these fuels is the upper temperature limit. Because anomalous behavior may occur in the critical region, it is desirable to avoid reaching critical temperature in the cooling system. We have estimated the order of magnitude of the coolant temperature rise in the following way. A calculation published by Rocketdyne[2)] indicates an overall coolant $\Delta T$ of 156°F for RP-1 in an Atlas rocket motor; this corresponds to a heat input of 79 Btu/lb. On the basis of the rough assumption that the heat input will be the same for the other fuels, a corresponding temperature rise can be calculated for each. The values obtained for $\Delta T$ ranged from

137°F for bicyclobutane to 197°F for SHELLDYNE. Even for bicyclobutane, with an estimated critical temperature around 360°F, the final temperature estimated in this way is 150°F below the critical.

As is shown in Figures 4 through 6 of this report, the low-boiling high-energy hydrocarbons give rise to higher flame temperatures than does RP-1. If the sum of the thermal resistances in the sequence gas film, carbon film, tube wall and liquid film does not change substantially when RP-1 is replaced by a new fuel, the heat flux to be dissipated by the new fuel in the regenerator will be changed proportionately to the difference between the flame temperature and the temperature of the liquid. If we approximate the temperature of the liquid coolant as approximately constant at 350°K, the data of Figure 6 suggest that the heat flux at the throat will be increased by about 10% if RP-1 is replaced by bicyclobutane and by 7-9% if the replacement fuel is bicyclopentane, spiropentane or 1,7-octadiyne. The final coolant temperatures estimated above from the Rocketdyne example for the Atlas engine would still be well below the critical temperatures.

This conclusion must be qualified, however, because of the fact that a double-pass heat exchange system is used in many rocket engines. In such a system, it is possible that the exit temperature is not the highest temperature attained by the coolant; a maximum may occur somewhere within the system, possibly in the vicinity of the throat. If the maximum is severe, it may be necessary to eliminate from consideration the lowest boiling hydrocarbons, such as bicyclobutane, at least for use as neat fuels.

One additional proviso is that coolant performance depends also on chemical stability under the conditions encountered in the heat exchanger. Whether the candidate fuels have adequate stability for this service, or can be given adequate stability by the use of additives, can be learned only by experiment.

## A. References for Section VI


1) Rocketdyne Report RM 1105/362, "Study of an Endothermic Fuel for the Atlas Rocket Motor", Second Quarterly Progress Report, Canoga Park, California, December 1964.

2) Ibid., First Quarterly Report, September 16, 1964.


# SECTION VII

# THERMAL STABILITY OF SOME CANDIDATE FUELS

## A. Acetylenes

Only limited information is available about the thermal stability of these fuels as liquids under the conditions of temperature and pressure that are of practical interest. Since all of the compounds under consideration in this report are deficient in hydrogen, they are liable in principle to undergo polymerization in the presence of free radical sources, including

 Figure 18 follows

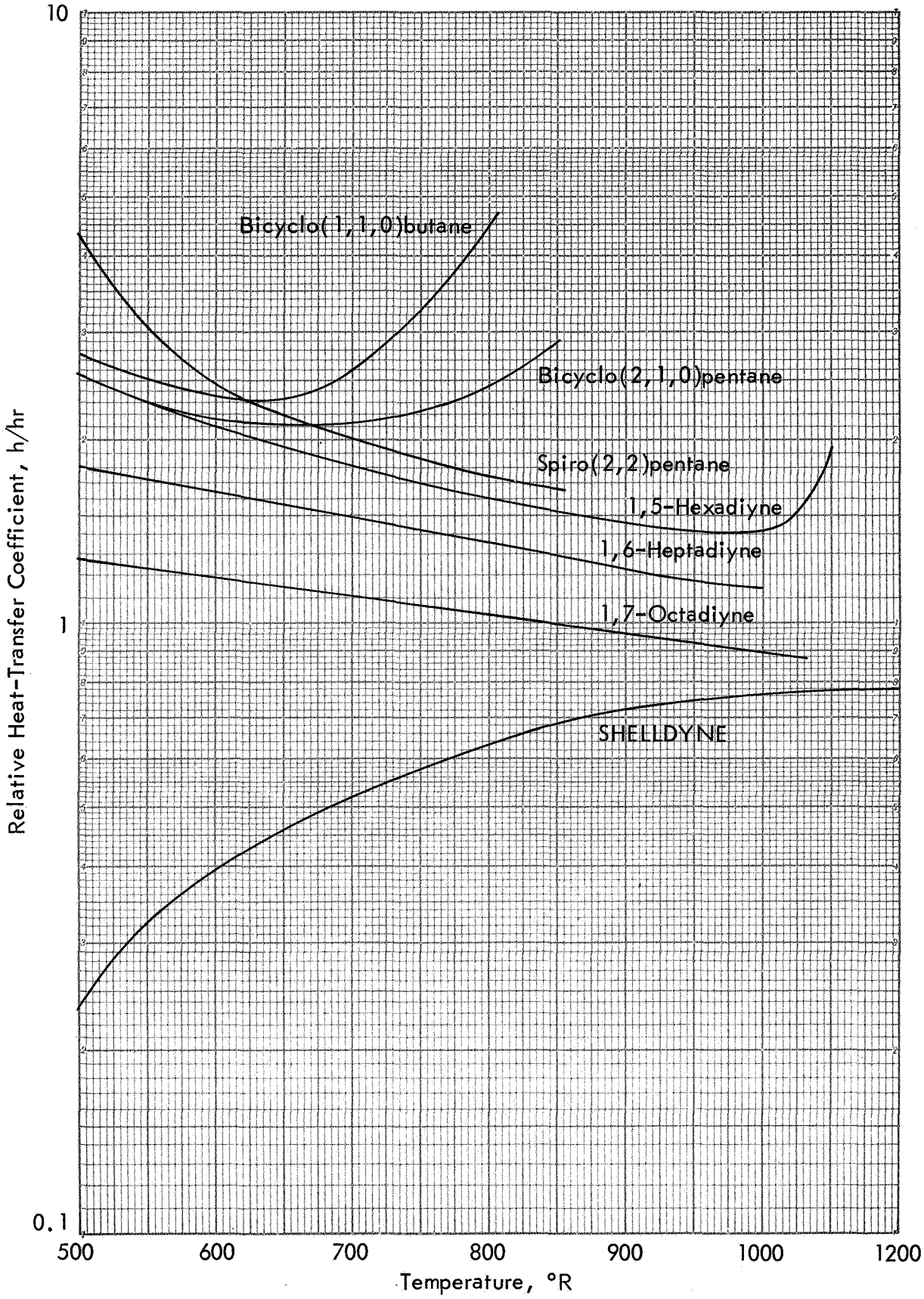


Figure 18. RATIO OF HEAT-TRANSFER COEFFICIENT TO RP-1

dissolved oxygen. In the case of the terminal diacetylenes, the propagation step in the polymerization process can be represented schematically as

$$R. + HC \equiv C - (CH_2)_n\, C \equiv CH \longrightarrow RCH = \dot{C}\,(CH_2)_n\, C \equiv CH$$

where R. represents a free radical. The more complex free radical resulting from this reaction can react with other acetylenes to generate branched linear polymeric free radicals of the general form

$$\begin{array}{ccccc} R & - [CH = C]_p & - & CH = C. \\ & \quad\;\; | & & \quad\;\; | \\ & \quad (CH_2)_n & & \quad (CH_2)_n \\ & \quad\;\; | & & \quad\;\; | \\ & \quad\;\; C \equiv CH & & \quad\;\; C \equiv CH \end{array}$$

Such a free radical can be converted into a stable molecule either by reaction with another radical like itself or by abstracting a hydrogen atom from another molecule. The resulting products, however, still contain double and triple carbon-carbon bonds and are susceptible to further polymerization reactions. These reactions can lead to the conversion of the initial linear soluble polymers into insoluble cross-linked materials that may form resinous films on hot surfaces such as those of heat-exchanger tubes. Such films will change the effective thermal conductivity of the tube-wall and can result in a higher wall-temperature on the liquid side of the heat exchanger. As a result, the polymerization reactions referred to above may be accelerated together with the entire chain of associated events. Self-acceleration results also fr m the fact that these chain processes are exothermic. Indeed acetylene itself undergoes these reactions so readily that the pure liquid tends to explode when it is confined under pressure at ordinary temperatures. The substituted acetylenes, in which the triple bonds are diluted with relatively unreactive paraffin chains, are much more stable. Stability increases with increasing length of the paraffin chain.

Thus, 1,5-hexadiyne has a moderate inpact sensitivity that can be relieved by dilution. The undiluted liquid was found to explode in an impact tester.[1] More recently it has been reported[2] that the liquid (bp 87°C) explodes when it is heated under pressure at 280°C, and that the vapor undergoes the following thermal isomerization reaction:

$$\begin{array}{ccc} H_2C & - & CH_2 \\ | & & | \\ C & & C \\ ||| & & ||| \\ C & & C \\ H & & H \end{array} \qquad\qquad \begin{array}{ccccc} H_2C & & & & CH_2 \\ & \diagdown\!\!\diagdown & & \diagup\!\!\diagup & \\ & & C & - & C \\ & & | & & | \\ & & HC & = & CH \end{array}$$

This first-order reaction has a rate constant of $8 \times 10^{-5}$ $sec^{-1}$ at 210°C and $3 \times 10^{-2}$ $sec^{-1}$ at 300°C; the activation energy is 34.4 kcal/mole. The reaction can be expected to be exothermic.

1) See references at end of Section.

The corresponding $C_7$ compound, 1,6-heptadiyne is much more stable. A preparation of this compound made under the 1952-3 contract[1] was not detonated by a No. 6 blasting cap at room temperature and was estimated to have a storage life of over a year at 200°F though it developed a yellow color after two months at that temperature. Its short-time decomposition temperature was found to lie between 550°F (290°C; dark brown color after 3 minutes) and 700°F (370°C; complete carbonization in 3 minutes).

The $C_8$ compound, 1,7-octadiyne was estimated to be much more stable than the $C_7$ compound on the basis of qualitative observations under the same contract;[1] this conclusion, however, is far from certain and requires confirmation.

It should be possible to enhance the thermal stability of these compounds considerably by minimizing the concentration of dissolved oxygen and by the addition of small amounts of various inhibitors such as alkyl phenols or aromatic amines. These compounds are able to interupt the polymerization chain reaction by transferring a hydrogen atom to the terminal free radical of the growing polymer. Whether such measures will stabilize the terminal diacetylenes sufficiently to prevent the formation of undesirable deposits on heat exchanger surfaces can be determined only by experiment.

## B. Cyclanes and Polycyclanes

At sufficiently high temperatures, these compounds undergo a thermal rearrangement to form olefins at measureable rates. The resulting olefins, in turn, can form polymers if a suitable source of free radicals is present. A considerable body of information is available about the kinetics of these rearrangement reactions in the dilute vapor phase. Very little information is available, however, about the thermal stability of the liquids.

A comprehensive review of the kinetic information available concerning the thermal decomposition of small-ring monocyclic compounds has recently been published by O'Neal and Benson.[3] These authors present a thorough discussion of the mechanistic implications of the data and a set of useful rules for predicting the rate constants and their temperature coefficients from the chemical structure. They promise a future paper in which the same analysis will be extended to polycyclic compounds.

Some of the kinetic information available is summarized in Table 18 in which the first-order rate constants are expressed in the form

$$k = A \exp(-E/RT) \ \mathrm{sec}^{-1}$$

Also given are values of the calculated temperatures at which the reaction rate attains 1% per minute; these provide an index of relative thermal stability of the vapors.

Table 18. RATE CONSTANTS FOR THERMAL DECOMPOSITION OF SOME SMALL-RING CYCLANES AND POLYCYCLANES

| Reactant | Products | Decomposition T[a] °C | Decomposition T[a] °F | $\log_{10}$ A | E, kcal/mole | Ref |
|---|---|---|---|---|---|---|
| 1) Cyclopropane | Propene | 470 | 880 | 15.45 | 65.6 | 1 |
| 2) Methylcyclopropane | Isobutene | 465 | 870 | 14.62 | 66.0 | 2,3 |
| | 1-Butene | | | 14.95 | 64.3 | 2,3 |
| | cis-2-Butene | | | 14.59 | 63.9 | 2,3 |
| | trans-2-Butene | | | 15.49 | 63.1 | 2,3 |
| | Overall | | | 15.45 | 65.0 | 3 |
| 3) 1,1-Dimethylcyclopropane | 3-Methylbutene-1 | 465 | 870 | 14.75 | 62.6 | 4 |
| | 3-Methylbutene-2 | | | 14.75 | 62.6 | |
| 4) Isopropenylcyclopropane | 1-Methylcyclopentene | 360 | 670 | 13.89 | 50.9 | 5 |
| 5) Bicyclopropyl | Cyclohexene | 420 | 790 | 16.8 | 70.8 | 6 |
| | All products | | | 15.36 | 60.7 | |
| 6) Cyclobutane | Ethylene | 430 | 810 | 15.62 | 62.5 | 7,8 |
| 7) Methylcyclobutane | Propene + Ethene | 425 | 800 | 15.38 | 61.2 | 9 |
| 8) Methylenecyclobutane | Ethene + Allene | 525 | 980 | 15.08 | 61.5 | 10 |
| | | 530 | 990 | 15.68 | 63.3 | 11 |
| 9) Spiropentane | Methylenecyclobutane (92%); allene + ethene (8%) | 370 | 700 | 15.86 | 57.6 | 12 |
| 10) 1,3-Dimethylbicyclo-(1,1,0)butane | 1,3-Dimethylbutadiene-1,3 | 250 | 500 | 13.91 | 40.4 | 13 |
| | | 250 | 525 | 14.45 | 43.8 | |
| 11) Bicyclo(2,1,0)pentane | Cyclopentene | (330)[b] | (620) | - | - | 14 |
| 12) Bicyclo(3,1,0)hexane | Cyclohexene | 460 | 860 | 13.29 | 57.4 | 15 |
| | 1-Methylcyclopentene | 485 | 905 | 13.89 | 61.2 | |
| 13) cis-1,2-Dimethylcyclopropane | trans-1,2-isomer | 480 | 900 | 15.25 | 59.42 | 16 |
| | 2-Methylbutene-1 | | | 13.93 | 61.0 | |
| | 2-Methylbutene-2 | | | 14.08 | 62.3 | |
| | Pentene-2 | | | 13.94 | 61.3 | |
| 14) Quadricyclene | Bicyclo(2,2,1)heptadiene-2,5 | 170 | 335 | 12.81 | 33.51 | 17 |
| 15) Bicyclo(3,1,0)-hexene-2 | Cyclohexadiene-1,3 | 335 | 640 | 14.28 | 50.20 | 18 |
| | Cyclohexadiene-1,4 | | | 14.095 | 50.20 | |
| 16) Cyclohexadiene-1,4 | Benzene + $H_2$ | 320 | 610 | 12.02 | 42.69 | 18 |

a) For calculated decomposition rate of 1%/min, approximately.

b) Temperature at which appreciable rate of decomposition is observed.

(Continued)

Table 18 (Contd). LIST OF REFERENCES


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10. R. L. Brandaur, B. Short and S. M. E. Kellner, J. Phys. Chem. 65, 2269 (1961).

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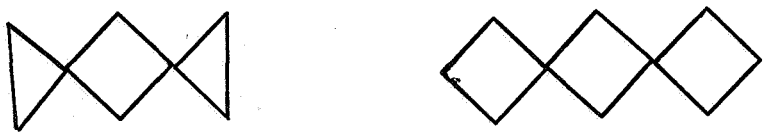
16. M. C. Flowers and H. M. Frey, Proc. Roy. Soc. (London) A257, 122 (1960); ibid. A260, 424 (1961).

17. H. M. Frey, J. Chem. Soc. 1964, 365-7.

18. R. J. Ellis and H. M. Frey, J. Chem. Soc. A1966, 553.

The initial step in these rearrangement reactions is believed by several authors to be the rupture of a carbon-carbon bond to form a biradical; this step should occur more readily with increasing strain in the ring system. This is consistent with the observed sequence of thermal stabilities, which increase in the order bicyclobutane, bicyclopentane, bicyclohexane, 1,2-dimethylcyclopropane. A minor reversal of this trend appears in the comparison between cyclopropane and cyclobutane.

From these data, spiropentane, bicyclopropyl (cyclopropyl cyclopropane) and the monocyclanes appear to be moderately stable in the vapor phase. For spiropentane, for example, the rate of decomposition is only 1% per hour at 600°F and the cyclobutanes are even more stable. This would suggest that the dispiranes, with structures (schematic) as shown below would also be fairly stable thermally in the vapor.



The authors who obtained the kinetic data listed in Table 18 did not report any evidence of polymer formation under their experimental conditions, though in most cases they looked for it. This implies that the lifetime of the postulated biradical reaction intermediate is shorter than or comparable to the time between gas-phase collisions. This does not guarantee, however, that polymerization will not occur when the same hydrocarbons are heated in the liquid phase where collision and intermolecular interactions are more frequent. In addition, the indicated reactions are exothermic and may become self-accelerating in the liquid phase under conditions of poor cooling. The resulting temperature rise could conceivably initiate polymerization reactions that did not occur rapidly at lower temperatures. It has been reported by Wiberg et al[4] that polymerization of some of the derivatives of bicyclobutane occurs readily in the presence of free radical initiators. The parent compound is less prone to polymerize, though it decomposes cleanly at a measureable rate to butadiene at 200°C. Chesick (ref. 13 of Table 18) reports that though 1,3-dimethylbicyclobutane decomposes cleanly in the vapor phase, it appeared to polymerize to some extent during passage at 35°C through a gas-liquid chromatographic column with copper fittings and packed with fire brick. Similarly, Frey (ref. 17 of Table 18) has reported that a slow polymerization of quadricyclene occurred over the course of several months storage of the liquid at room temperature, with the result that part of the liquid was converted to a non-volatile white solid. Only experiment will reveal whether similar polymerizations would be troublesome when an experimental energetic fuel is exposed to conditions corresponding to those in the heat-exchanger section of a rocket motor.

No kinetic data have been found in the literature for the thermal decompositions of tricyclo (3, 1, 0, 0,$^{2,4}$) hexane or of cyclopropylacetylene. We would expect the tricyclohexane, however, to be relatively unstable by analogy with the compound tricyclo (4, 2, 0, 0,$^{2,5}$) octane (called Ladderane on account of its structure, which resembles a series of three square boxes). The latter compound isomerizes at 150°C to form

cyclooctadiene; in the liquid phase a dimer of cyclooctadiene, $C_{16}H_{24}$, is formed with a melting point of 121°C.

Cyclopropylacetylene was studied to some extent by Happel and Marsel[6] who found it to be relatively insensitive to thermal shock, but somewhat sensitive to impact. We have seen no report of the preparation of dicyclopropyl acetylene.

SHELLDYNE, which may be of interest as a high-density blending agent, has been tested for thermal stability by A. C. Nixon et al.[5] The extent of decomposition was measured after passage of the vapor through a 1/4 in. OD stainless steel tube at a controlled flow rate and temperature. Under these conditions appreciable decomposition occurred with some conversion to light gases and coke at 800°F and contact times of less than a second. The average effective rate constant from a series of runs near this temperature was 0.34 $sec^{-1}$; from rates at other temperatures the activation energy was estimated to be 41 kcal/mole. Slightly lower rate constants were obtained in experiments in which the vapors were passed through a 5/8 in. ID stainless steel tube packed with quartz chips. It appears that the stainless steel surface provided some catalytic activity for the formation of coke, since pyrolysis in Pyrex tubes was found in another investigation to proceed cleanly at comparable rates but with no coke formation.

Hydrogenation of SHELLDYNE to SHELLDYNE H decreases its density by only 1.7% but decreases the rate of thermal decomposition substantially; the conversion of the hydrogenated material at 1,200°F was comparable to that of the unhydrogenated material with similar residence time at 800°F. For comparison with the data of Table 18 a very approximate description of the rate data can be given as

$$k = 10^{9.29} \exp(-30{,}800/RT) \ sec^{-1}$$

$$k_h = 10^{9.22} \exp(-41{,}000/RT) \ sec^{-1}$$

for the unhydrogenated and hydrogenated compounds, respectively. On this basis the temperature for a decomposition rate of 1%/min is estimated to be 470 and 780°F (245 and 420°C) respectively for the two materials. Thus SHELLDYNE appears to be comparable in stability to the bicyclobutanes, while SHELLDYNE H is comparable to bicyclopropyl and the cyclobutanes. It is to be emphasized that both the rates and the products of the thermal decomposition reactions of these hydrocarbons may be different in the liquid phase from what they are in the vapor phase and may be modified by metallic surfaces.

## C. References to Section VII


1) Shell Development Company Report No. S-13526, Contract Noas 52-808-C, ONR/Butler, September 1953.

2) H. J. Wristers, J. Am. Chem. Soc. 89, 342 (1967).

3) H. E. O'Neal and S. W. Benson, J. Phys. Chem. 72, 1966 (1968).

4) K. E. Wiberg, G. M. Lampman et al, Tetrabedron 21, 2749 (1965).

5) Shell Development Company Report No. S-14062, Contract No. AF 33(615)-3789, Quarterly Progress Report No. 7, December 1967 - February 1968.

6) J. Happel and C.J. Marsel, "Acetylenic Compounds for Rocket Fuels", New York University Report NYU-175.9, December 1, 1952, Contract Nonr-285(04).

## SECTION VIII

## COST AND AVAILABILITY

### A. Introduction

Unlike the reference fuel RP-1, which is a kerosene available in large quantities at a price of less than two cents per pound, the compounds discussed in this report are synthetic chemicals whose cost will be much higher, often by orders of magnitude. Ethylene at around 3.5 ¢/lb and butadiene at 10-12¢/lb are produced in quantity. A mixture of allene and methylacetylene is marketed commercially in cylinders by Dow Chemical Company at a reasonably modest price as a fuel for use in welding torches, the supply of this mixture could be increased substantially. All of these compounds, however, have disadvantages as prospective replacements for RP-1 on the basis of density, boiling point or chemical stability.

None of the remaining energetic hydrocarbons considered in this report is made commercially on a substantial scale. Some of them have been prepared only on a research scale and a few [tetrahedrane, dicyclopropylacetylene and dispiro(2,1,2,1)octane] have never been made to our knowledge. The terminal diacetylenes ($C_6$, $C_8$, $C_9$ and $C_{10}$) are produced on a small scale by Farchan Research Laboratories for sale as laboratory chemicals at a price of the order of $100 for 0.5 kg.

The hydrogenated form of SHELLDYNE, which might find use as a high-density blending agent, is not produced commercially but a practical synthetic route is known. Its potential selling price and scale of manufacture are currently under review by Shell Oil Company.

We have made very approximate preliminary estimates of the probable costs of producing 1,7-octadiyne or spiro(2,2)pentane on a commercial scale. The latter was selected as an example of a high-impulse relatively stable hydrocarbon for which a reasonably efficient synthetic route appears in principle to be achievable. Its major disadvantage is its low density, about 79% that of RP-1. With regard to the estimated costs, it should be noted that the basic costs of production given do not include interest on capital, amortization of capital or profit.

In comparison with spiropentane, 1,7-octadiyne has a higher density by a factor 1.085 and gives a stoichiometric specific impulse that is lower by the factor 1.010. A reasonably efficient synthetic route for its preparation is known. We chose it for economic evaluation over its lower homologues for the following reasons: the $C_5$ compound is difficult to prepare and probably has a relatively poor thermal and shock stability. The $C_6$ compound requires a more complicated preparative method than is used for the higher homologues, though the desired product can be obtained in high yield, possibly greater than 90%.[1] The $C_6$ compound has also a relatively high melting point (-4°C), presumably because of its limited molecular flexibility. It is reported to have a moderate impact sensitivity that can be relieved by dilution. The undiluted material was found to detonate in an impact tester.[1]

1) See References at the end of this Section.

The $C_7$ compound has a wide liquid range (mp -84°C, bp 112°C). In work done under the 1952-3 contract[1] it was estimated to have a storage life of over one year at 200°F, though it developed a yellow color after 2 months at that temperature. It was not detonated by a No. 6 blasting cap. Its short time decomposition temperature was found to lie between 550°F (290°C) (dark brown color after 3 min) and 700°F (370°C) (complete carbonization in 3 min). Its major drawback is that it has been made only in relatively poor yield (10% to 34% has been reported) by the conventional synthesis from sodium acetylide and 1,3-dibromopropane in liquid ammonia. Unless these yields can be improved the cost of the $C_7$ compound will be higher than that of the $C_8$ compound by severalfold.

The $C_8$ compound was estimated on the basis of qualitative observations in the earlier work at Shell Development Company[1] to be somewhat more stable thermally than the $C_7$ compound, though this conclusion is far from certain. It was prepared on moderate scale in 83% yield from 1,4-dichlorobutane. It is possible that this yield could be improved. The only known disadvantage of this material is that its freezing point is -22°C; this may be low enough, but could be lowered by blending. Its cost of manufacture is estimated below. It should be emphasized that the cost of development quantities (100-1000 lb) will be higher than these estimates by at least an order of magnitude.

## B. Estimated Cost of Manufacture of 1,7-Octadiyne and of Spiro(2,2)pentane (Preliminary)

The major elements determining the cost of producing a chemical substance are:

(A) Cost of Raw Materials and Process Materials

(B) Processing Costs

Operation: labor, materials, overhead
Maintenance: labor, materials, overhead
Utilities

(C) Capital Costs

Process Units
Utilities

Accurate estimates of (A) depend on accurate knowledge of the yields attainable in the contemplated reactions. These yields and information about the rates of the reactions involved also have an effect on (B) and (C), since these factors determine the volume of material to be handled to produce a desired quantity of product. (B) and (C) are also affected by constraints on materials of construction such as may be imposed by a corrosive environment or by extreme conditions.

For the estimates presented here, operating costs and capital costs were estimated by analogy with existing evaluated processes. These estimates involve a good deal of chemical and engineering judgment; they should be regarded as highly preliminary and much less precise or certain than estimates based on pilot plant data and a preliminary plant design.

## 1. 1,7-Octadiyne and 1,6-Heptadiyne

The process steps are outlined on Figure 19; raw materials are sodium, ammonia and 1,4-dichlorobutane; the reaction medium is liquid ammonia. Yields of the octadiyne achieved on a 100 gram scale in earlier work[1] were 80% based on dichlorobutane, 72.5% on acetylene, and 74.5% on sodium; these yields have been assumed. Corresponding yields of the heptadiyne on a laboratory scale were much lower: approximately 10% basis dichloroalkane. Since the cost of these materials is dominated by raw material costs, the heptadiyne will be much more expensive than the octadiyne by the present route unless yields can be substantially improved by experimentation.

Prices assumed per pound for raw materials are $0.19 for sodium, $0.10 for acetylene, and $0.34 for purchased dichlorobutane. Carbide-based acetylene is somewhat more expensive, ca $0.20/lb. Cost estimates have been made not only on the basis of purchased dichlorobutane, but also on the basis of dichlorobutane manufactured onsite from furfural at $0.135/lb and anhydrous HCl at $0.010/lb. This option lowers the cost of raw materials by 21 to 19¢ per pound of product but increases capital requirements considerably.

Table 19. PROVISIONAL ESTIMATES OF MANUFACTURING COST FOR 1,7-OCTADIYNE

| Case | I | II | III |
|---|---|---|---|
| Scale, MM lb/yr | 20 | 60 | 60 |
| Option[a] | A | A | B |
| Raw Materials, ¢/lb product | 69.0 | 69.0 | 48-50 |
| Operating Costs, ¢/lb product | 6.8-8.7 | 5.1-6.4 | 5.1-6.4 |
| Unamortized Manufacturing Cost, ¢/lb | 76-78 | 74-75 | 53-56 |
| Capital Investment, $ MM | 3.4-6.4 | 7.8-14.4 | 20-34 |
| $ per annual pound of product | 0.17-0.32 | 0.13-0.24 | 0.33-0.57 |

a) A = Purchased 1,4-dichlorobutane;
B = Manufactured 1,4-dichlorobutane.

The processing steps on which the cost estimates were based are described as follows: A solution of sodamide in ammonia is formed by addition of sodium metal to liquid ammonia at -10°C, under nitrogen, in the presence of catalytic amounts of ferric nitrate. The hydrogen evolved is vented. Acetylene gas is reacted with the sodamide solution at -10°C to form mono-sodium acetylide in solution; reaction time is about four hours. The sodium acetylide solution is mixed with 1,4-dichlorobutane and the mixture is stirred 8 hours at about 0°C (75 psig). All operations are under nitrogen. Ammonia is flashed off, condensed and recycled. Water is added to the bottoms to extract chloride and a phase separation is carried out. The organic phase is distilled in the presence of inhibitors at reduced pressure (100 mm Hg). A product fraction is collected, inhibited, and stored under nitrogen. Bottoms from the distillation are burned.

The resulting estimated costs are summarized in Table 19.

 Figure 19 follows

1. Sodamide Formation

$$\underset{(FW = 23)}{Na} + \underset{(MW = 17)}{NH_3} \xrightarrow[\substack{NH_3(\ell) \\ -10°C \\ 50\ psig}]{Fe^{+++}} \underset{(FW = 39)}{NaNH_2} + \underset{(1/2\ MW = 1)}{1/2\ H_2}$$

2. Sodium Acetylide Formation

$$\underset{(FW = 39)}{NaNH_2} + \underset{(MW = 26)}{C_2H_2} \underset{\substack{NH_3(\ell) \\ -10°C \\ 50\ psig \\ ca\ 4\ hr}}{\rightleftharpoons} \underset{(FW = 48)}{NaC_2H} + NH_3$$

3. Alkylation

a) $$\underset{(2 \times FW = 96)}{2\ NaC_2H} + \underset{(MW = 127)}{C_4H_8Cl_2} \xrightarrow[\substack{NH_3(\ell) \\ 0°C \\ 75\ psig \\ ca\ 8\ hr}]{} \underset{(MW = 106)}{C_8H_{10}} + \underset{(2 \times FW = 106)}{2\ NaCl}$$

b) $$\underset{(2 \times FW = 96)}{2\ NaC_2H} + \underset{(MW = 113)}{C_3H_8Cl_2} \xrightarrow[\substack{NH_3(\ell) \\ 0°C \\ 75\ psig}]{} \underset{(MW = 92)}{C_7H_8} + \underset{(2 \times FW = 106)}{2\ NaCl}$$

Figure 19. CHEMICAL STEPS AND PROCESS EQUATIONS
1,7-Octadiyne and 1,6-Heptadiyne

## 2. Spiropentane and Methylenecyclobutane (Clasical Route)

The process steps involved in the classical route to spiropentane are indicated schematically in Figure 20. Basically, pentaerythritol, a tetra-basic alcohol, which may be either purchased commercially or prepared by condensation of formaldehyde with acetaldehyde in the presence of lime, is converted to the tetrahalide; the tetrahalide is reduced with metallic zinc in the presence of sodium carbonate to form spiropentane and zinc oxide. This step is carried out in the presence of minor amounts of iodine, which is reduced to iodide.

The high cost of zinc and of iodine demands that these intermediates be recovered. An essential part of the process, therefore, is the recovery of zinc by reduction of zinc oxide with carbon at high temperatures and the recovery of iodine by oxidation of iodide ion with cheaper chlorine.

The available literature studies of this process all involve reduction of the tetrabromide with zinc; even in this case the yield of spiropentane is very sensitive to the conditions employed (solvent, temperature) in the reaction.[2] Thus the assumption made here that the chloride can be used in place of the more expensive bromide is an optimistic one. The yield of spiropentane assumed (85% basis pentaerythritol tetrachloride) is also optimistic in view of the range of yields that have been reported from experiments on reduction of the tetrabromide. Nevertheless, the preparation of pentaerythritol tetrachloride is a known process, either by means of stoichiometric quantities of phosphorus pentachloride or thionyl chloride-pyridine[2] or, more economically, with concentrated hydrochloric acid in the presence of lesser amounts of aliphatic carboxylic acids.[2][3] Moreover, the zinc dehalogenation of 1,3-dichloropropane to cyclopropane is known.[4]

In spite of the optimistic assumptions described above, the projected cost of making spiropentane by the classical route is still high. The basic reason for this lies in the fact that one mole of pentaerythritol, with a weight of 136 units, can yield no more than 68 mass units of spiropentane. Thus the raw material cost per pound of spiropentane from pentaerythritol must be at least twice the price per pound of pentaerythritol. In addition, for each mole of spiropentane produced, the stoichiometry requires that at least 4 moles of HCl and 2 moles of $Na_2CO_3$ be consumed and at least 2 moles of zinc oxide be converted to zinc; appreciable amounts of iodine must also be recovered.

The major by-product in the dehalogenation of pentaerythritol tetrahalides with zinc is methylene cyclobutane. This is itself a strained hydrocarbon; both its density and its "stoichiometric" specific impulse, however, are lower than those of spiropentane. If an efficient cyclodimerization process could be worked out, however, it would provide a route to dispiro(3,1,3,1)decane. Under some reaction conditions, methylene cyclobutane is the major product from the dehalogenation reaction under discussion. Several studies have been published[2][5][6] of the conditions required to maximize the yield of either methylene cyclobutane or spiropentane.

The processing steps on which the cost estimate was based are as follows: pentaerythritol is treated at elevated temperature and pressure with an excess of concentrated (36%) aqueous hydrochloric acid in the presence

 Figure 20 follows

1. Pentaerythritol Chloride Formation

$$C(CH_2OH)_4 + 4\,HCl \xrightarrow[0.14\ CH_3COOH]{\Delta,\ P} C_5H_8Cl_4 + 4\,H_2O$$

MW = 136 FW = 36.5 MW = 210

2. Spiropentane Production

$$C_5H_8Cl_4 + 2\,Zn + 2\,Na_2CO_3 \xrightarrow[\Delta]{C_2H_5OH \cdot H_2O} C_5H_8 + 2\,ZnO + 4\,NaCl + 2\,CO_2$$

$C_5H_8Cl_4$: MW = 210; Zn: FW = 65.4; $Na_2CO_3$: FW = 106; 0.17 $I_2$; $C_5H_8$: MW = 58; ZnO: FW = 81.4

3. Zinc Recovery

$$ZnO + C \xrightarrow{\Delta\Delta} Zn + CO$$

FW = 81.4 FW = 65.4

4. Iodine Recovery

$$2\,I^{\ominus} + Cl_2 \longrightarrow I_2 + 2Cl^{\ominus}$$

MW = 71.0 MW = 253.8

Figure 20. SPIROPENTANE: CHEMICAL STEPS AND PROCESS EQUATIONS

of small amounts of acetic acid. The insoluble product, pentaerythritol tetrachloride, is isolated, washed and carried forward to spiropentane production. The reaction liquor is recycled after appropriate draw-off and addition of makeup anhydrous HCl. Yield of tetrachloride based on pentaerythritol is assumed to be 85% of theory.

Pentaerythritol tetrachloride (PETC) in ethanol-water azeotrope is mixed with an aqueous solution of iodine and sodium carbonate. The mixture is held at reflux, and zinc powder added stepwise over a period of twelve hours. Spiropentane (bp 38.5°C) and its isomers and carbon dioxide are evolved. Spiropentane is condensed, redistilled, collected, dried and stored. The reaction liquor (slurry) is settled, filtered, and ZnO-Zn solids sent to zinc recovery. The filtrate is diluted with water, ethanol-water azeotrope taken overhead, and the aqueous bottoms sent to iodine recovery. Recovery of spiropentane basis the tetrachloride is assumed (optimistically) to be 85% of theory.

Recovered ZnO and Zn solids from spiropentane production are dried, mixed with finely divided coke, and changed to 1000°C furnaces. Zinc vapor is condensed from the reducing atmosphere. Purchased "60% concentrate" zinc sulfide ore is roasted, sintered, and mixed with coke for makeup feed. By-product sulfuric acid may be recovered, but is not credited. Recovery of zinc from total charge is taken as 93% of theory.

Stripped aqueous reaction liquor from spiropentane production, after separation of zinc solids, is charged to a packed tower along with excess liquid chlorine and contacted with a counter-current flow of air. Volatilized iodine is absorbed in sulfuric acid, reduced with sulfur dioxide, then regenerated with the theoretical amount of chlorine and recovered by filtration. Recovery of iodine from the feed liquor is taken as 98% of theory. Makeup iodine is purchased as $I_2$.

### 3. Pentaerythritol Supply and Other Material Costs

For the spiropentane process under consideration, usage of pentaerythritol corresponds to 2.78 lb/lb spiropentane produced. Supplies for 20 MM lb/yr and 60 MM lb/yr spiropentane units thus total 56 MM lb/yr and 167 MM lb/yr pentaerythritol, respectively, and correspond roughly to 50% and 150% of the total projected 1967 U.S. Pentaerythritol capacity.[7] It is assumed in the present evaluation that 56 MM lb/yr could either be purchased from U.S. and import sources or be produced while usage of 167 MM lb/yr would demand the construction of pentaerythritol production units.

The following information is available concerning pentaerythritol (PE) supply:

PE production in 1964 (U.S.) was 69 MM lb; sales were 64 MM lb at 24¢/lb. U.S. capacity in 1965 was 80 MM lb, with projected 1967 capacity of 110 MM lb. Imports are primarily from Canada, with some from Italy and Japan. Imports in 1965 totaled 14 MM lb. Prices in 1965 were: Canadian product 19.5-20¢/lb, Italian 19.8¢/lb, Japanese (lower grade) 16.8¢/lb. Recent (1966) domestic quotations are 24¢/lb delivered. Domestic producers are Celanese Corporation, Commercial Solvents, Delaware Chemical, Hercules Powder, Heyden Chemical, Reichhold Chemical, and Trojan Powder. Over 90% of the PE produced

goes into competition with glycerine in surface coatings (themselves highly competitive). Small amounts go into tetranitrate for explosives. PE and glycerine are considered almost interchangeable as alkyd modifiers.

Unamortized costs of producing PE at volumes of 60 MM lb/yr and 170 MM lb/yr are estimated roughly at 12.1¢/lb and 11.5¢/lb, respectively. Plant capital costs are taken as $10.0 MM and $20.7 MM for these units.

Costs assumed for other raw materials, in cents/pound, are 1.5 for sodium carbonate, 10.0 for acetic acid, 1.0 (optimistic) to 5.0 (pessimistic) for anhydrous HCl, 4.5 for ZnS concentrate, 1.0 for coke, 3.0 for chlorine, 4.5 for sulfur dioxide, 1.0 for sulfuric acid, and 102.0 for makeup iodine. The unamortized cost per pound for zinc and iodine charged to the spiropentane production unit (makeup and recovery costs) was estimated to fall within the following ranges: At a scale of 20 MM lb spiropentane/year, 6.1 to 9.4 cents for zinc and 11.9 to 14.8 cents for iodine; at a scale of 60 MM lb spiropentane/year, 5.6 to 7.8 cents for zinc and 11.5 to 13.8 cents for iodine.

The total unamortized cost thus estimated per pound of spiropentane produced and the estimated capital required are summarized in Table 20.

An alternative route to spiropentane may eventually come from the type of chemistry now under investigation by Skell.[8] These studies, involving addition of active carbon fragments ($C_1$ and $C_3$) to olefins, are at a very early stage of development; scale-up of the techniques used may be difficult and expensive.

## C. Routes to Other Energetic Hydrocarbons

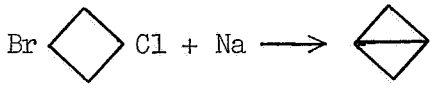
Of the hydrocarbon fuels that show high potential performance, one of the most effective is cubane. Since this hydrocarbon can be regarded as the tetramer of acetylene, it is not impossible that an inexpensive synthesis may someday be found. At present, however, it has been made only by a synthesis of many steps involving relatively costly reagents.[9][10] It also has a relatively high melting point (130°C), presumably as a result of its highly symmetrical structure. It may be soluble enough, however, to be used as a blending agent. Methyl and especially dimethylcubane should have a much lower melting point; they also show a high potential performance. These have not been made, to our knowledge. At present, the cubanes can not be regarded as practical fuels; they do indicate, however, the magnitude of potentially attainable gains in performance.

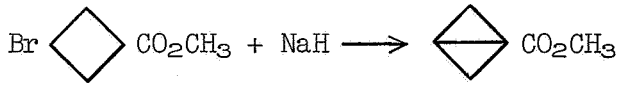
Tetrahedrane and its derivatives have not been made, to our know knowledge, though its synthesis has been attempted. This fact and its lower estimated density and boiling point make it of less interest in comparison with the cubanes. Its estimated heat of formation per carbon atom is even higher than that of acetylene; if this estimate is reliable, it may account for the failure of efforts to make tetrahedrane.

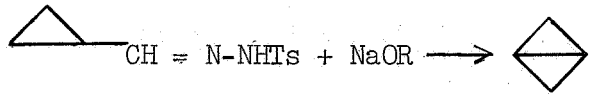
An excellent recent review of the chemistry of polycyclic systems containing 3- and 4-membered rings has been given by Seebach;[11] his article is a good source of references to the original literature. The chemistry of bicyclobutane and its derivatives has been recently reviewed by Wiberg and his co-workers;[12] among the synthetic methods mentioned are the following:

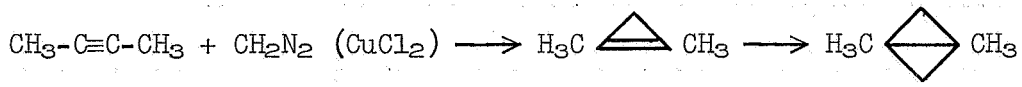
Table 20. SUMMARY OF ESTIMATED MANUFACTURING COSTS FOR SPIROPENTANE

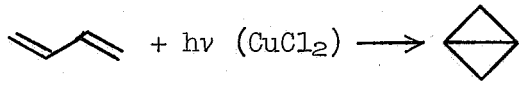
| Case | I | II | III | IV | V |
|---|---|---|---|---|---|
| Scale, MM lb spiropentane/yr | 20 | 20 | 20 | 60 | 60 |
| On-stream Factor | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
| Pentaerythritol Source | Mfd. | Purch. | Purch. | Mfd. | Mfd. |
| Costs Estimated | Min | Min | Max | Min | Max |
| Unamortized Manufacturing Cost, ¢/lb spiropentane | | | | | |
| Raw and Process Materials (with associated process costs) | 93.5 | 115.0 | 141.6 | 85.5 | 108.6 |
| Other Operating Costs | 6.2 | 6.2 | 6.2 | 4.8 | 4.8 |
| Total Unamortized Cost | 99.7 | 121.2 | 147.8 | 90.3 | 113.4 |
| Capital Requirements, $MM | | | | | |
| Spiropentane Unit | 5.9 | 5.9 | 5.9 | 12.2 | 12.2 |
| Tetrachloride Unit | 14.3 | 14.3 | 14.3 | 28.8 | 28.8 |
| Zinc Recovery | 9.5 | 9.5 | 17.9 | 21.7 | 39.7 |
| Iodine Recovery | 3.2 | 3.2 | 6.3 | 6.4 | 12.8 |
| Pentaerythritol Manufacturing | 10.0 | — | — | 20.7 | 20.7 |
| Total Capital Capital, $MM | 42.9 | 32.9 | 44.4 | 89.8 | 114.2 |
| Capital per Annual Pound of Spiropentane Produced, $ | 2.15 | 1.65 | 2.22 | 1.50 | 1.90 |

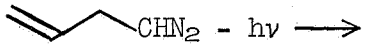


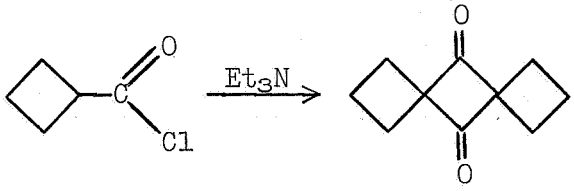




The quantum yield in the photochemical cyclization of butadiene is quite low. Recently a bicyclobutane dicarboxylic ester has been prepared by electrochemical reduction of a symmetrical half-ester of cyclobutane tetracarboxylic acid.[13]

The only example known of a tricyclo(3,1,0,$0^{2,4}$)hexane is a hexamethyl derivative prepared by the sensitized photodimerization of 1-methyl-3,3-dimethylcyclopropene.[14] It should be possible to find other methods for synthesizing derivatives of this highly strained system.

Synthetic routes to spiranes and polyspiranes were investigated and reviewed some years ago by a group headed by E. R. Buchman[15] at the California Institute of Technology. One of the fairly general routes that was used by them and has since been used by others (see the review by Vogel)[16] is the so-called Walborsky reaction, exemplified below as a route to dispiro(3,1,3,1)-decane:




The resulting dispirodiketone has been successfully reduced to the hydrocarbon either with hydrazine sulfate and excess sodium ethylate (Wolf-Kishner reduction) or by reaction with methyl mercaptan and zinc chloride to convert the carbonyl oxygens to dimercaptyl groups, followed by reduction with hydrogen over Raney nickel. Alternative and cheaper routes to the dispiranes would be useful and may be attainable.

Synthesis of a number of cyclopropyl derivatives, including cyclopropyl cyclopropane, has been reported by Slabey, Wise and Gibbons of the Lewis Flight Propulsion Center.[17]

A number of syntheses of strained polycyclic hydrocarbons have recently been reported in the literature; these hydrocarbons include, in addition to compounds considered in this report, bicyclo(2,2,0)hexane, bicyclo(2,1,1)hexane, bicyclo(1,1,1)pentane, tricyclo(2,1,0,$0^{2,5}$)pentane, and tricyclo(3,1,0,$0^{2,6}$)hexane. For references and a discussion of nomenclature see Meinwald and Crandall.[18] At the present state of development of their synthetic chemistry, these compounds are likely to be very expensive.

Cyclopropyl acetylene was prepared by Happel and Marsel[19] by the reaction of cyclopropyl halide and sodium acetylide. We have seen no report of the preparation of dicyclopropyl acetylene, but its synthesis either from cyclopropyl acetylene or via disodium acetylide should be possible. Alternative but more expensive syntheses of cyclopropyl acetylene and of methylcyclopropyl acetylene (1-methyl, 1-ethinylcyclopropane) have been reported by Russian investigators.[20][21]

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## SECTION IX

## CONCLUSIONS AND RECOMMENDATIONS

Significant gains in booster payload can be achieved with energetic hydrocarbons as replacements for RP-1 provided the mass-flow rate of fuel can be enhanced over the existing design. A study of the feasibility of increasing the mass-flow rate of fuel in existing engines as a function of fuel density and viscosity appears to be needed to define the permissible range of these properties for acceptable fuels, and to aid in the choice of fuels whose properties and preparation should be studied further.

Among the candidate fuels, spiropentane and 1,7-octadiyne have been sufficiently studied with regard to preparative chemistry to provide a basis for the development of a manufacturing process; the first appears potentially to be about twice as costly as the second. If adequate mass-flow rates appear to be attainable with these and if their potential performance appears to justify their cost, sufficient amounts should be prepared for an experimental evaluation of their physical properties and thermal stability (including the effectiveness of stabilizers) over the range of pressures and temperatures of practical interest. The preparative program could be used to provide additional data for the development of a manufacturing process. At this stage, sufficient information should be available to decide whether or not to embark on process development.

For the longer term, hydrocarbons such as dispiro(2,1,2,1)octane or dispiro(3,1,3,1)decane with higher density than RP-1 and only moderately low H/C ratios may deserve consideration. Following an exploration and evaluation

of their physical properties, a decision could be made whether to embark on a program of research directed toward the discovery of cheaper methods of synthesis.

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## APPENDIX 1

## SPECIFIC IMPULSE AND OPERATING TEMPERATURES VS O/F RATIO FOR VARIOUS HYDROCARBONS

The curves shown in Figures A1-1 to A1-13 illustrate the variation of specific impulse for individual hydrocarbons with oxygen/fuel weight ratio, $(O/F)_W$, calculated for both equilibrium and frozen expansion. Each of the Figures A1-1 to A1-11 presents data for hydrocarbons with a common value of the hydrogen/carbon atom ratio, r, but different values of x, the heat of formation per gram atom of carbon. It should be noted that some of the curves are for fictitious hydrocarbons with a combination of x and r that does not exist among the specific hydrocarbons listed in Tables 2 through 5 of the text. It should also be noted that the value of x used for some of the hydrocarbons in constructing Figures A1-1 and A1-13 differs slightly from the value assigned in Table 2 of the text; the values in that table have been revised from our earlier estimates in a number of cases.

Figures A1-14 to A1-19 illustrate the change in specific impulse as oxygen/fuel ratio is varied above and below the stoichiometric value for hydrocarbons with values of r equal to 1.0, 1.5 and 2.0 over a range of values of x. In general, the mixture ratio for maximum impulse varies from oxygen-rich to oxygen-lean as x increases at a constant value of r.

Figures A1-20 to A1-30 show the variation of specific impulse with LOX/fuel volume ratio, $(O/F)_V$, calculated for individual hydrocarbons. Since these curves were calculated early in the course of our work, there are some discrepancies between the densities chosen for the hydrocarbons in these calculations and the revised values given in Table 2 of the text. The values used for both $\rho$ and x in the calculations are shown on Figures A1-20 to A1-30 and should be compared with those quoted in Table 2 if there is interest in the precise placement of a particular curve.

Figures A1-31 to A1-38 show plots of the combustion chamber temperature vs oxygen/fuel weight ratio for various values of x, the heat of formation per carbon atom. Each of these figures is concerned with a fixed value of the hydrogen/carbon atom ratio r. The values of r considered are 1.00, 1.143, 1.50, 1.60 and 2.0. On each chart two lines are shown intersecting the curves; these lines represent approximate loci for maximum specific impulse for either frozen expansion (F) or equilibrium expansion (E).

Corresponding charts for the throat and exhaust temperatures have not been prepared; approximate values can be estimated from the chamber temperatures and the data plotted in Figures 4 through 7 of the text.

 Figures A1-1 through A1-38 follow

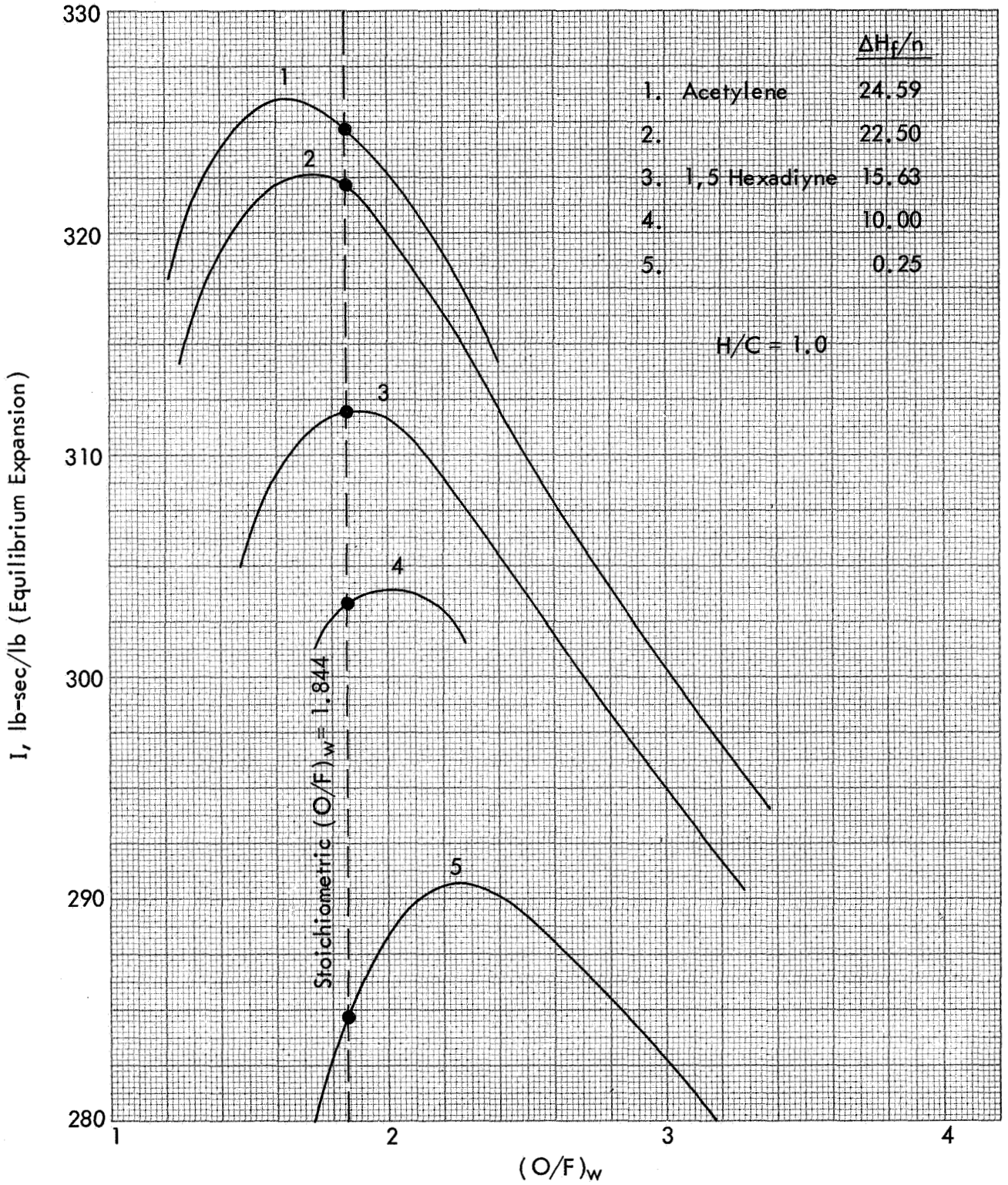


Figure A1-1. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
1000 psia/atm

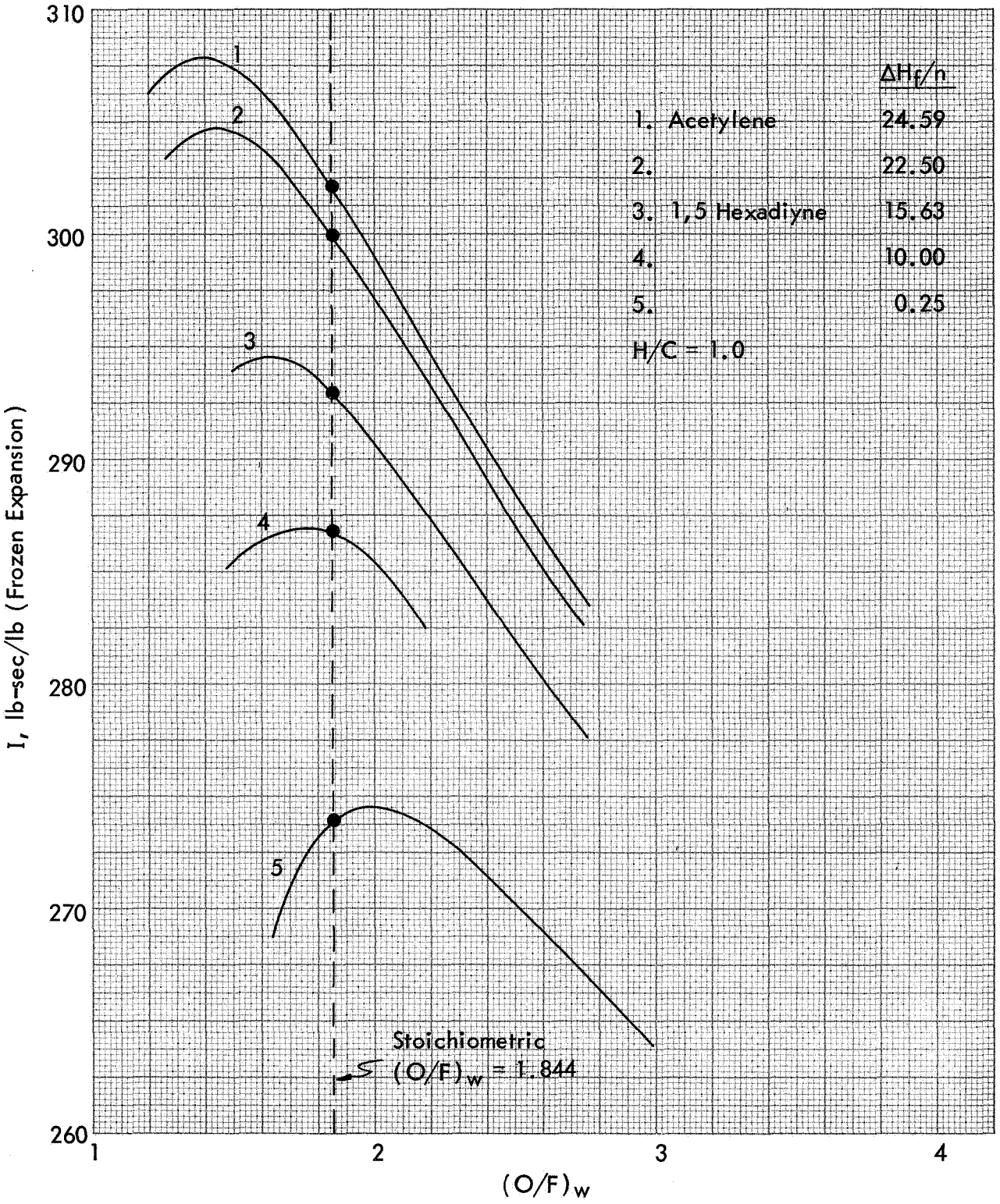


Figure A1-2. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
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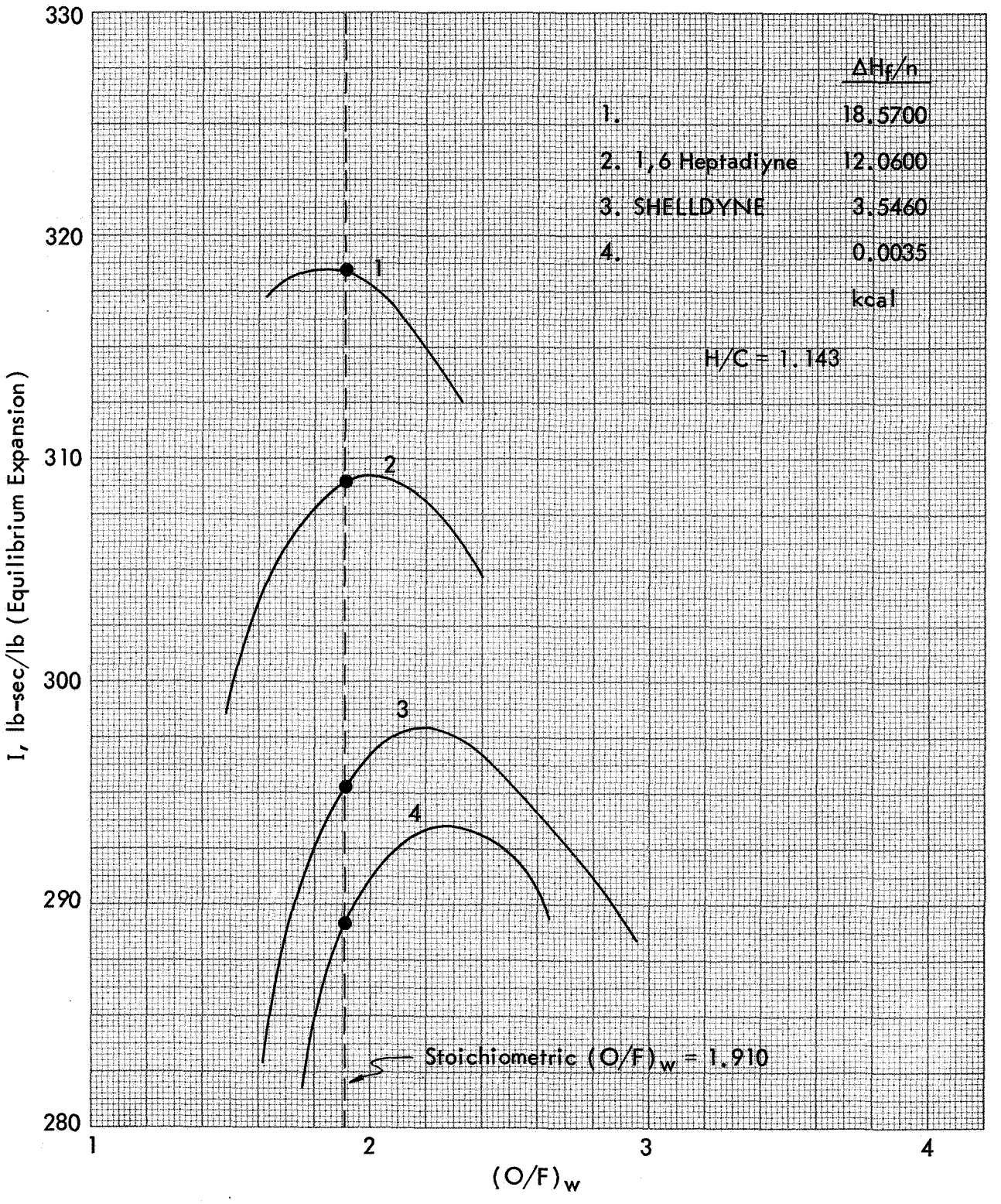


Figure A1-3. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
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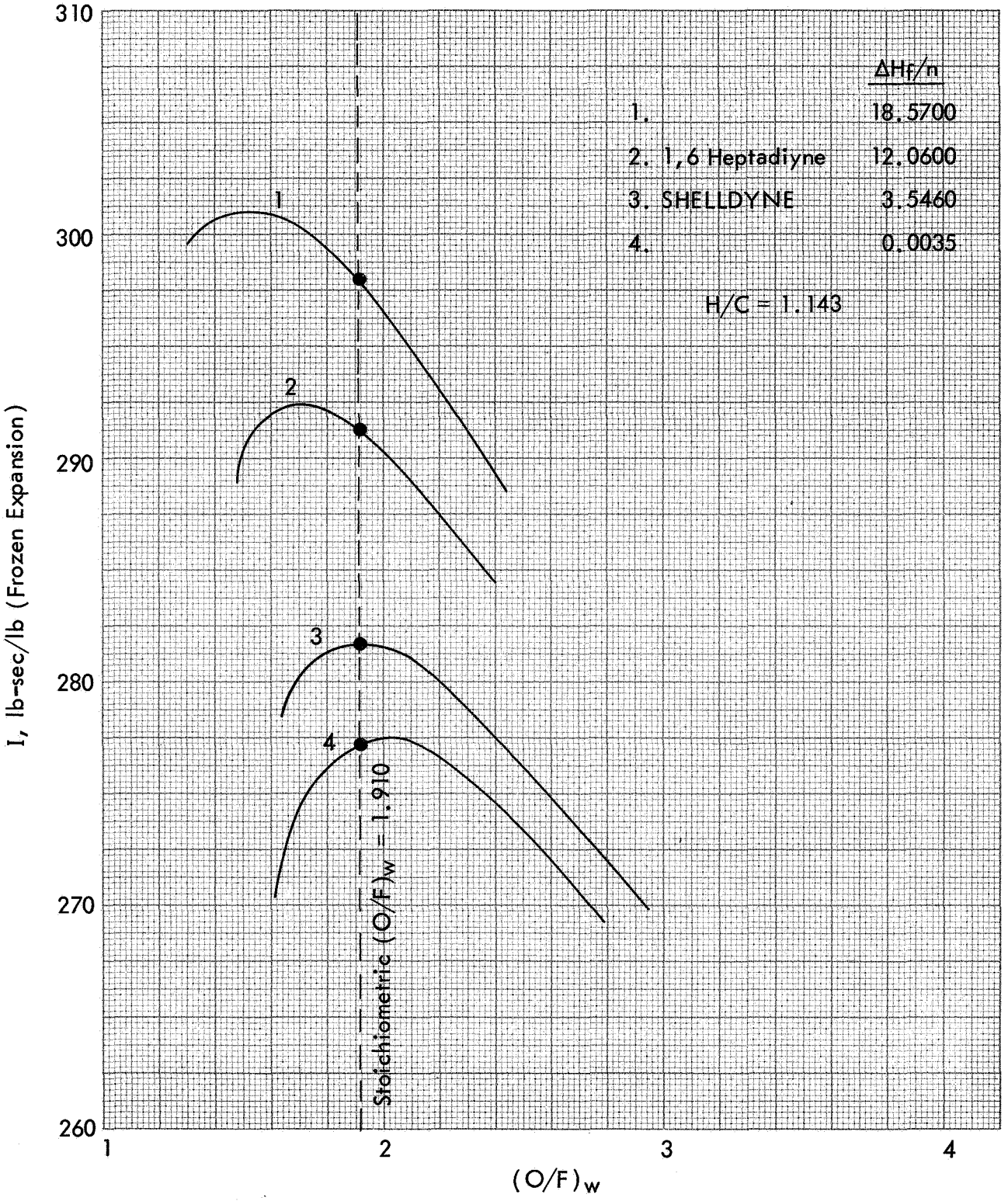


Figure A1-4. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
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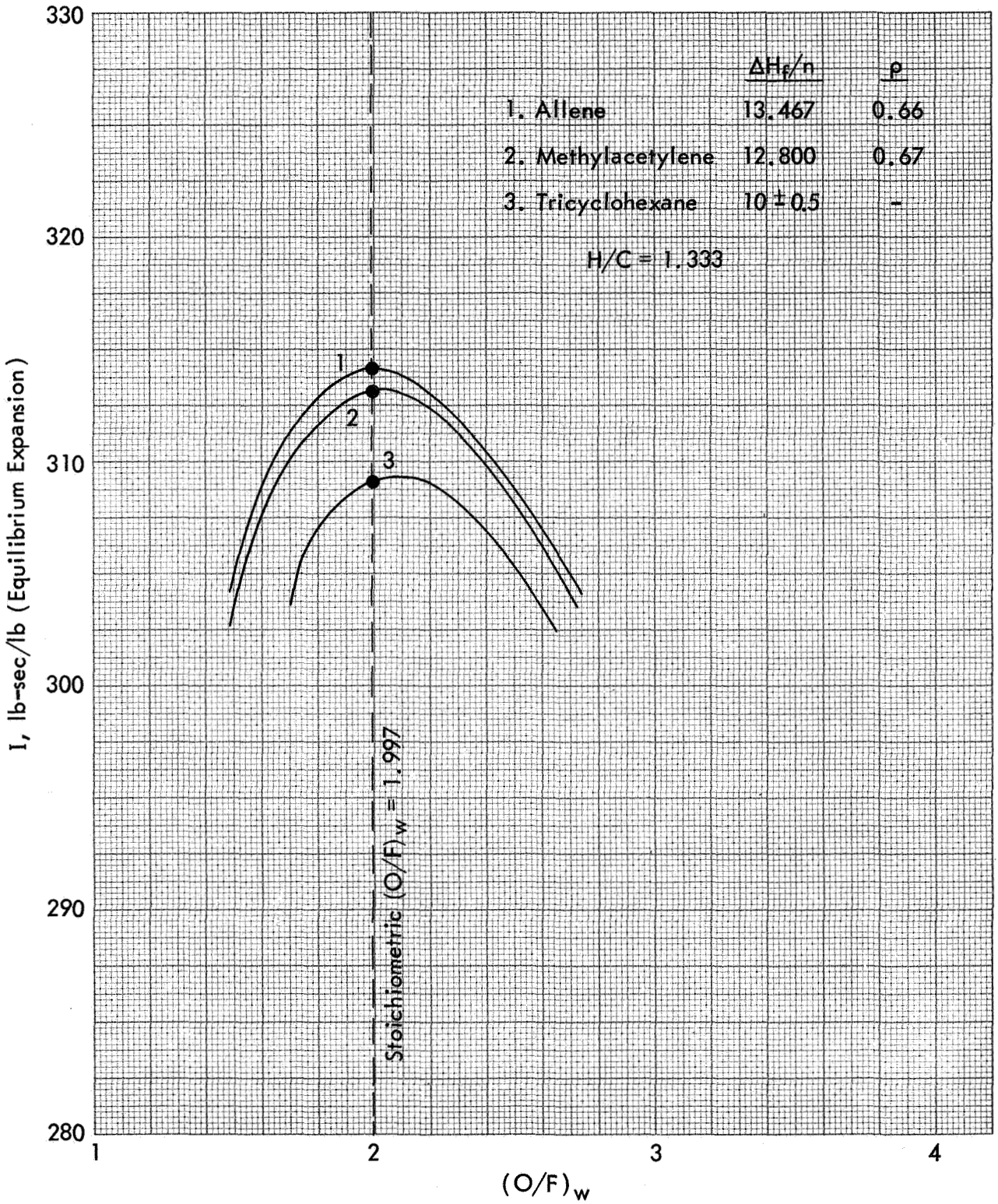


Figure A1-5. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
1000 psia/atm

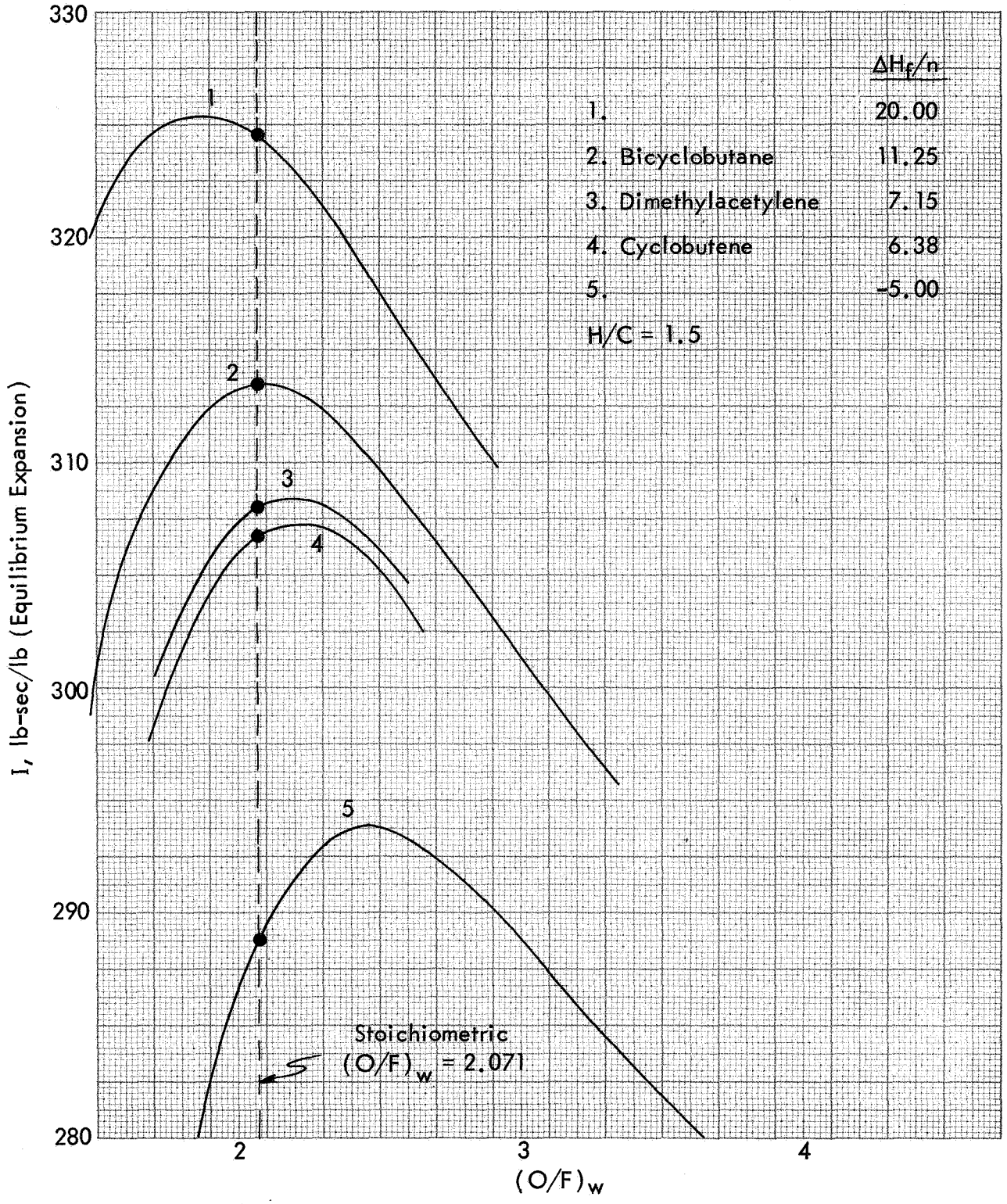


Figure A1-6. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
1000 psia/atm

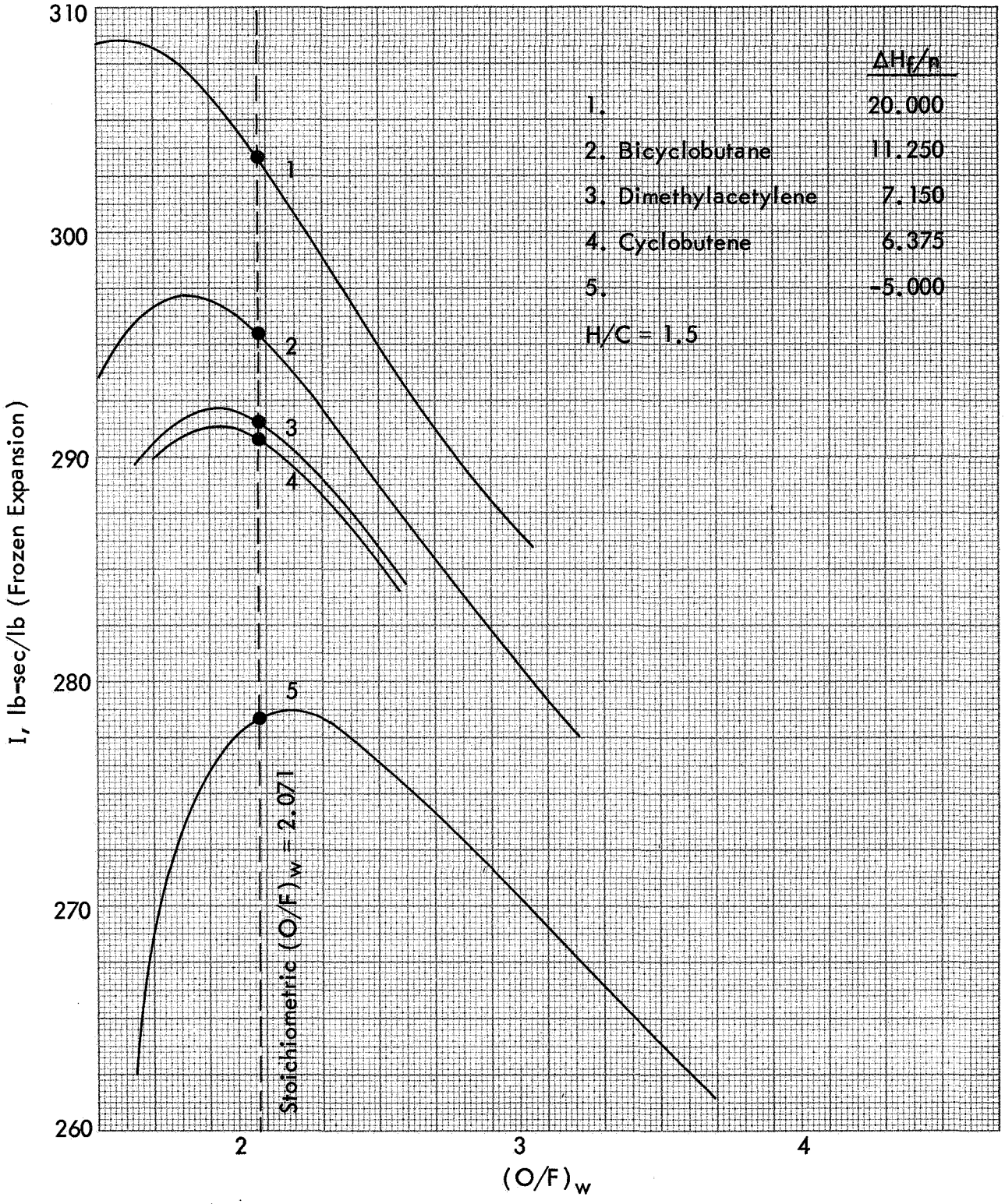


Figure A1-7. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBON

1000 psia/atm

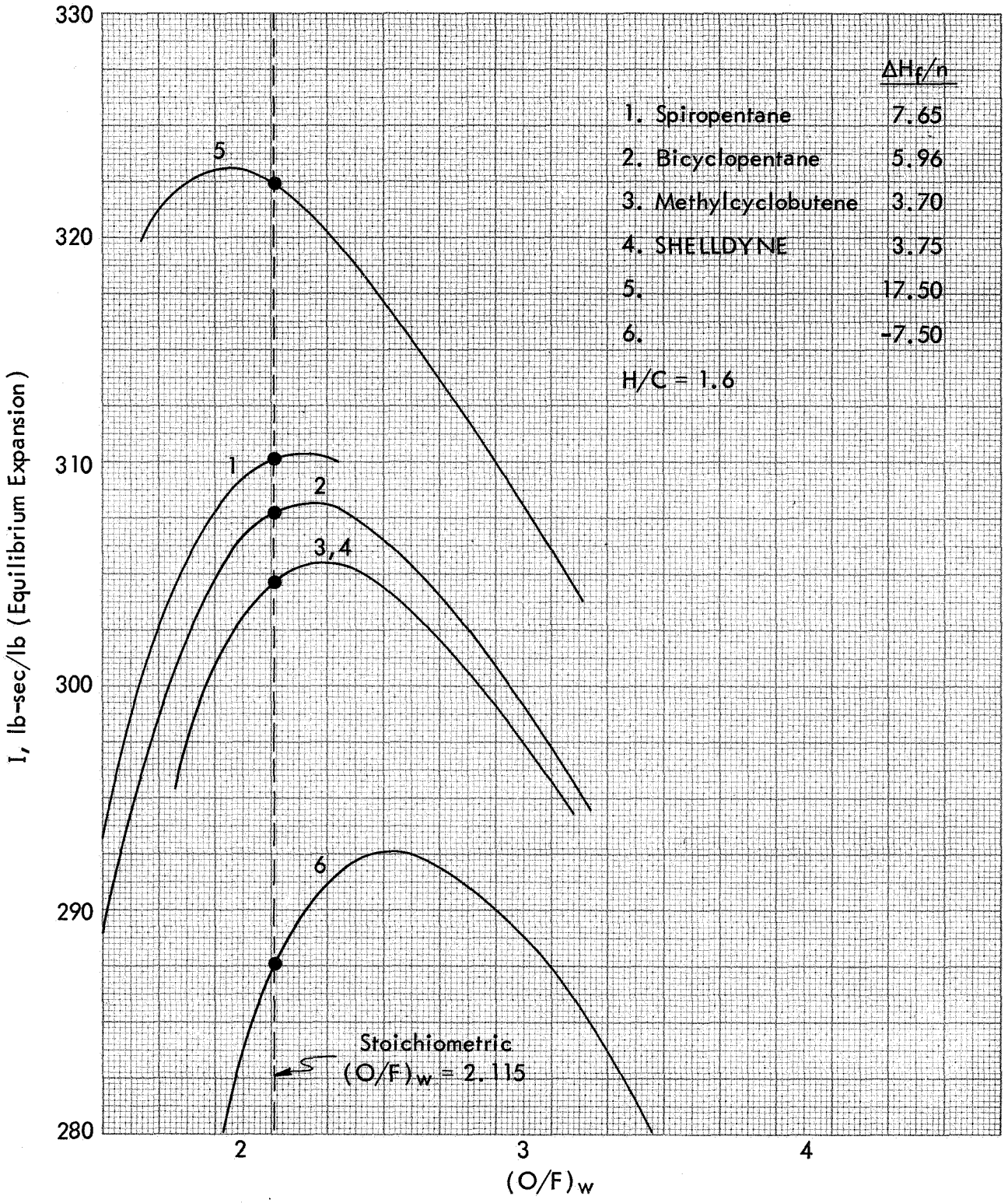


Figure A1-8. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
1000 psia/atm

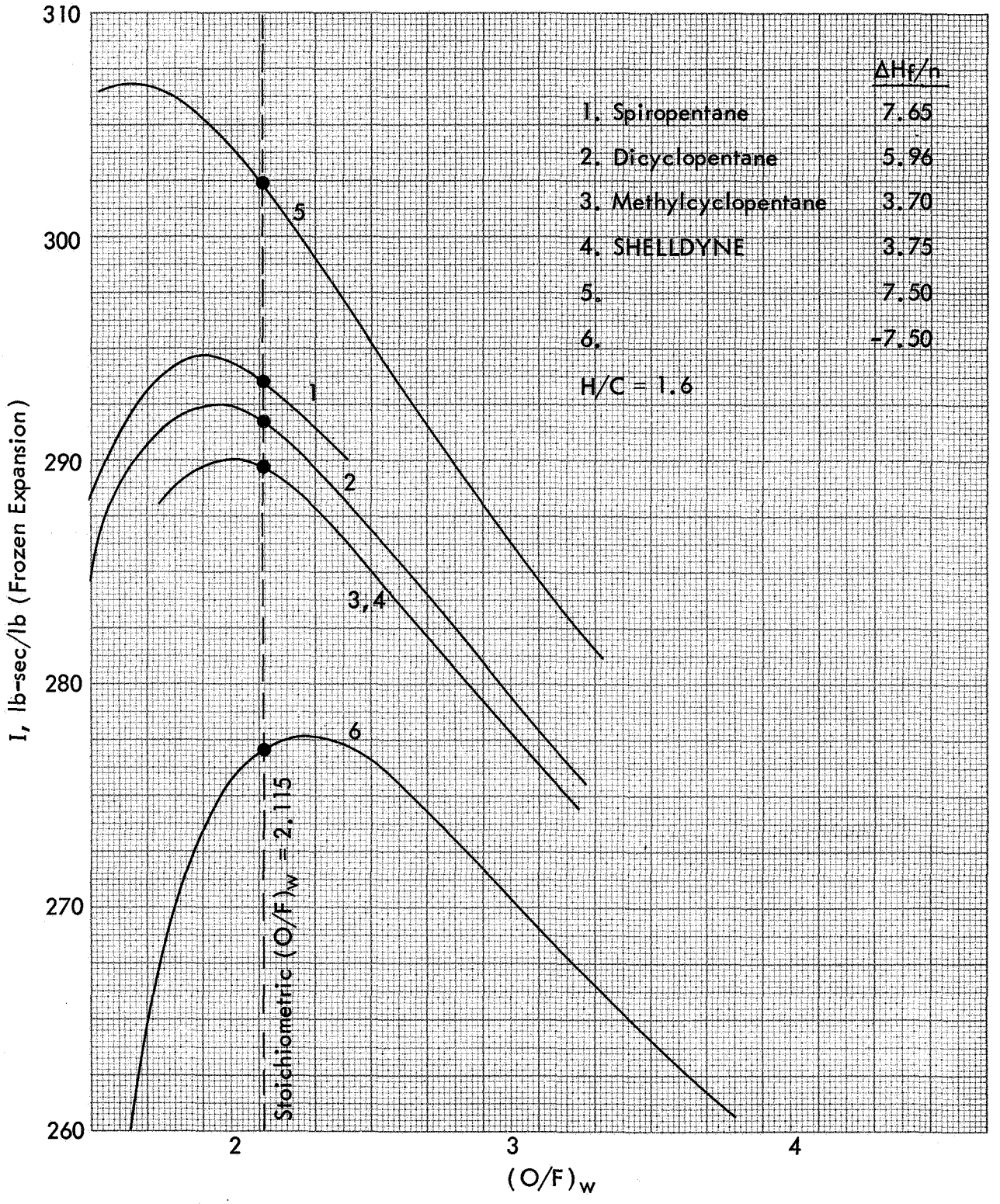


Figure A1-9. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
1000 psia/atm

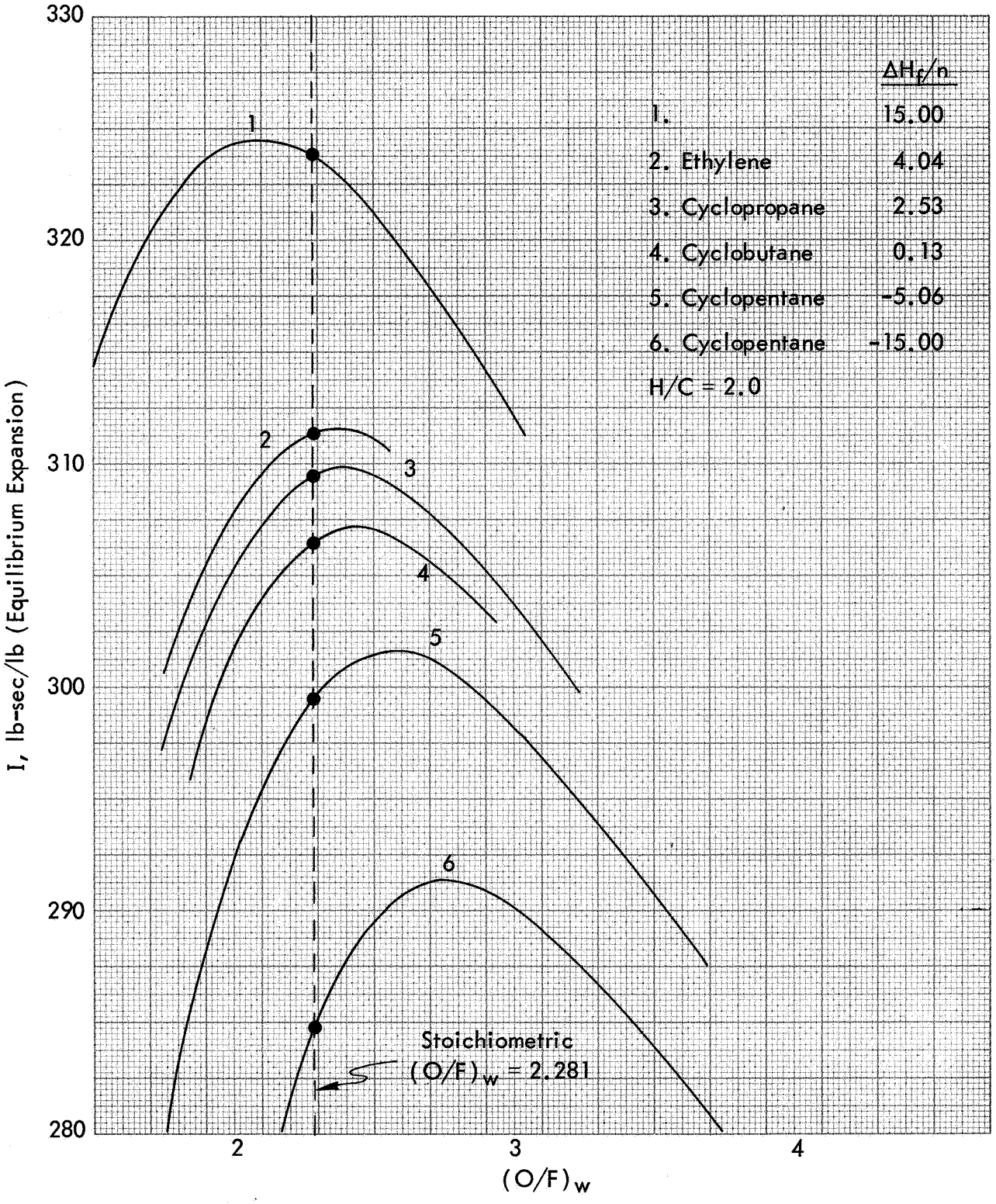


Figure A1-10. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
1000 psia/atm

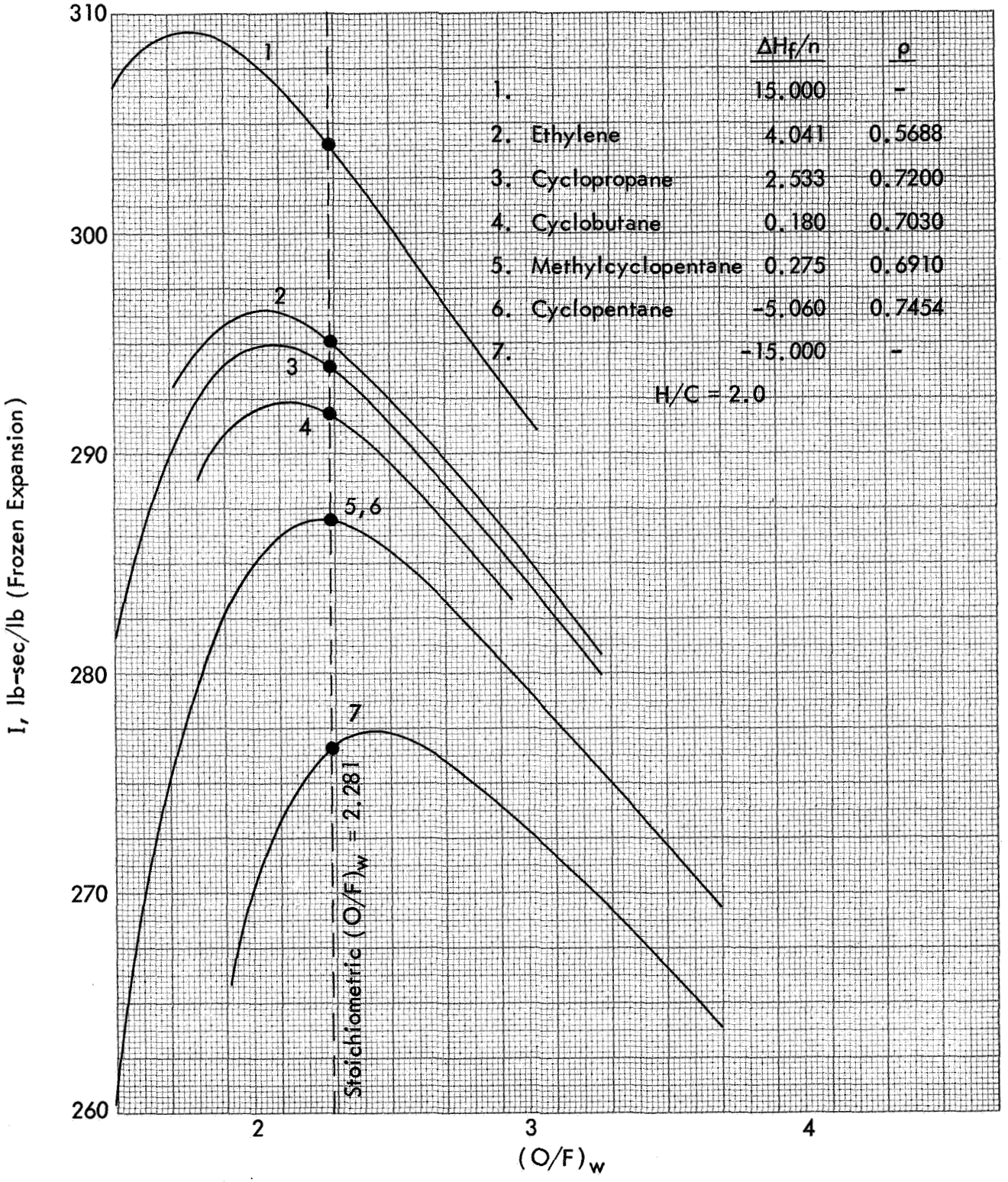


Figure A1-11. SPECIFIC IMPULSE vs $(O/F)_w$ FOR HYDROCARBONS
1000 psia/atm

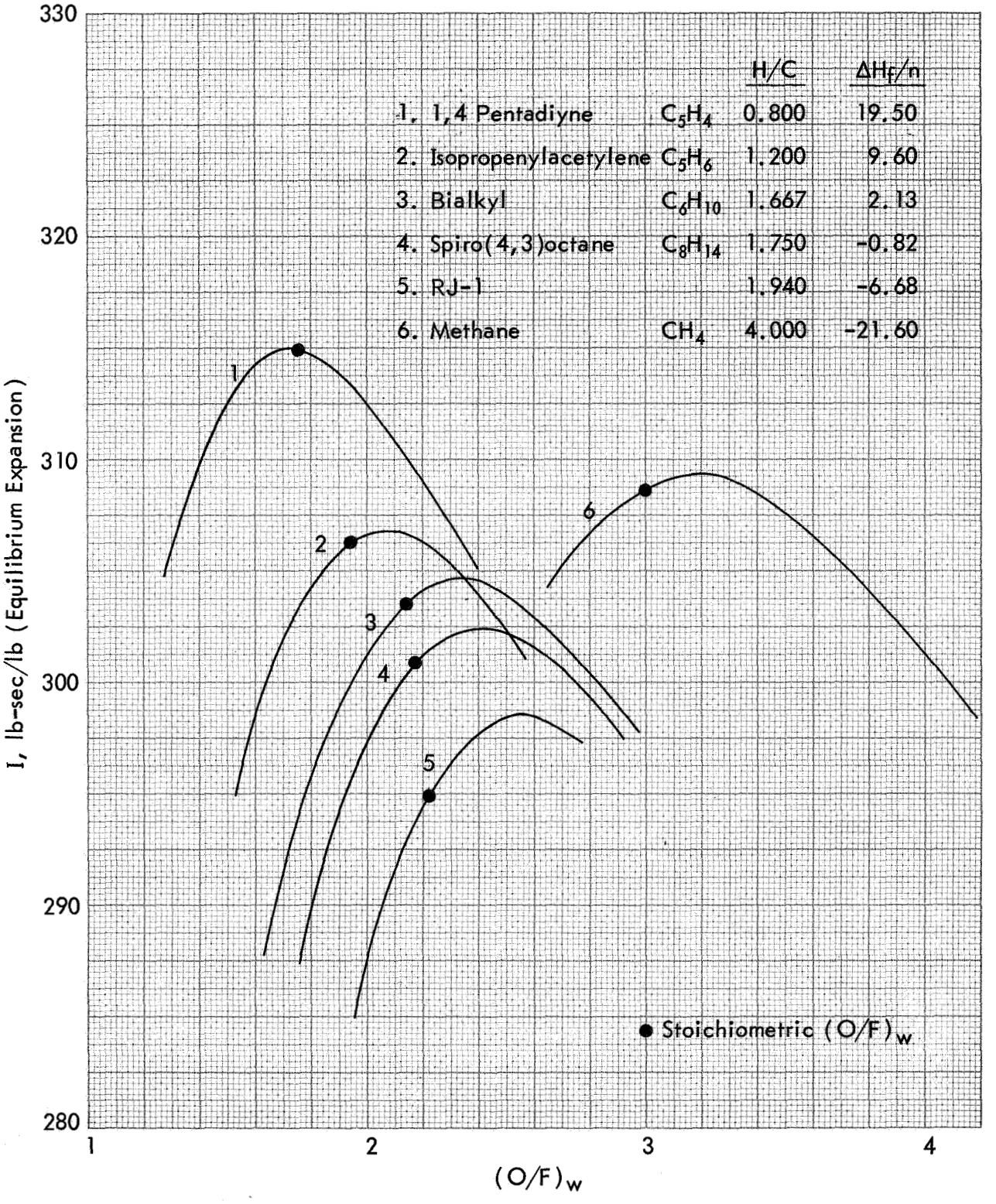


Figure A1-12. SPECIFIC IMPULSE vs $(O/F)_W$ OF HYDROCARBONS
1000 psia/atm

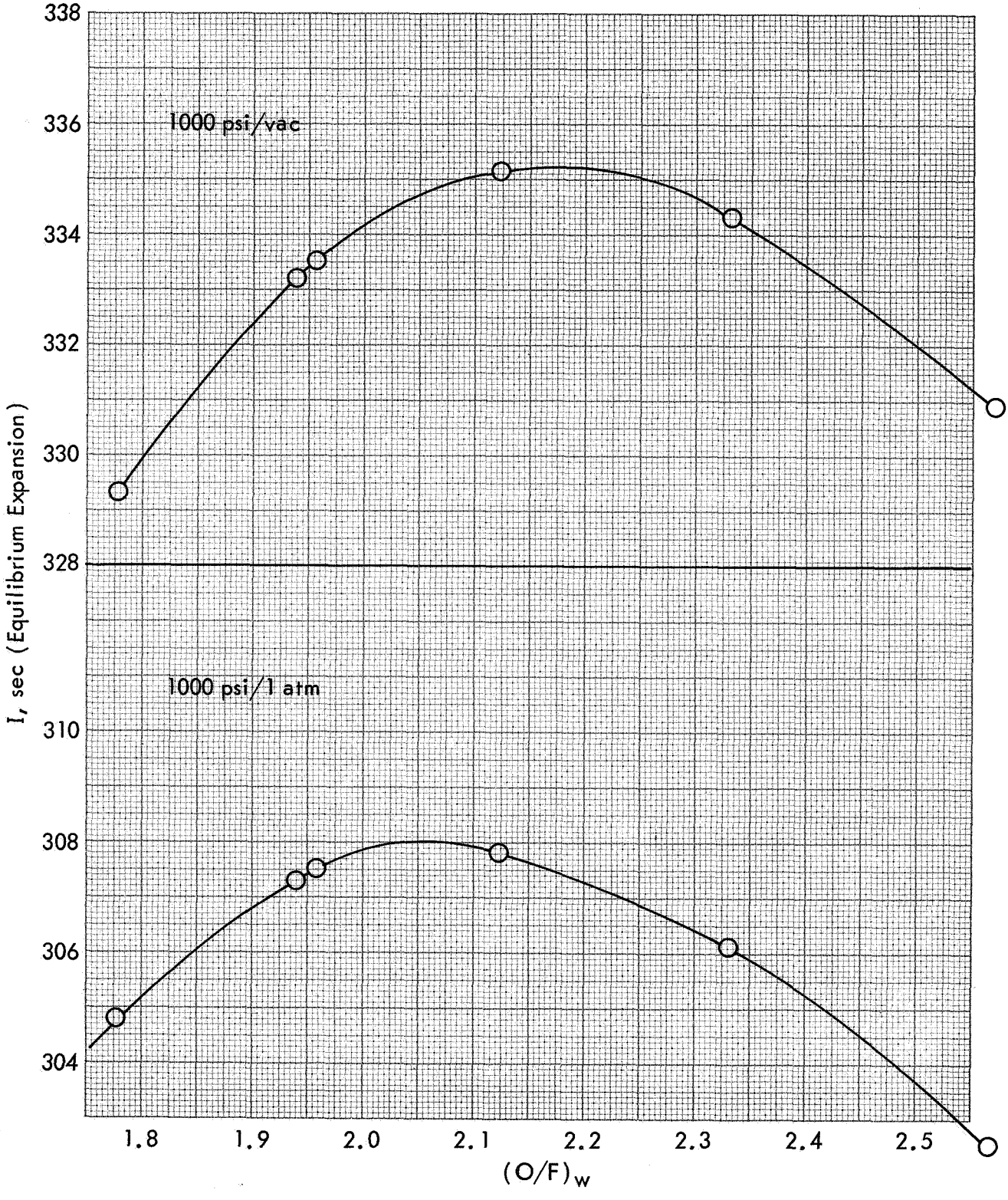


Figure A1-12a. SPECIFIC IMPULSE vs $(O/F)_W$ FOR 1,7 OCTADIYNE, $C_8H_{10}$
Assuming x = 9.80 kcal/gm Atom Carbon

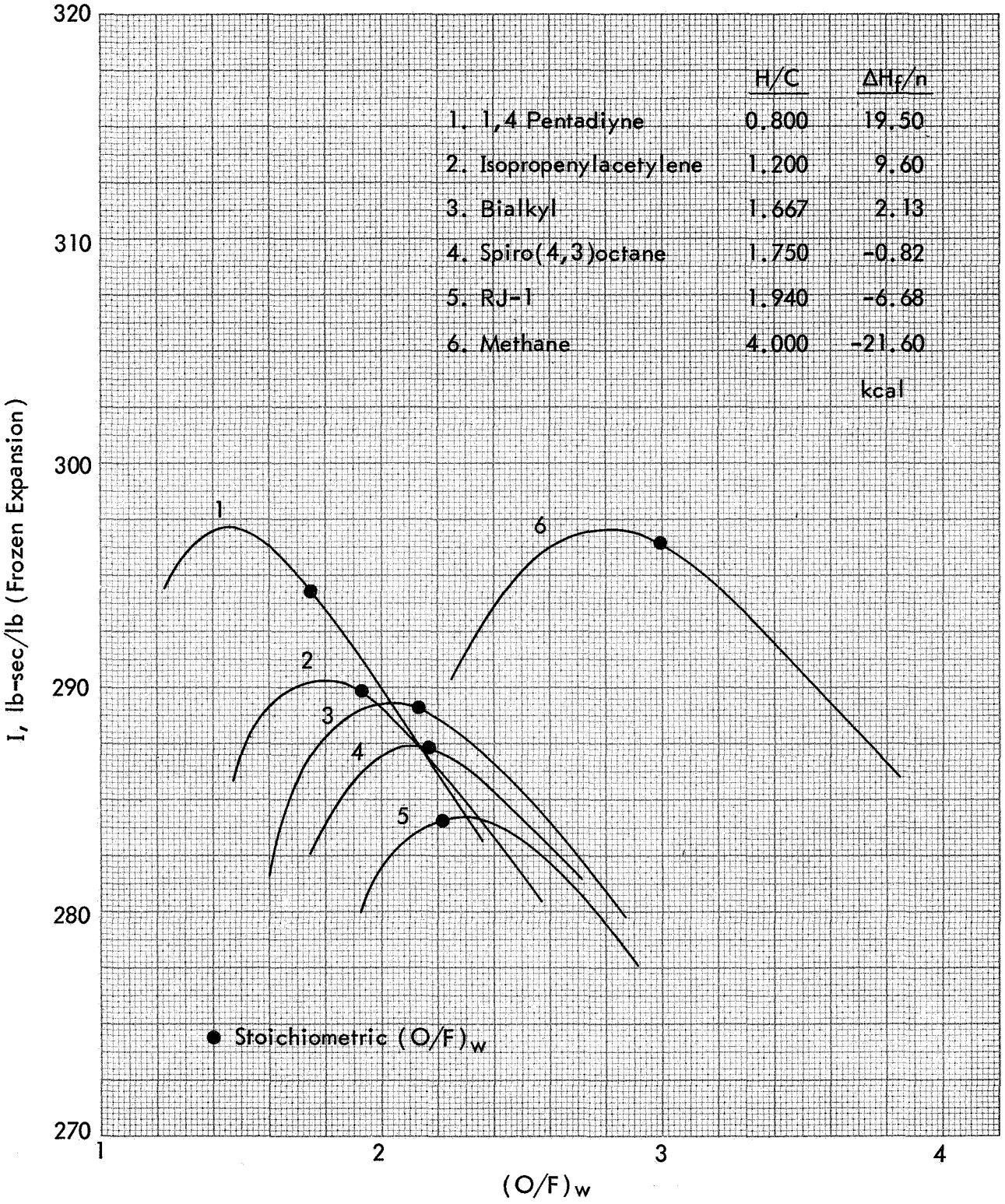


Figure A1-13. SPECIFIC IMPULSE vs $(O/F)_W$ FOR HYDROCARBONS
1000 psia/atm

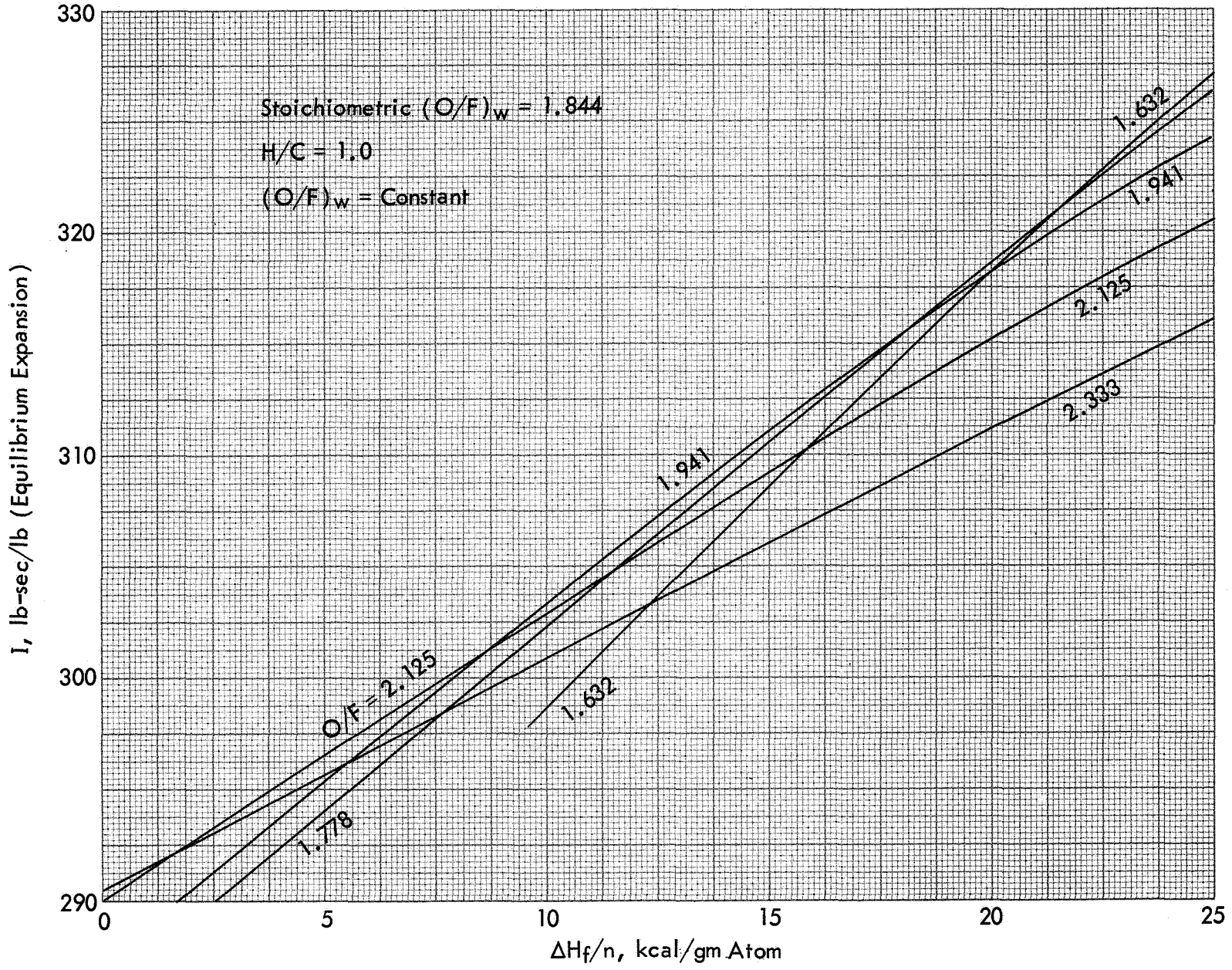


Figure A1-14. SPECIFIC IMPULSE vs $\Delta H_f/n$ FOR HYDROCARBONS

1000 psia/atm

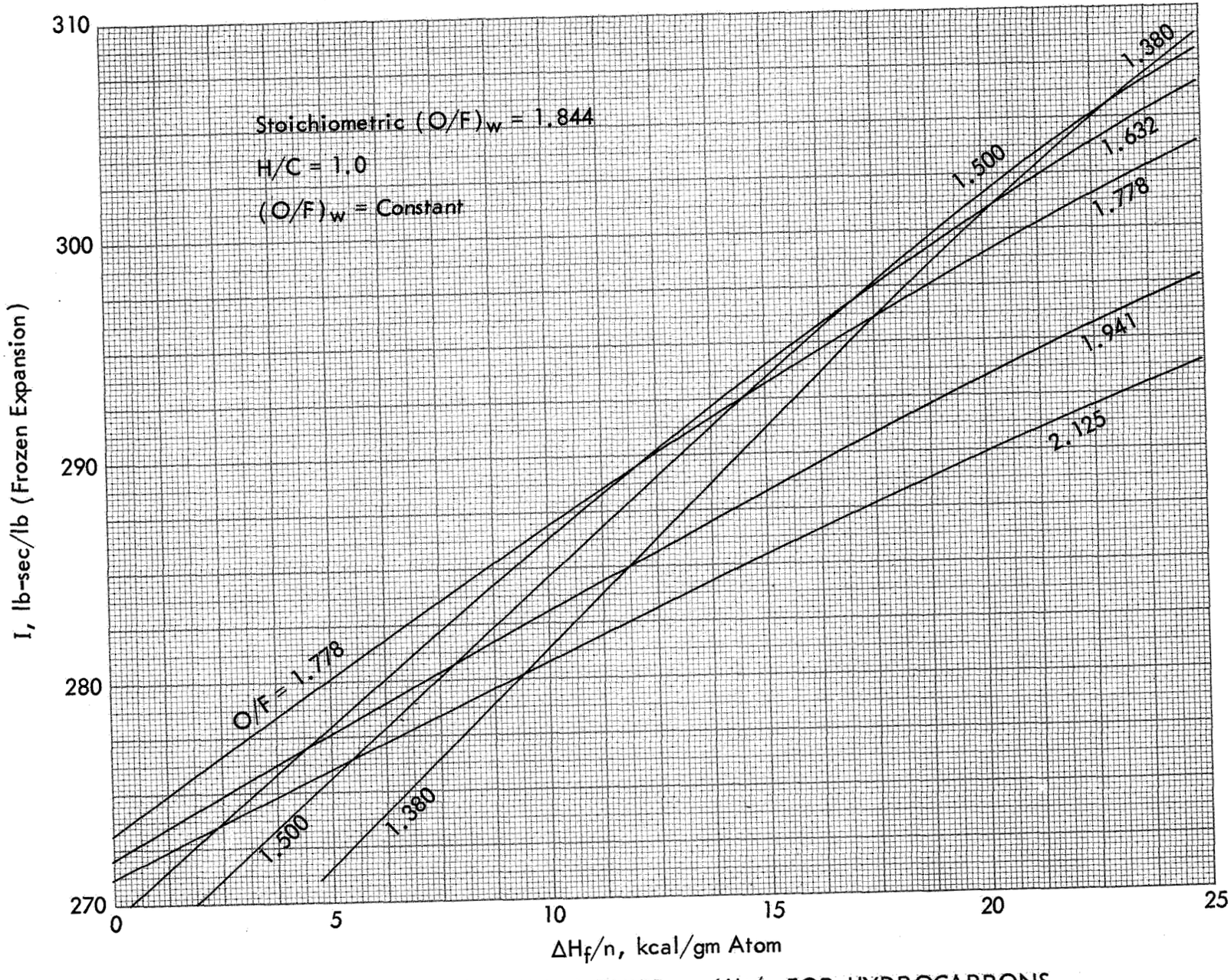


Figure A1-15. SPECIFIC IMPULSE vs $\Delta H_f/n$ FOR HYDROCARBONS
1000 psia/atm

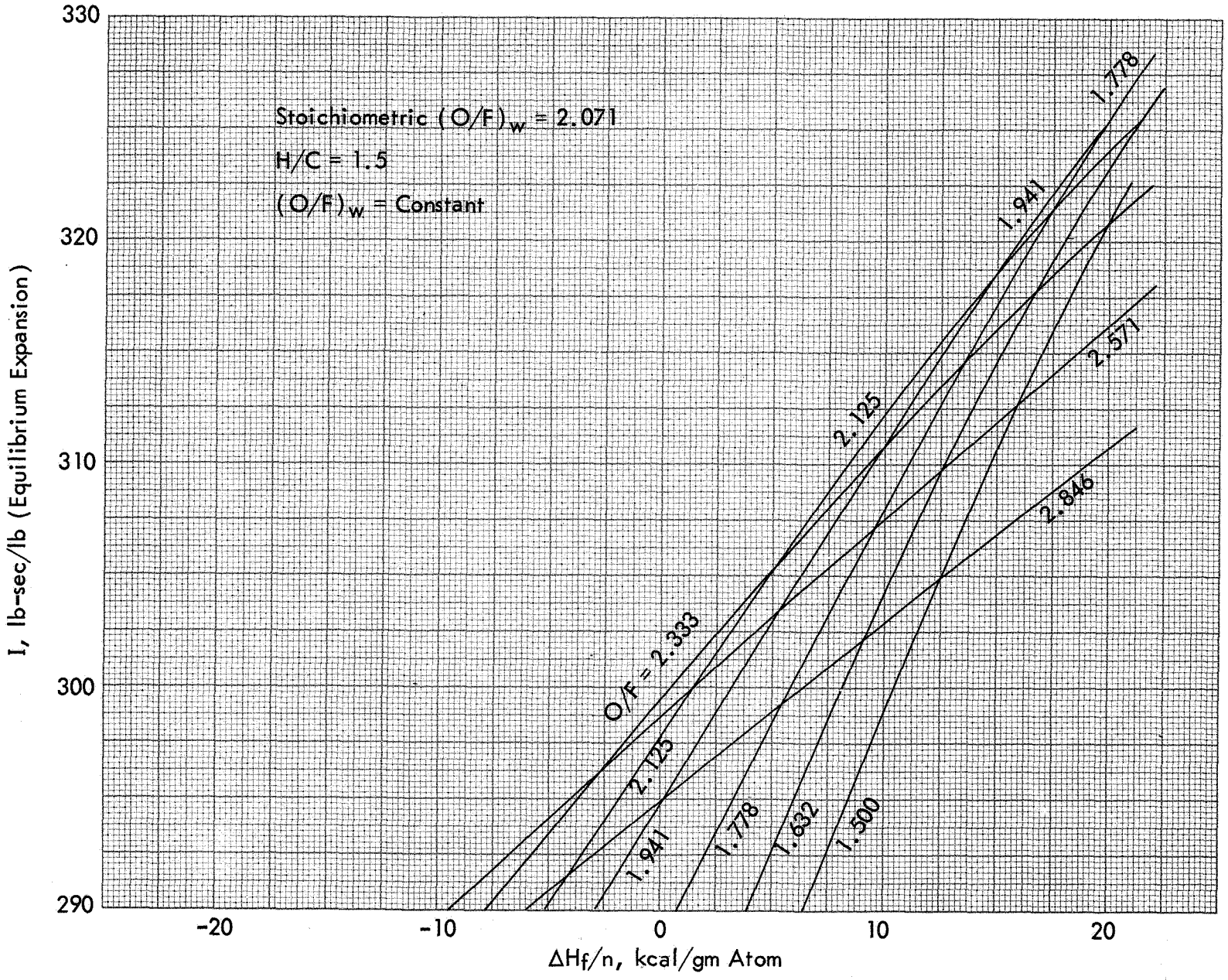


Figure A1-16. SPECIFIC IMPULSE vs $\Delta H_f/n$ FOR HYDROCARBONS
1000 psia/atm

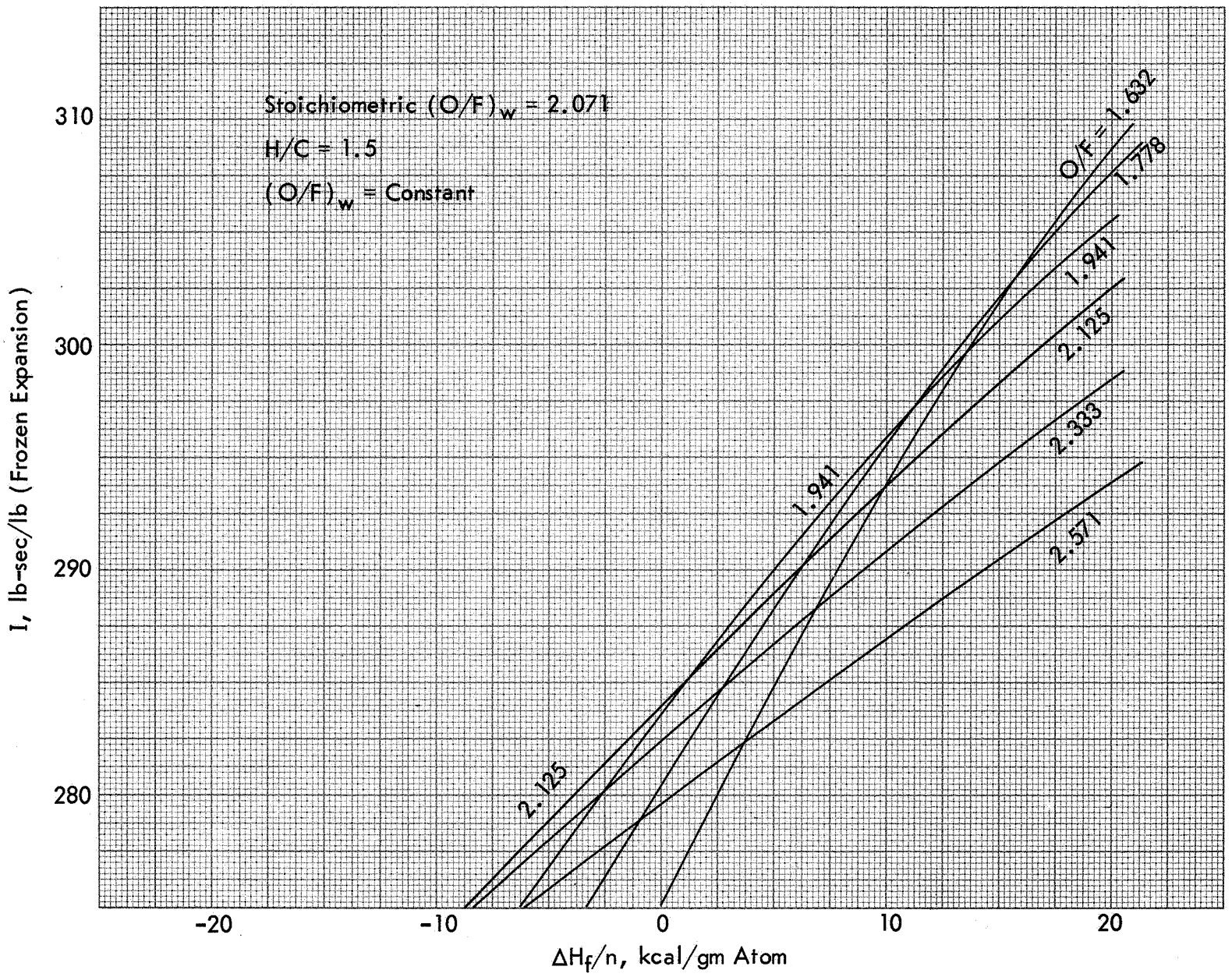


Figure A1-17. SPECIFIC IMPULSE vs $\Delta H_f/n$ FOR HYDROCARBONS
1000 psia/atm

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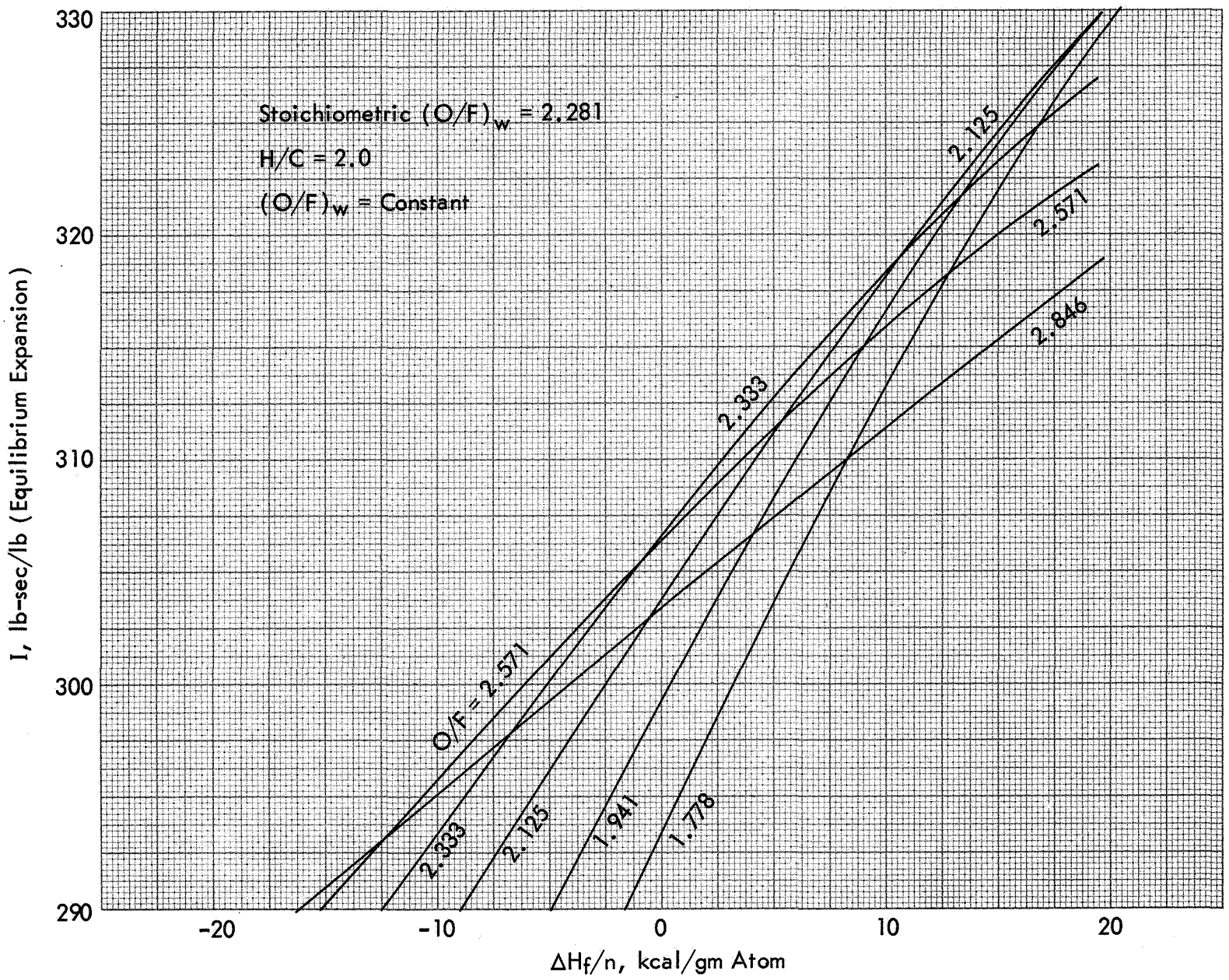


Figure A1-18. SPECIFIC IMPULSE vs $\Delta H_f/n$ FOR HYDROCARBONS
1000 psia/atm

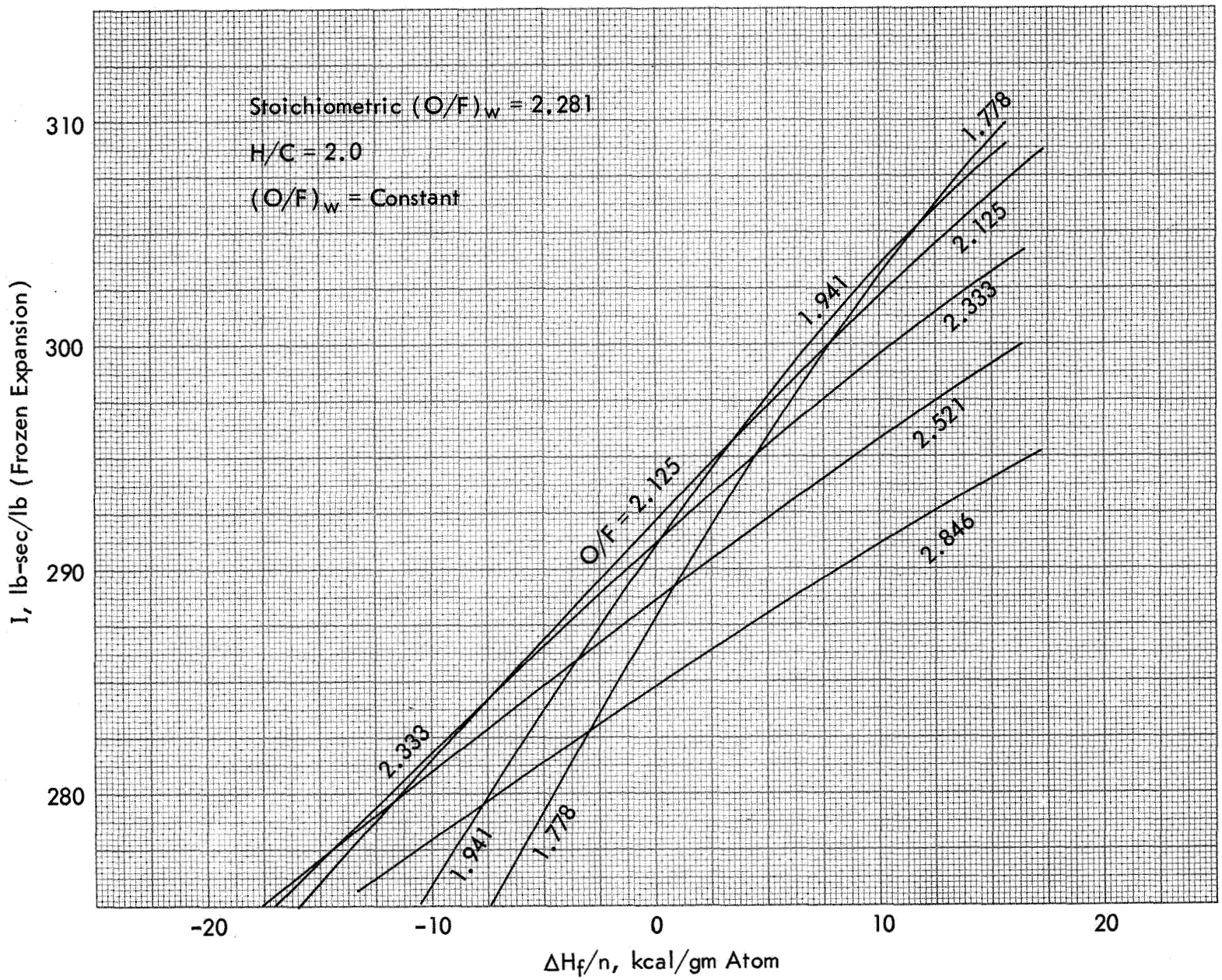


Figure A1-19. SPECIFIC IMPULSE vs $\Delta H_f/n$ FOR HYDROCARBONS
1000 psia/atm

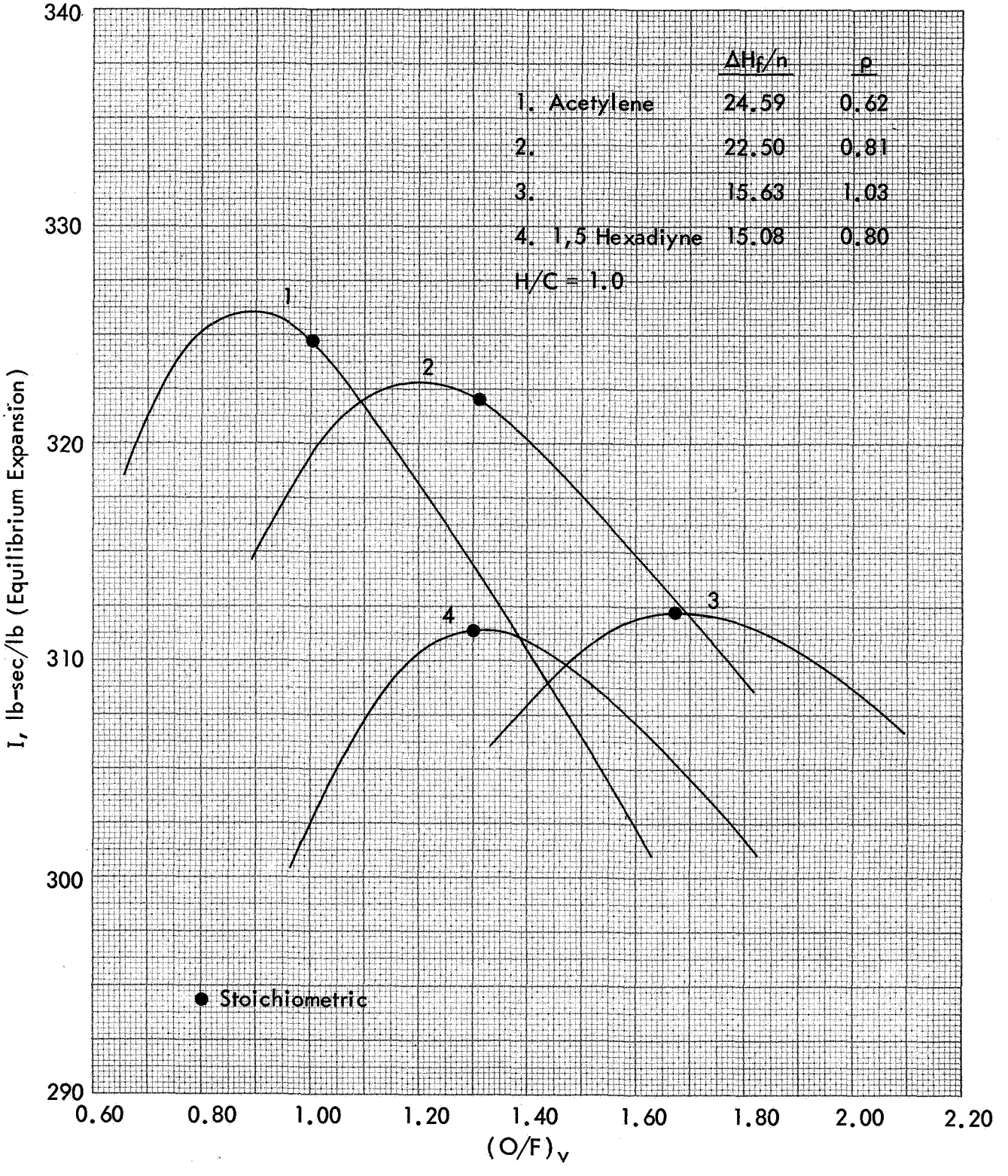


Figure A1-20. SPECIFIC IMPULSE vs $(O/F)_v$ FOR HYDROCARBONS
1000 psia/atm

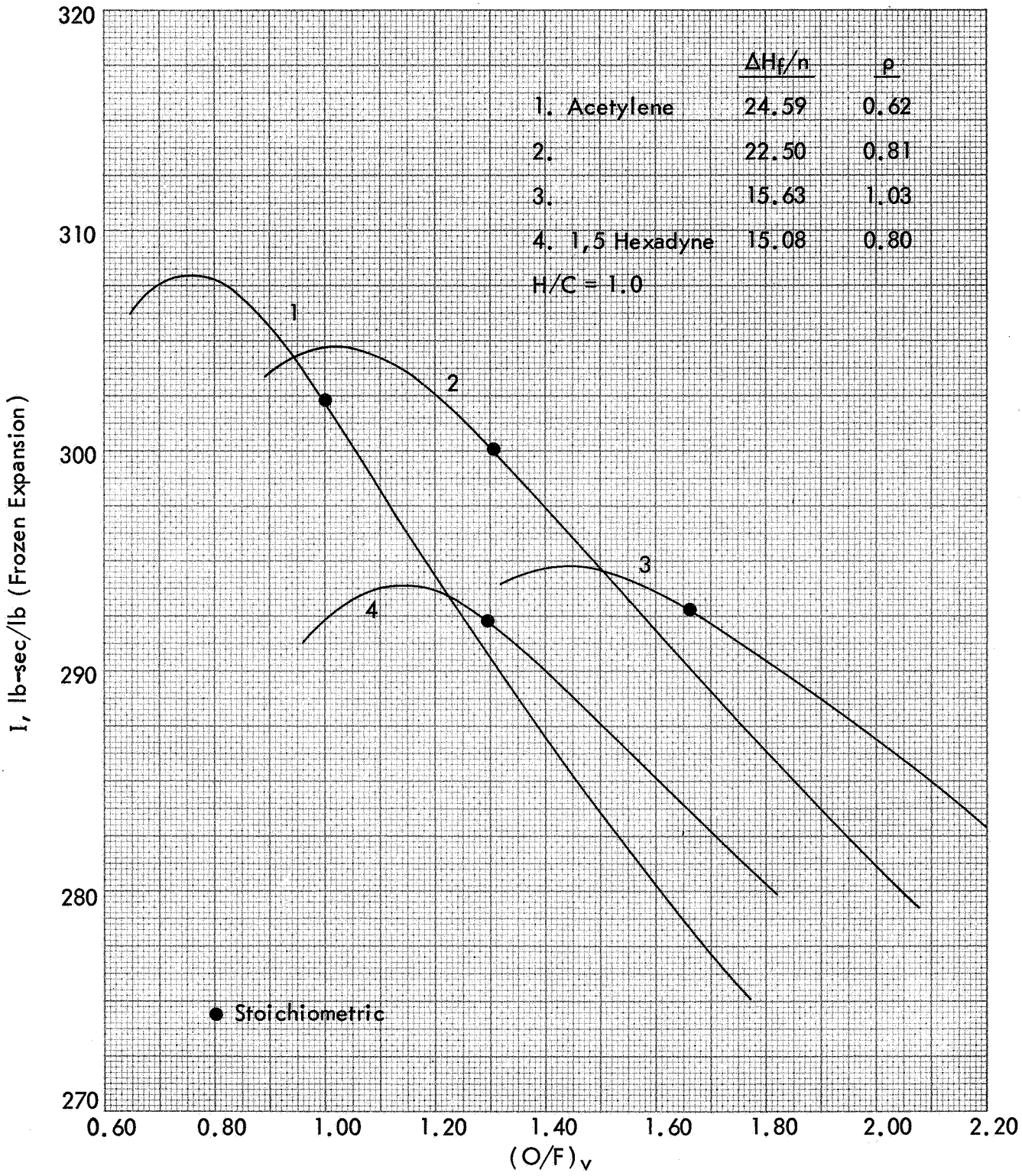


Figure A1-21. SPECIFIC IMPULSE vs $(O/F)_V$ FOR HYDROCARBONS
1000 psia/atm

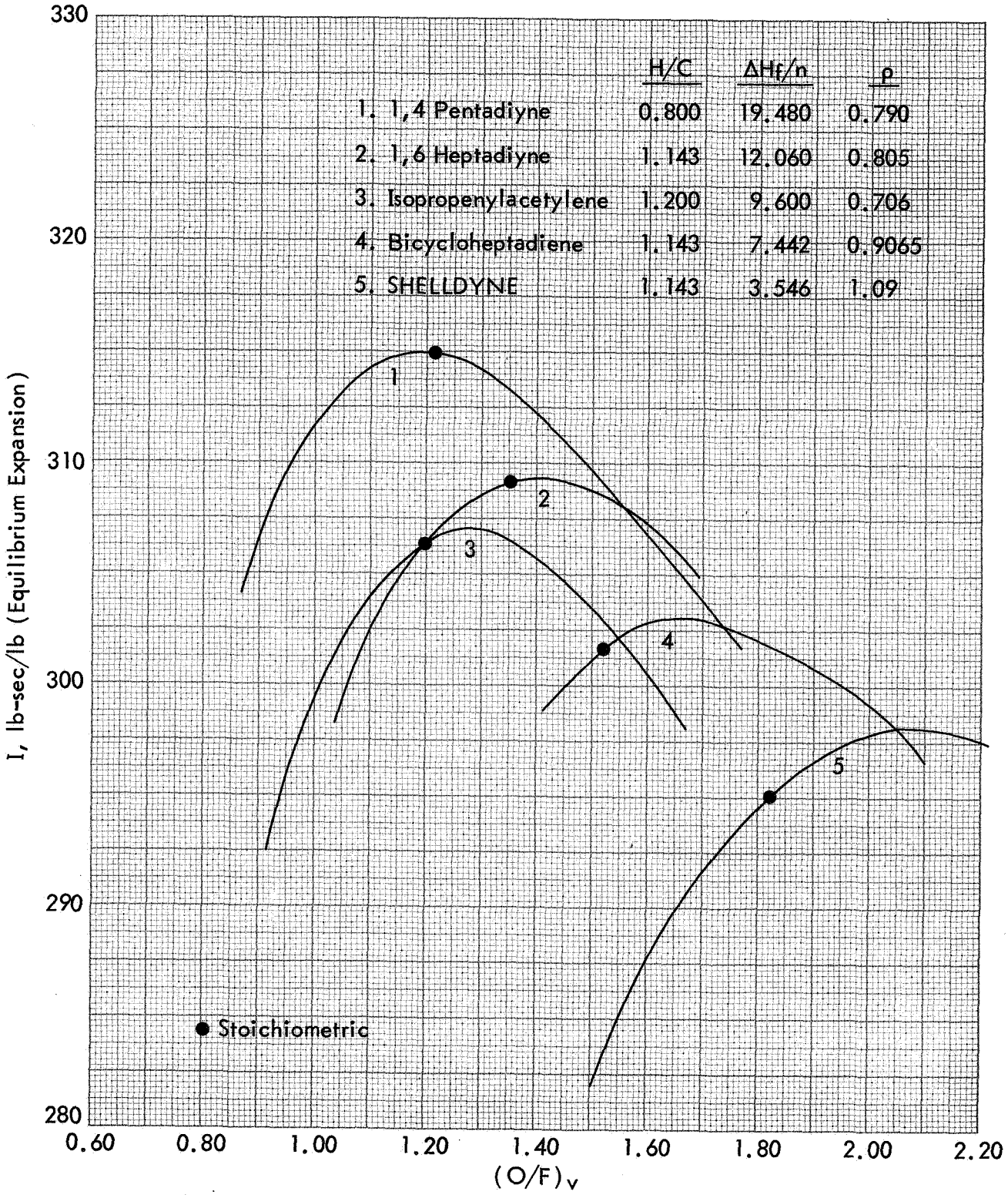


Figure A1-22. SPECIFIC IMPULSE vs $(O/F)_v$ FOR HYDROCARBONS
1000 psia/atm

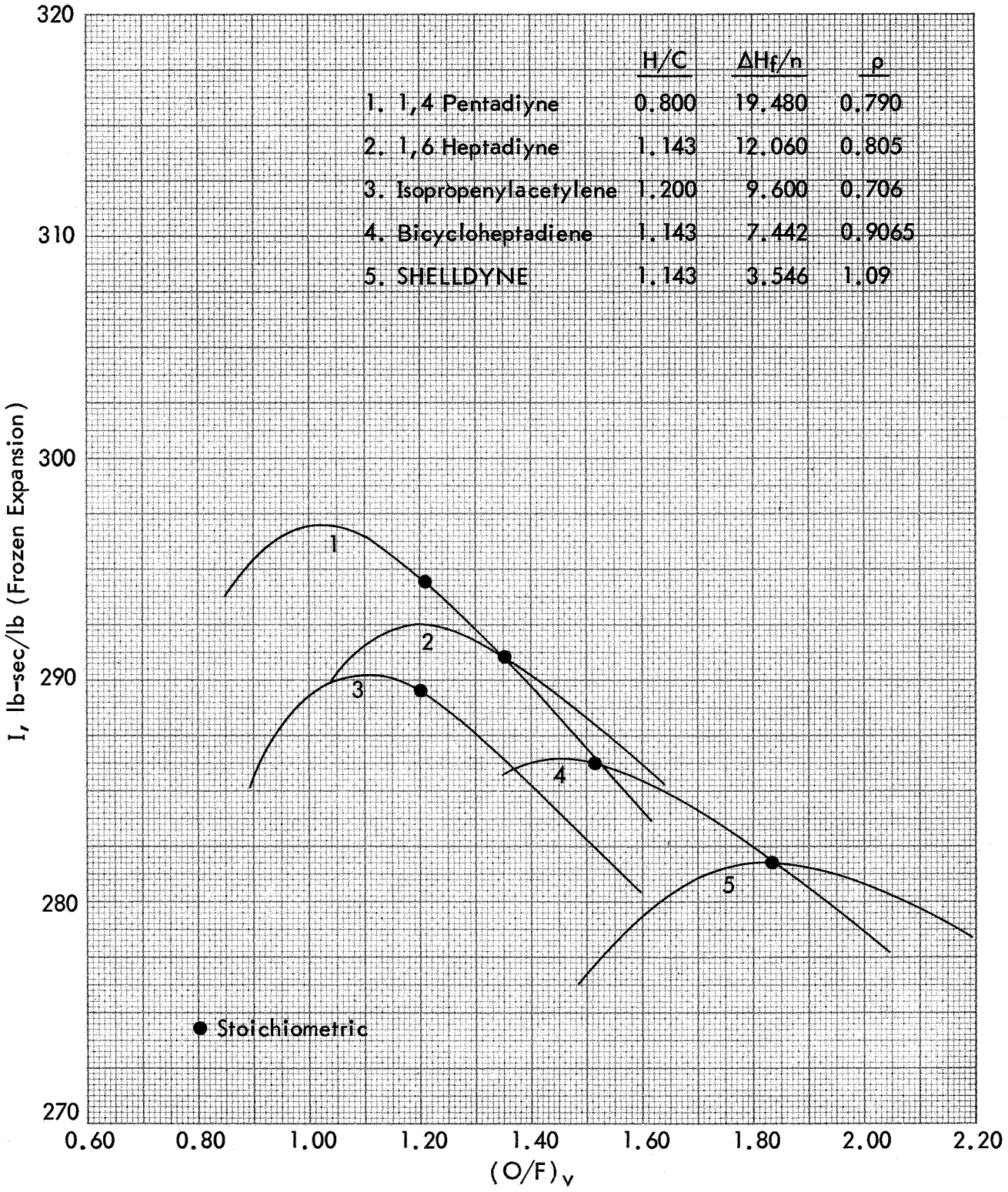


Figure A1-23. SPECIFIC IMPULSE vs $(O/F)_V$ FOR HYDROCARBONS
1000 psia/atm

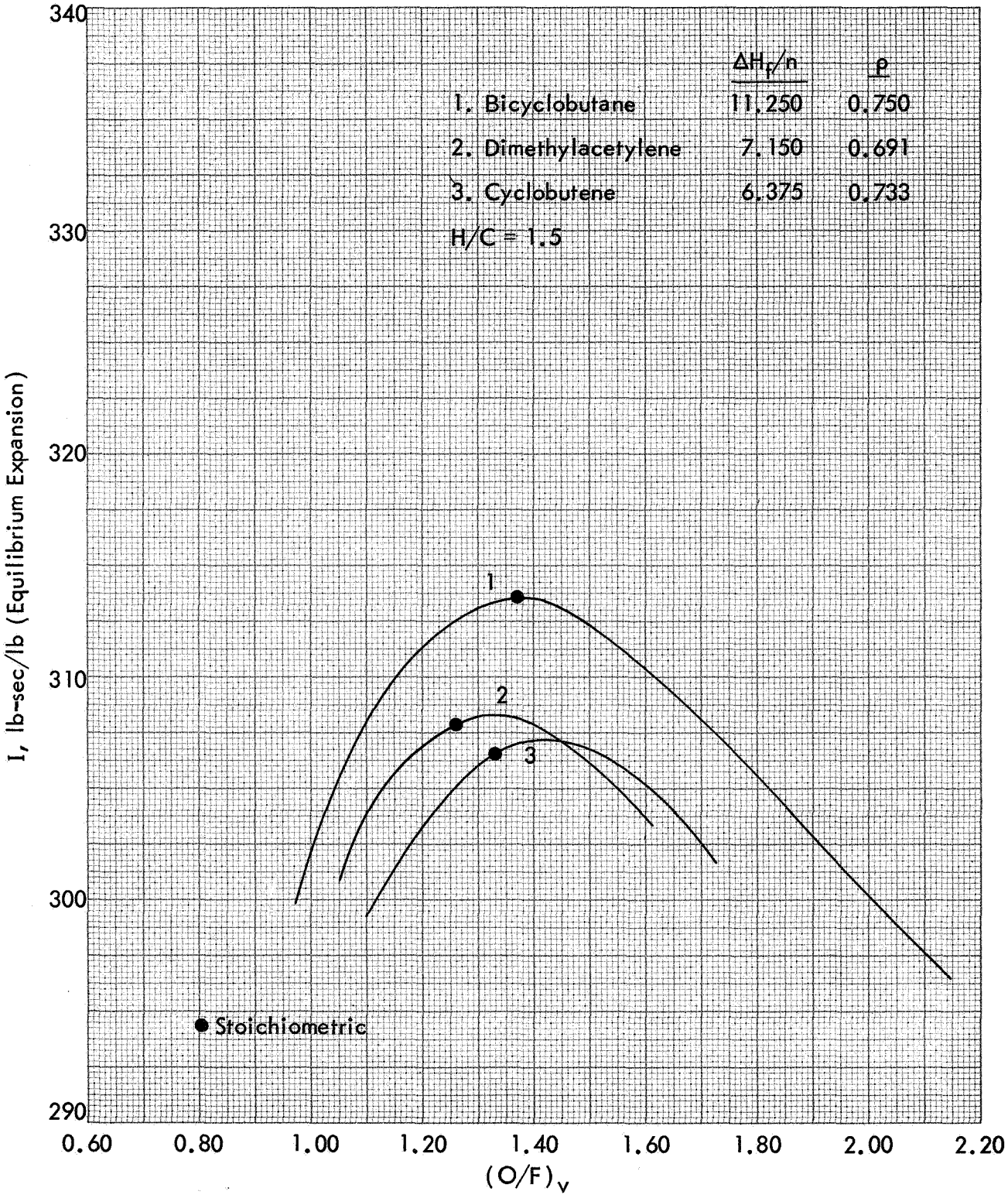


Figure A1-24. SPECIFIC IMPULSE $(O/F)_V$ FOR HYDROCARBONS
1000 psia/atm

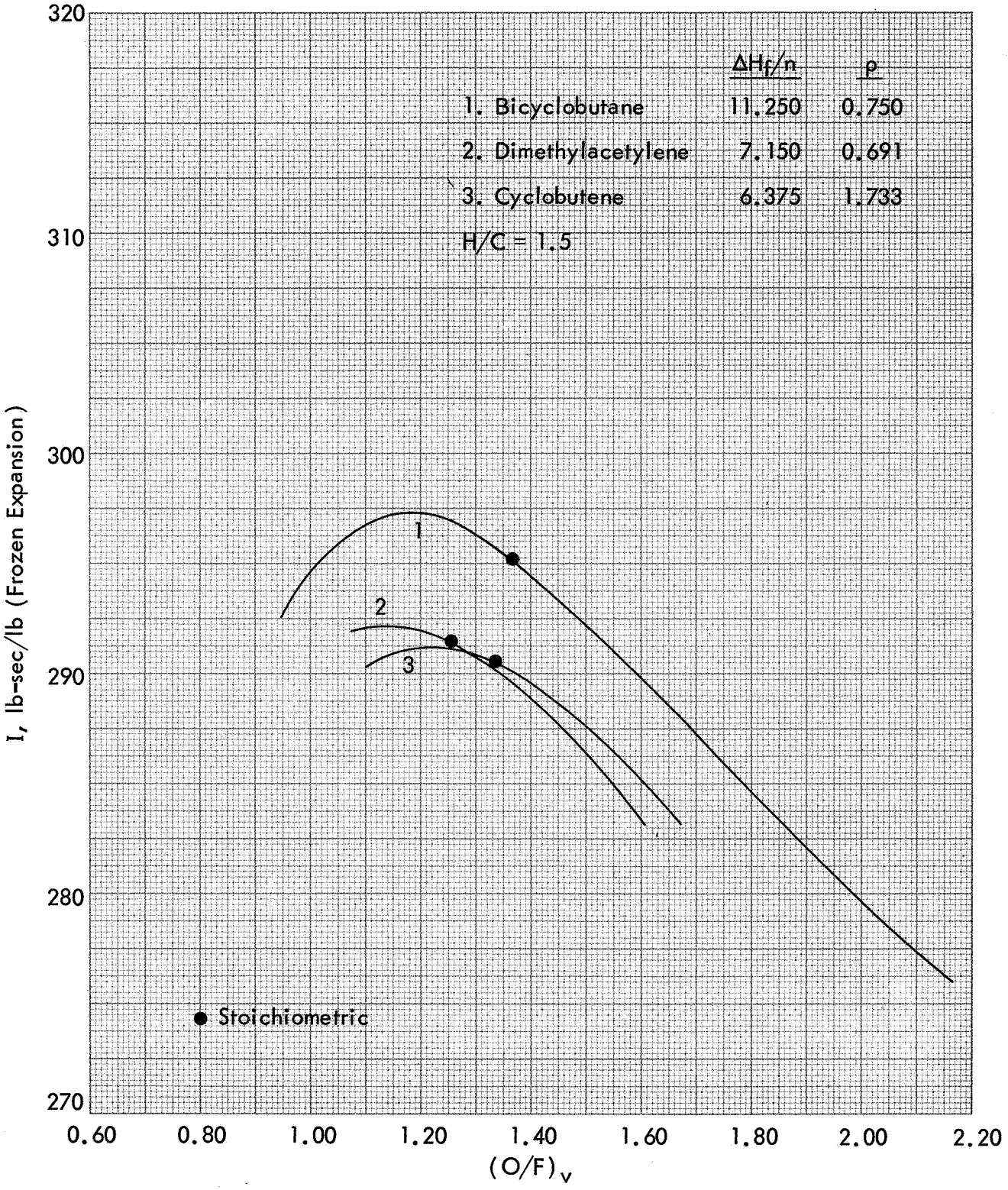


Figure A1-25. SPECIFIC IMPULSE vs $(O/F)_v$ FOR HYDROCARBONS
1000 psia/atm

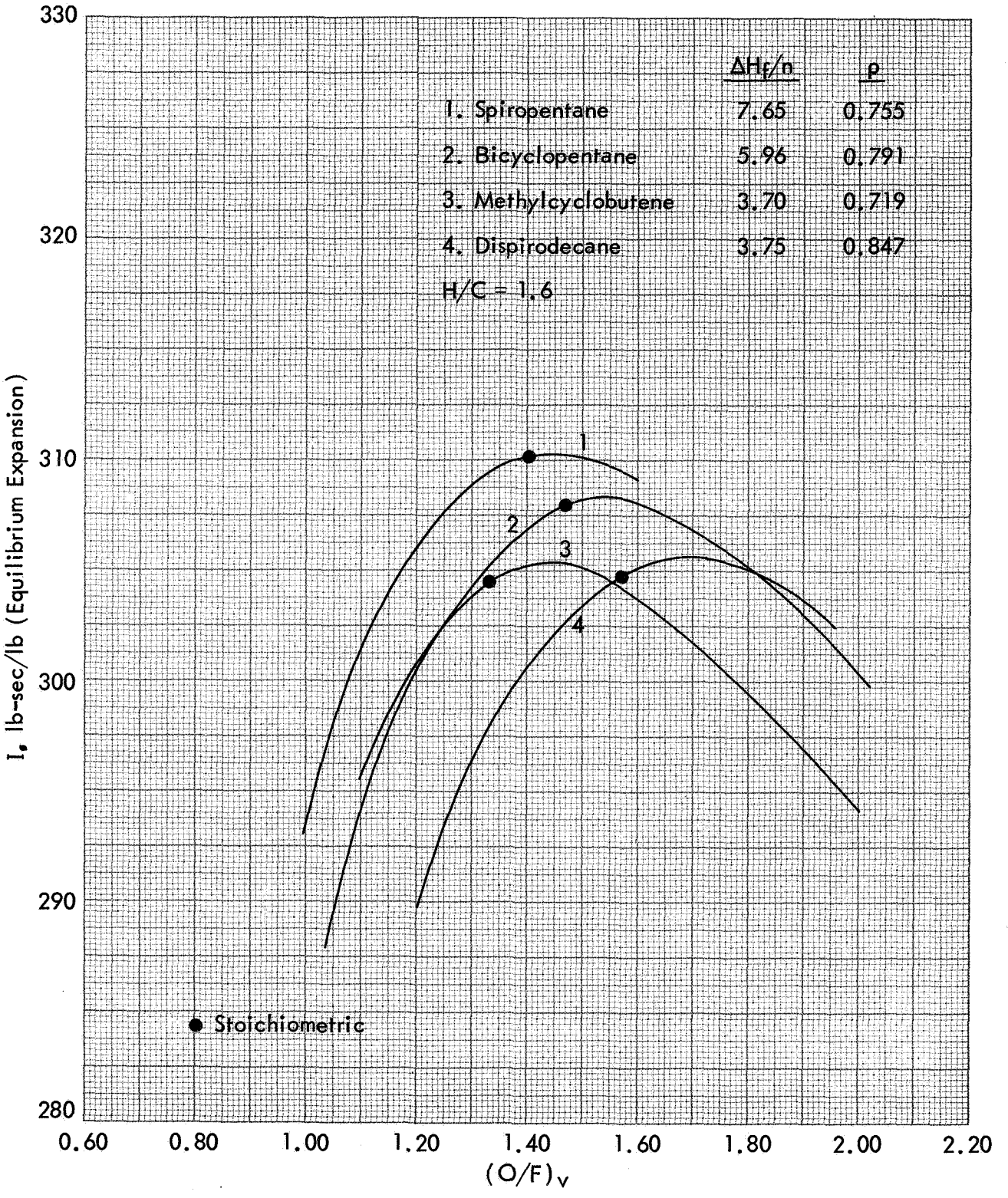


Figure A1-26. SPECIFIC IMPULSE vs $(O/F)_v$ FOR HYDROCARBON

1000 psia/atm

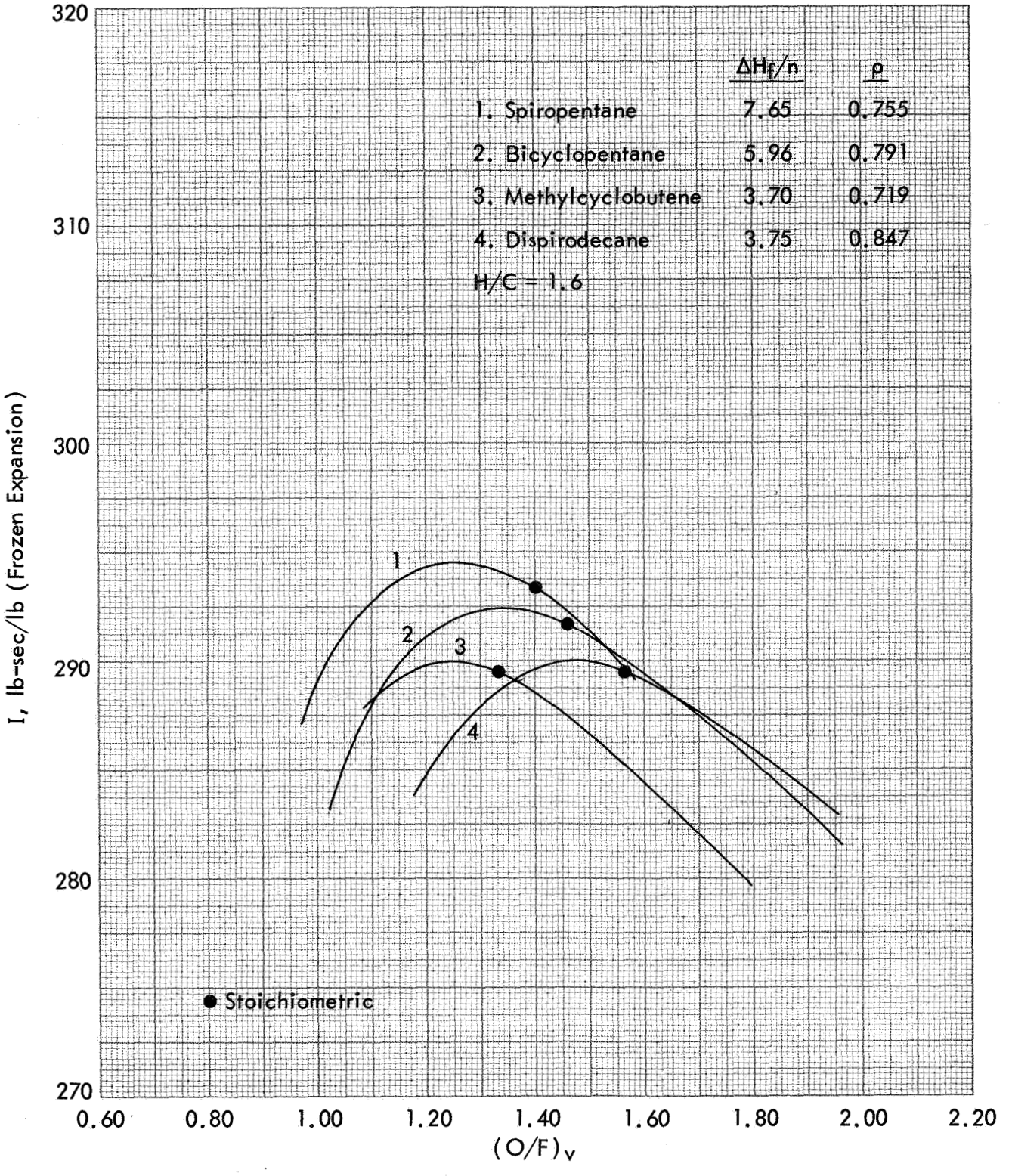


Figure A1-27. SPECIFIC IMPULSE vs $(O/F)_v$ FOR HYDROCARBONS
1000 psia/atm

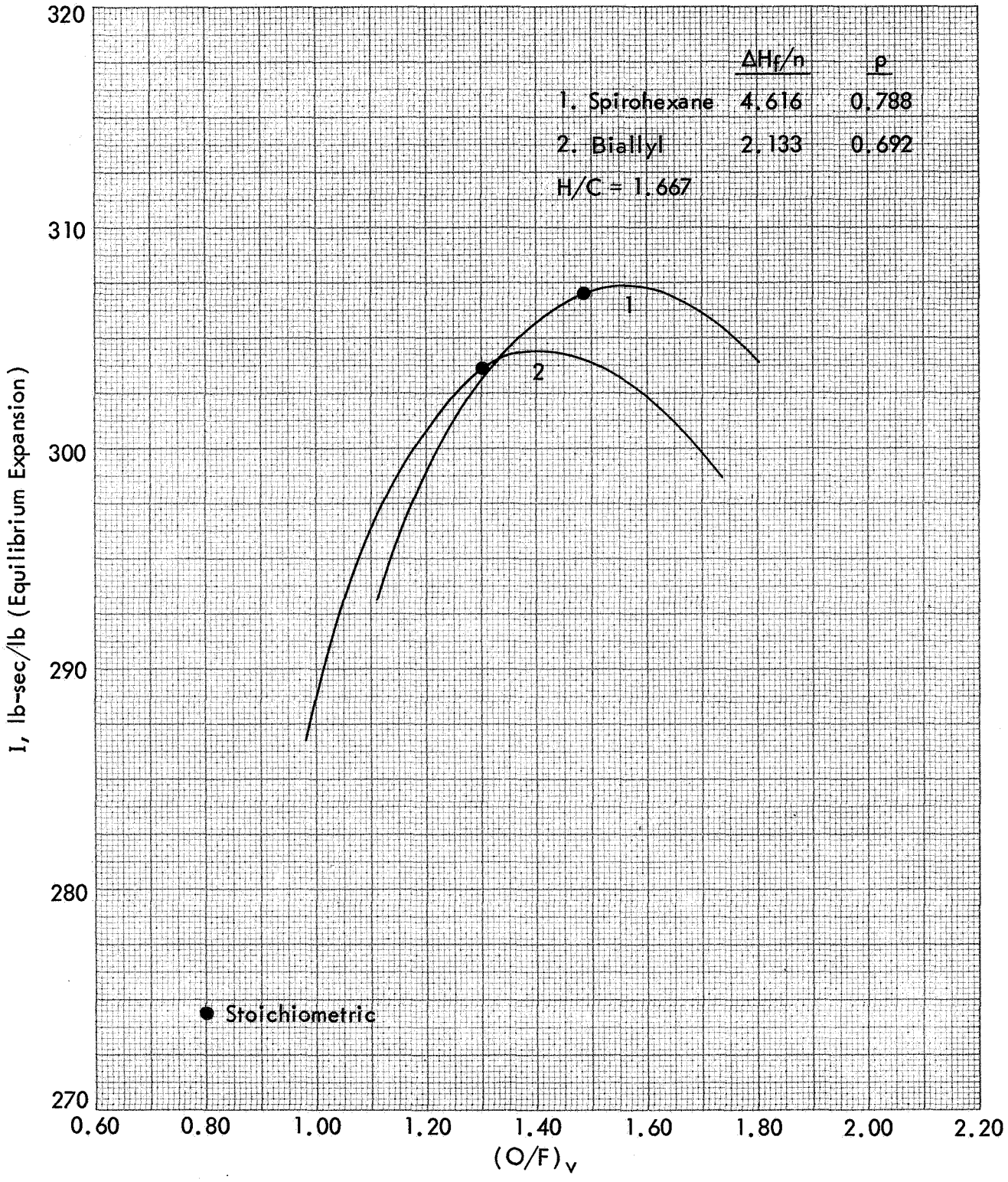


Figure A1-28. SPECIFIC IMPULSE vs $(O/F)_V$ FOR HYDROCARBONS
1000 psia/atm

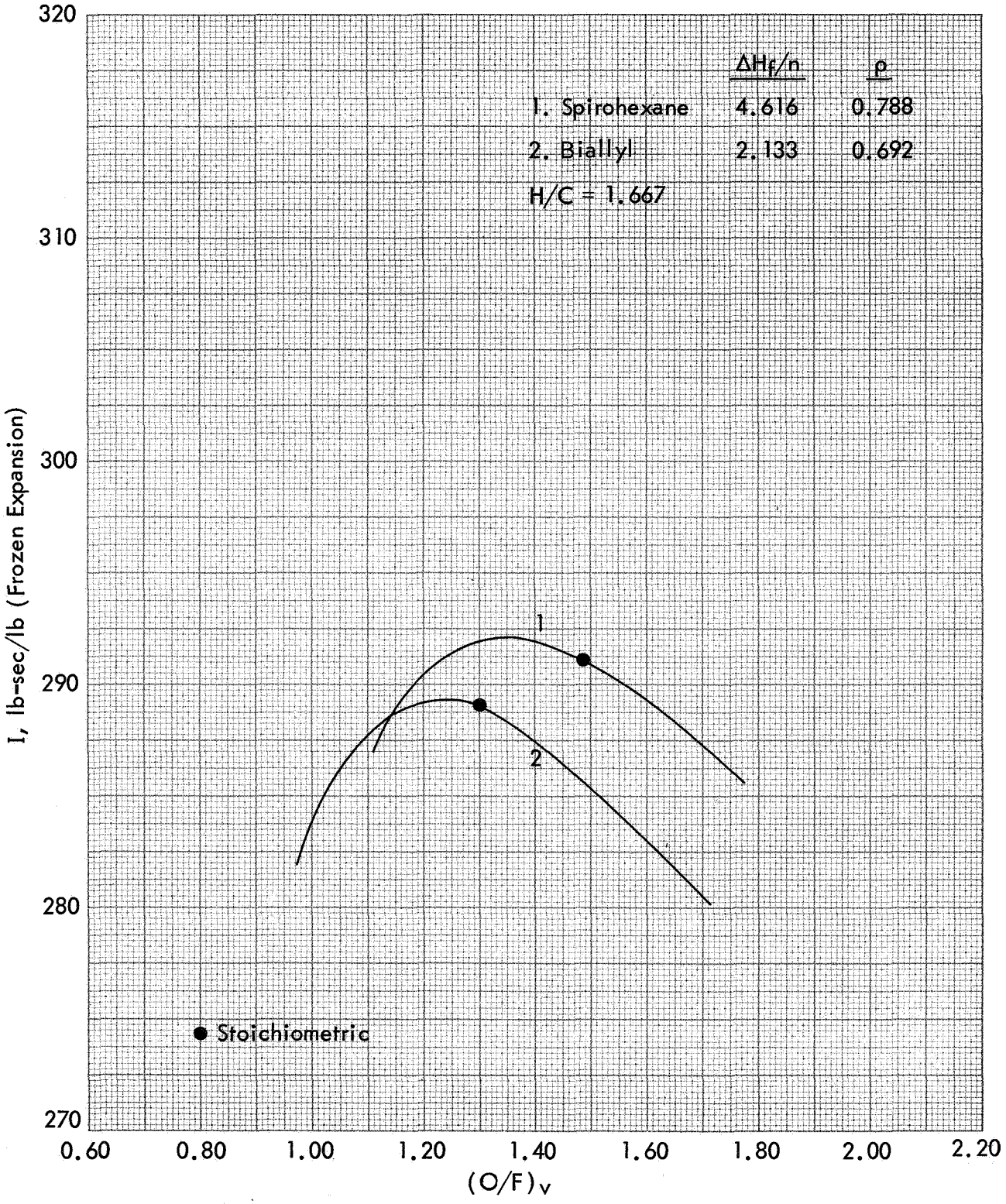


Figure A1-29. SPECIFIC IMPULSE vs $(O/F)_v$ FOR HYDROCARBONS
1000 psia/atm

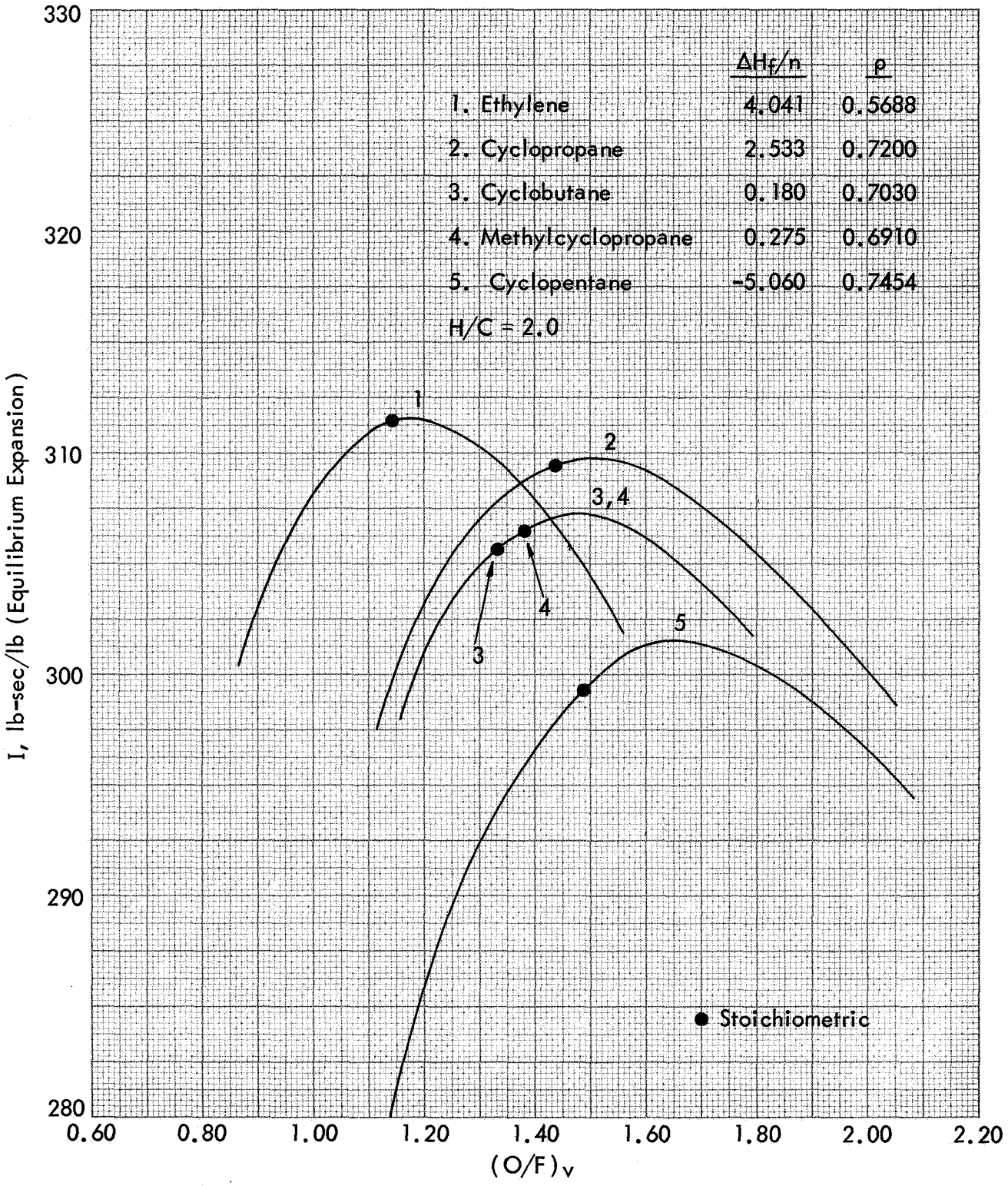


Figure A1-30. SPECIFIC IMPULSE vs $(O/F)_V$ FOR HYDROCARBONS
1000 psia/atm

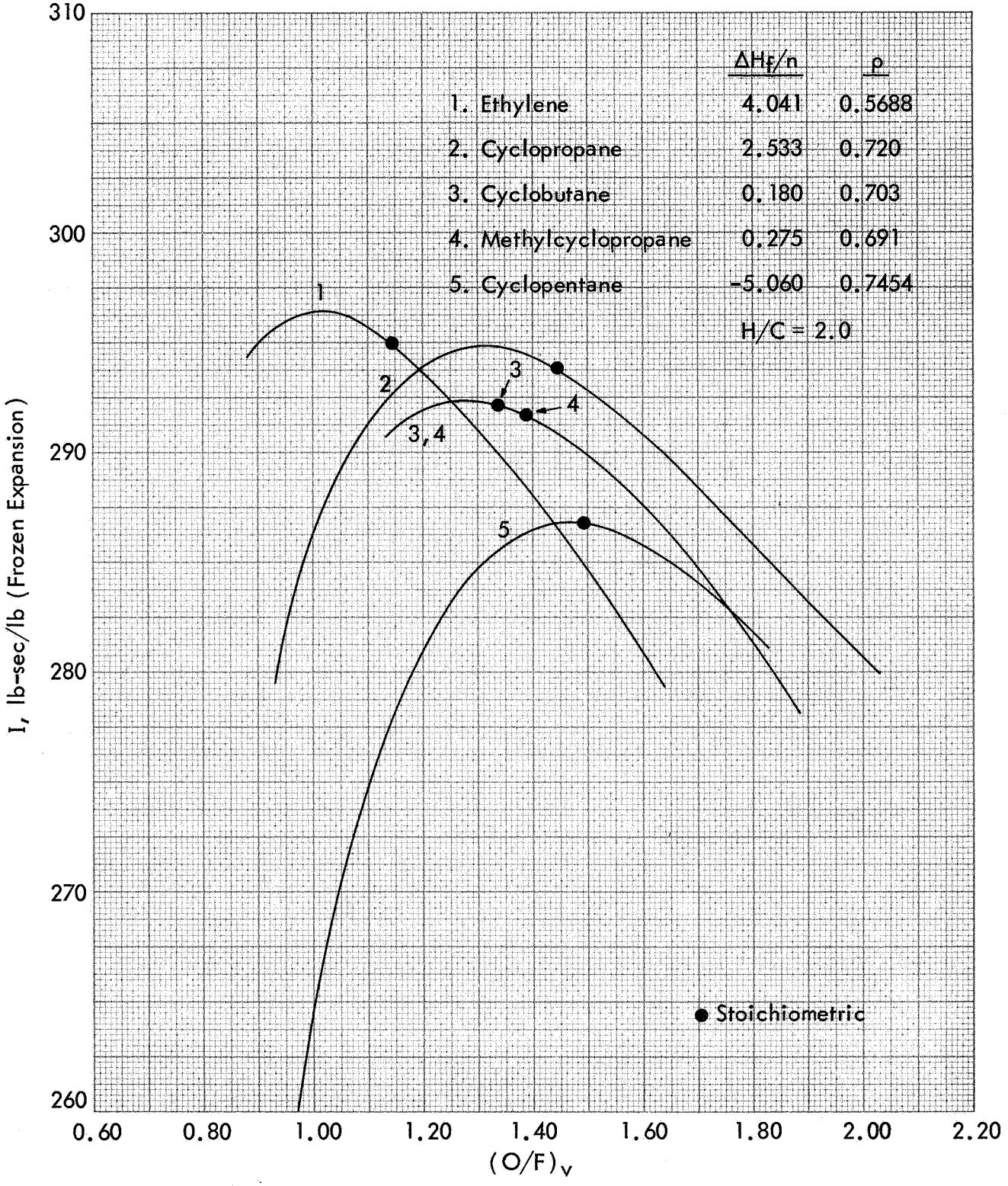


Figure A1-31. SPECIFIC IMPULSE vs $(O/F)_v$ FOR HYDROCARBONS
1000 psia/atm

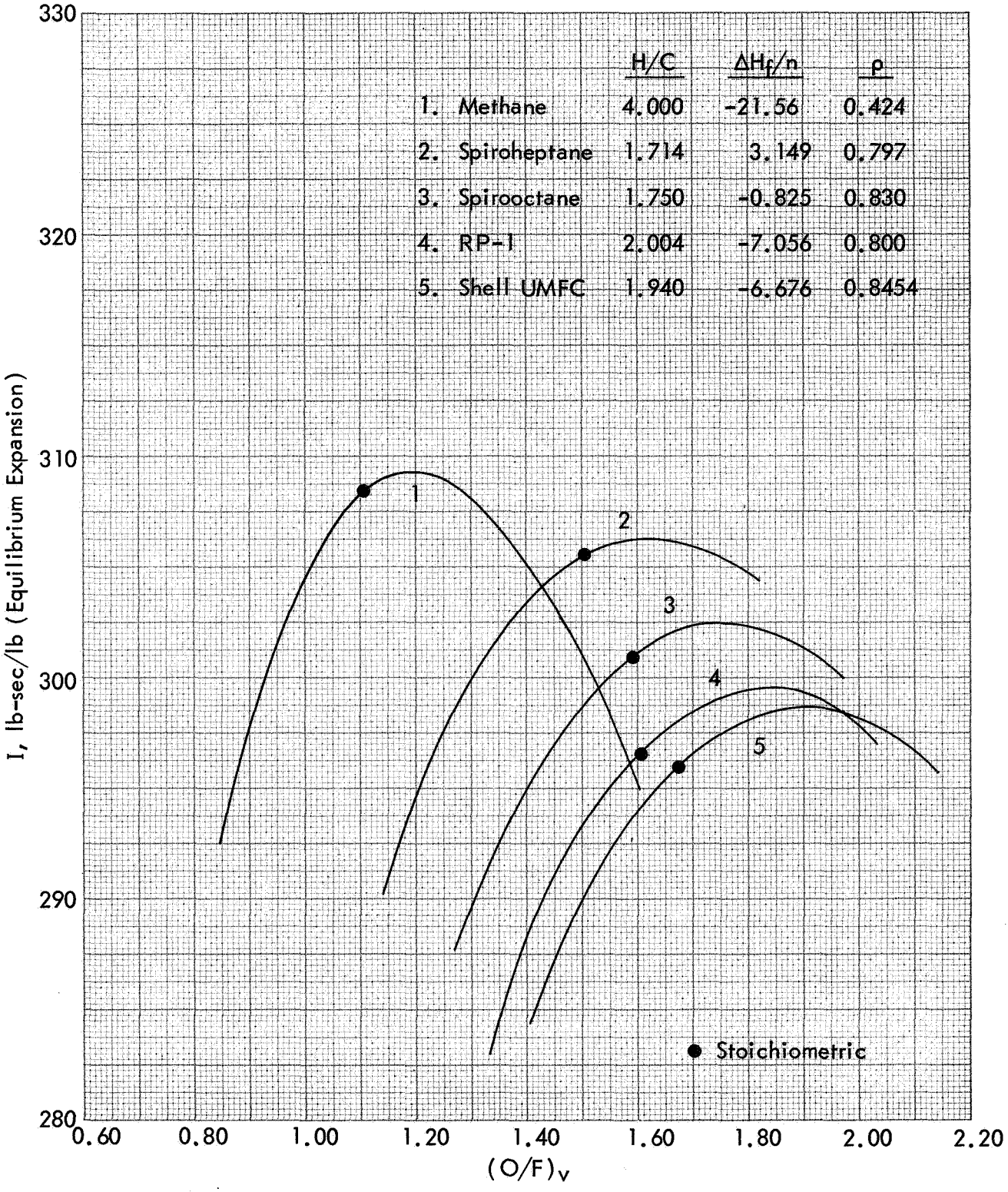


Figure A1-32. SPECIFIC IMPULSE vs $(O/F)_V$ FOR VARIOUS HYDROCARBONS
1000 psia/atm

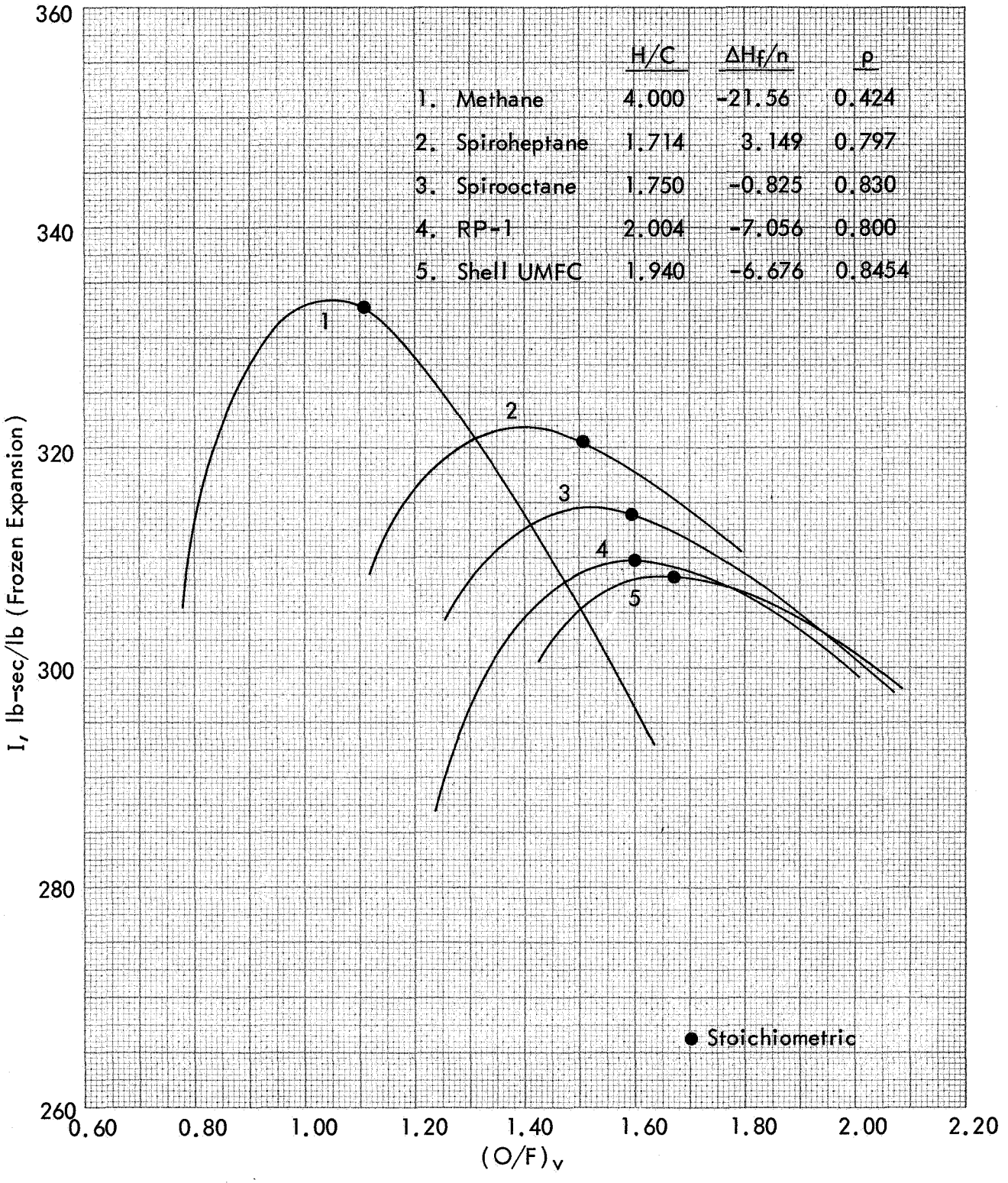


Figure A1-33. SPECIFIC IMPULSE vs $(O/F)_V$ FOR VARIOUS HYDROCARBONS
1000 psia/atm

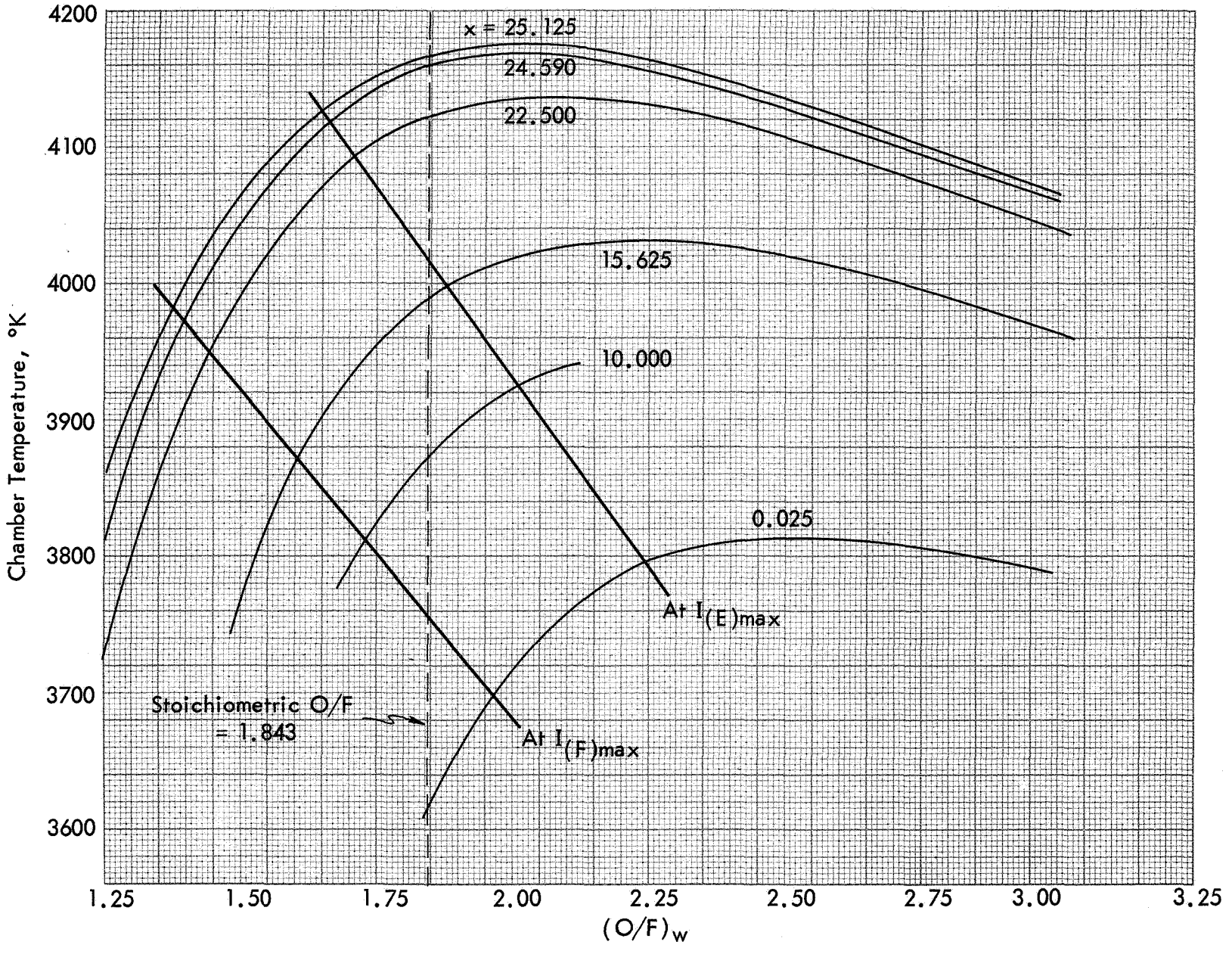


Figure A1-34. CHAMBER TEMPERATURE FOR HYDROCARBONS $C_nH_n$ AT VARIOUS O/F RATIOS

1000 psia/atm

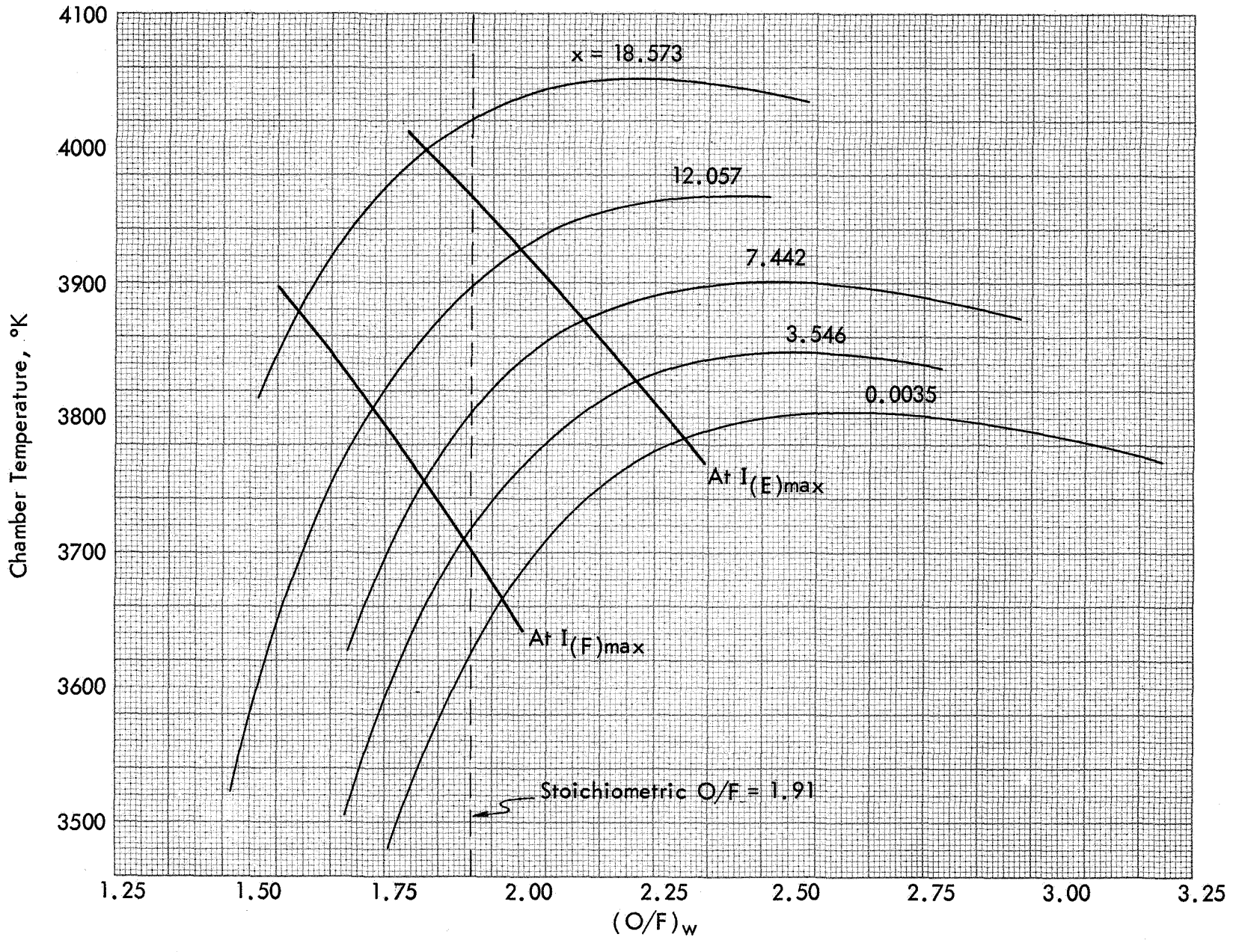


Figure A1-35. CHAMBER TEMPERATURE FOR HYDROCARBONS $C_nH_{1.143n}$ AT VARIOUS O/F RATIOS

1000 psia/atm

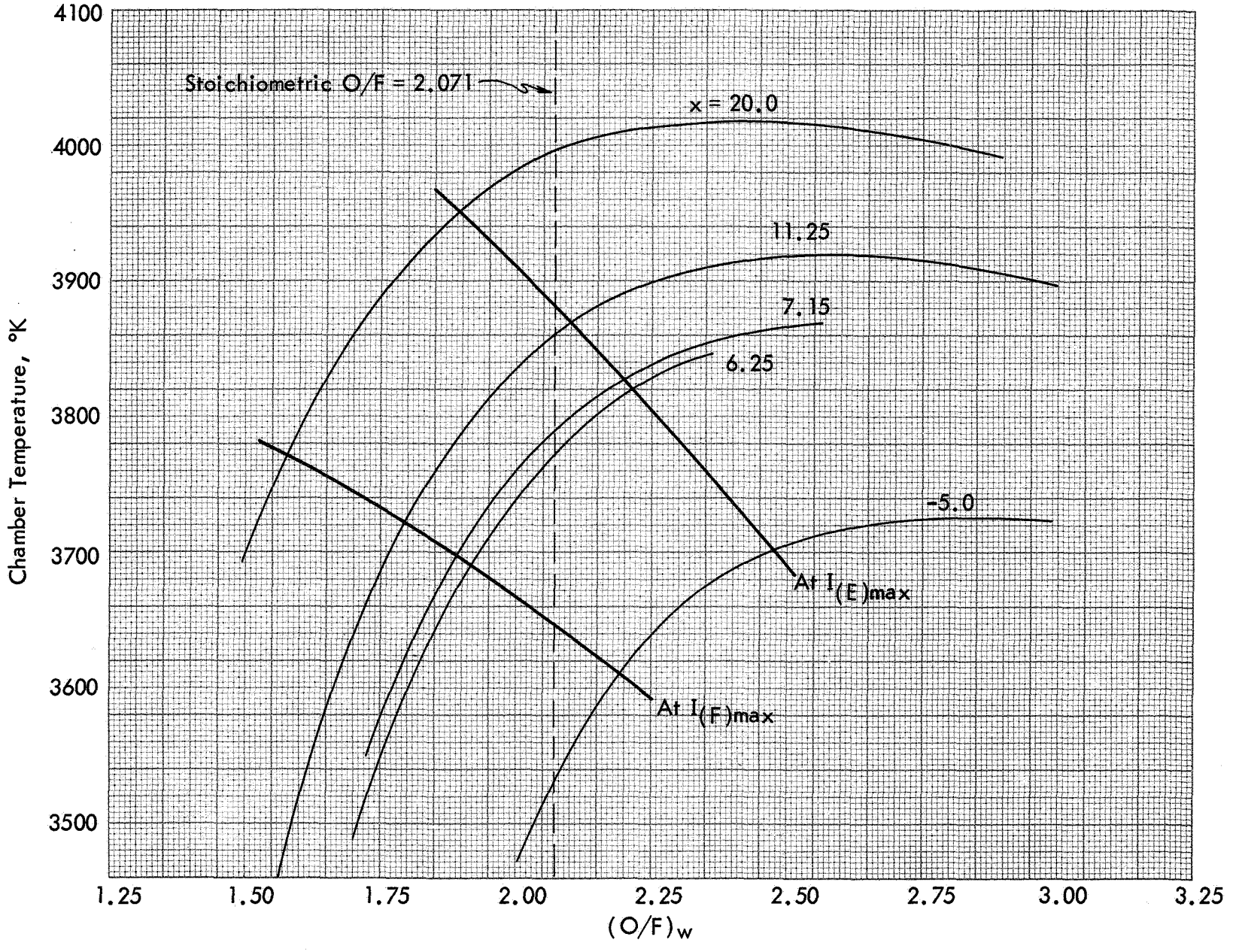


Figure A1-36. CHAMBER TEMPERATURE FOR HYDROCARBONS $C_nH_{1.5n}$ AT VARIOUS O/F RATIOS

1000 psia/atm

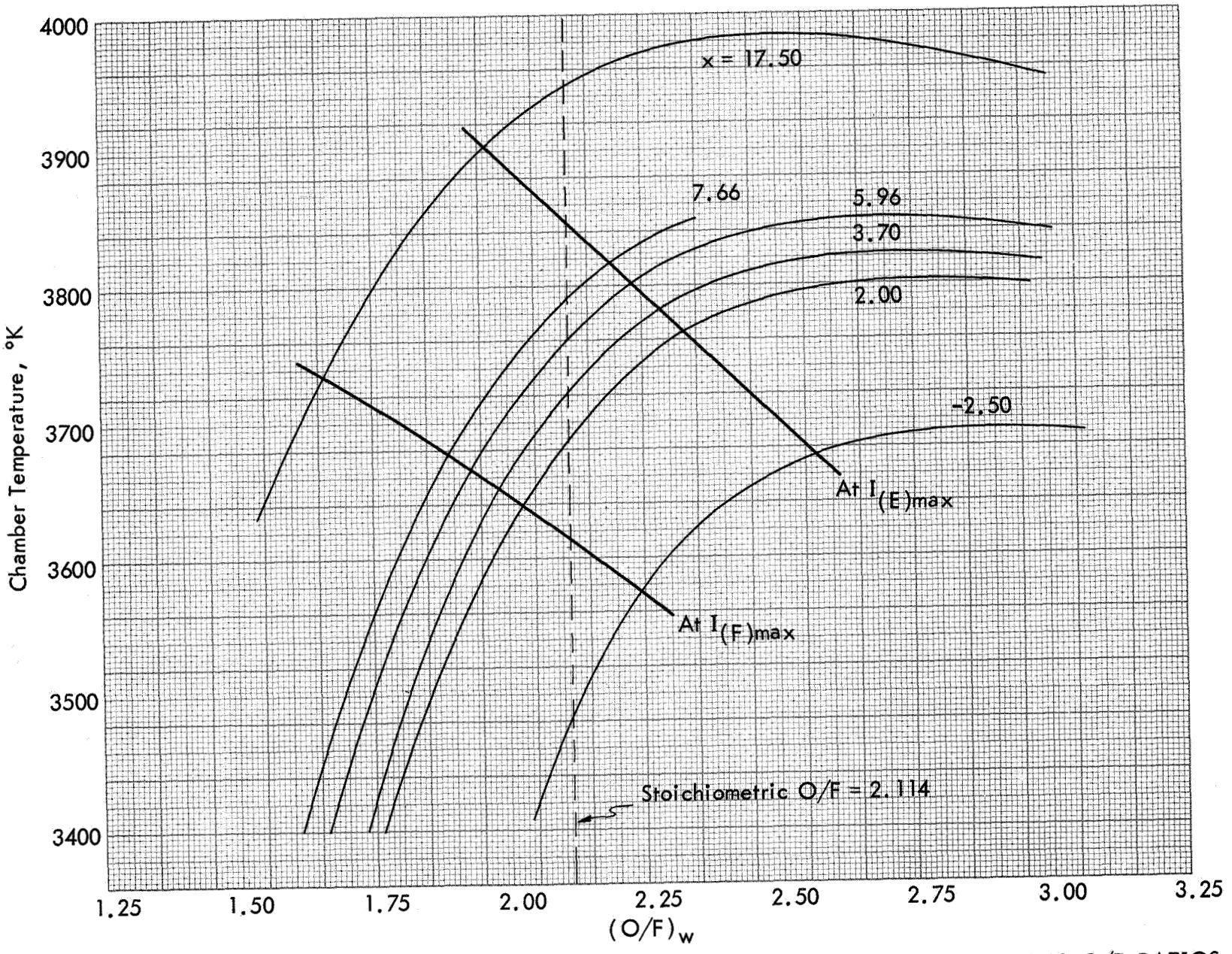


Figure A1-37. CHAMBER TEMPERATURE FOR HYDROCARBONS $C_nH_{1.6n}$ AT VARIOUS O/F RATIOS

1000 psia/atm

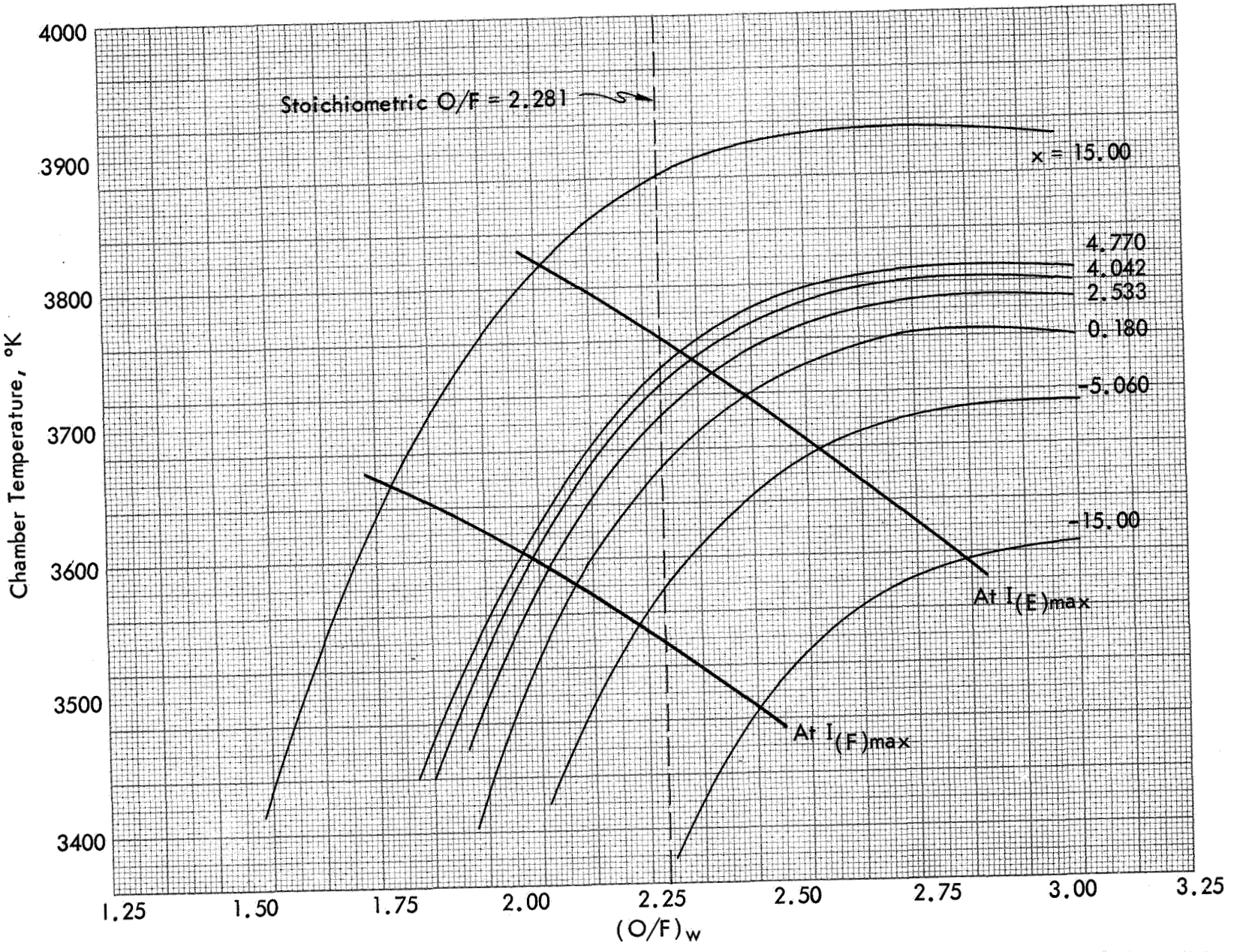


Figure A1-38. CHAMBER TEMPERATURE FOR HYDROCARBONS $C_nH_{2n}$ AT VARIOUS O/F RATIOS

1000 psia/atm

## APPENDIX 2

## SOURCES OF DATA (HEAT OF FORMATION AND DENSITY) AND METHODS OF ESTIMATION

The following Table A2-1 lists the sources of the values given in Table 3 of the text for heats of formation at 298°K, $\Delta H_f^{298}(\ell)$ and $\Delta H_f^{298}(g)$, the liquid density $\rho$, the melting point $T_M$ and the boiling point $T_B$. In each column for a given property there is a number referring to one of the references in the subsequent Table A2-2. A number followed by the symbol +E indicates that the value given was extrapolated from an experimental datum for that compound given in the numbered reference, e.g., 2 + E. For example, the density given in the cited reference is often at 20°C; the +E indicates an estimated correction to 25°C. The column following the reference column for heat of formation [$\Delta H_f^{298}(\ell)$] is labeled "Method". The symbol C in that column indicates a measured heat of combustion; the symbol H indicates a measured heat of hydrogenation; the symbol E indicates a theoretical estimate. If the heat of hydrogenation was measured in solution in a polar solvent, as is often the case, the result of the measurement was taken as a measure of $\Delta H_f(\ell)$ without allowance for the difference between the heat of solution and the heat of condensation of the hydrocarbon vapor under consideration. If the symbol in the reference column is E, without any accompanying number, the value used was estimated in the course of this project. The methods of estimation used are described in a section following the list of references. If the space in a column is blank, no estimate of the relevant quantity has been made.

The compounds are listed in accordance with a structural classification; for this purpose, cubane and tetrahedrane are classified as polyhedral compounds. Other classifications are acetylene derivatives, spiranes and dispiranes, bicyclanes and tricyclanes, monocyclanes and cyclenes and miscellaneous which includes polyenes. For cross-reference, each compound is numbered in accordance with the numbers assigned in Tables 3 and 4.

References are given to sources of data concerning some compounds that are listed in Table A2-1 but not in text Table 3. The values referred to here were used as base data in the estimation of some of the properties listed in Table 3 for which experimental data are lacking or were not found in our search of the literature. That search was not exhaustive; experimental data of which we are not aware may be available for some of the compounds listed.

### Methods for Estimating Heats of Formation at 25°C

#### Heat of Formation of Vapor in Acyclic Systems

Methods for estimating the standard heats of formation $\Delta H_f(g)$ (25°C) of hydrocarbon vapors were published simultaneously many years ago by Franklin[1)] and by Souders, Matthews and Hurd;[2)] a similar method for estimating $\Delta H_f(g)$ at any temperature over a wide range has been suggested more recently by Verma

1) See references at end of Appendix 2.

## Table A2-1. SOURCES OF DATA ON HYDROCARBONS: DENSITY, HEAT OF FORMATION, BOILING AND MELTING POINTS

### References to Table A2-2.

| Hydrocarbons, by Structural Type | Empirical Formula | | Number | | References | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Density, ρ, g/ml | Heat of Formation | | | Transition Temperature | |
| | C | H | Table 3 | Table 4 | | $\Delta H_f(g)$, kcal/mole | $\Delta H_f(l)$, kcal/mole | Method | $T_B$, °C | $T_M$, °C |
| I. Polyhedral Hydrocarbons | | | | | | | | | | |
| Tetrahedrane | 4 | 4 | 2 | 5 | E | | 3 | E | E | |
| Cubane | 8 | 8 | 1 | 1 | 1 (S) | 2 | 2 (S) | C | 2 | 2 + E |
| Methyl Cubane | 9 | 10 | 3 | 2 | E | E | E | | | |
| Dimethyl Cubane | 10 | 12 | 4 | 3 | E | E | E | | | |
| II. Acetylene Derivative | | | | | | | | | | |
| Acetylene | 2 | 2 | 21 | 44 | 12 | 12 | 12 | C | 12 | 12 |
| Methylacetylene | 3 | 4 | 28 | 38 | 12 | 12 | 12 | C | 12 | 12 |
| Dimethylacetylene | 4 | 6 | 40 | 40 | 12 | 12 | 12 | C | 12 | 12 |
| 1,4-Pentadiyne | 5 | 4 | 8 | 17 | E | E | E | | | |
| Isopropenylacetylene | 5 | 6 | 46 | 43 | 6,11 + E | E | E | | 11 | 6,7 |
| Cyclopropylacetylene | 5 | 6 | 14 | 23 | 4,5 | E | E | | 4,5 | 6 |
| 1,5-Hexadiyne | 6 | 6 | 13 | 16 | 7,37 + E | E | E | | 7,9 | 7 |
| 1-Ethynyl 1-Methylcyclopropane | 6 | 8 | | | 5 | E | E | | 5 | |
| 1,6-Heptadiyne | 7 | 8 | 15 | 18 | 7,8,37 + E | E | E | | 7,8 | 7,8 |
| 1,7-Octadiyne | 8 | 10 | 19 | 15 | 7,37 + E | E | E | | 6,7 | 7 |
| Dicyclopropylacetylene | 8 | 10 | 7 | 8 | E | E | E | | E | |
| Di(methylcyclopropyl)acetylene | 10 | 14 | 17 | 13 | E | E | E | | E | |
| III. Spiranes and Dispiranes | | | | | | | | | | |
| Spiro(2,2)pentane | 5 | 8 | 24 | 29 | 15 | 15 | 15,16 | C | 16 | 33 |
| Spiro(3,2)hexane | 6 | 10 | 23 | 19 | E | E | E | | E | |
| Spiro(3,3)heptane | 7 | 12 | 26 | 20 | E | E | E | | 14 | |
| Dispiro(2,1,2,1)octane | 8 | 12 | 9 | 9 | E | E | E | | | |
| Spiro(4,3)octane | 8 | 14 | 37 | 28 | E | E | E | | E | |
| Spiro(4,4)nonane | 9 | 16 | | | 13 | | 13 | C | 13,14 | |
| Dispiro(3,1,3,1)decane | 10 | 16 | 16 | 12 | E | E | E | | | |
| Spiro(5,4)decane | 10 | 18 | | | 13 | | 13 | C | 13 | |
| Spiro(5,5)undecane | 11 | 20 | | | 13 | | 13 | C | 13 | |
| Spiro(6,5)dodecane | 12 | 22 | | | 13 | | 13 | C | 13 | |
| IV. Bicyclanes and Tricyclanes | | | | | | | | | | |
| Bicyclo(1,1,0)butane | 4 | 6 | 11 | 22 | E | 18 + E | E | | 17 | |
| Bicyclo(2,1,0)pentane | 5 | 8 | 22 | 21 | 35 + E | | 19 | H | 35 | |
| Tricyclo(3,1,0,$0^{2,4}$)hexane | 6 | 8 | 5 | 7 | E | E | E | | | |
| 1,3-Dimethylbicyclo(1,1,0)butane | 6 | 10 | 42 | 39 | E | 18 + E | 18 | H | | |
| Cyclopropylcyclopropane | 6 | 10 | 25 | 24 | 33 + E | | 33,E | C | 33 | 33 |
| Bicyclo(3,1,0)hexane | 6 | 10 | 29 | 26 | E | | 20 | C | 36 | |
| 1-Methyltricyclo(3,1,0,$0^{2,4}$)hexane | 7 | 10 | 12 | 11 | E | E | E | | | |
| Bicyclo(2,2,1)heptane | 7 | 12 | | | | | 26 | C | | 26 |
| 1,4-Dimethyltricyclo(3,1,0,$0^{2,4}$)hexane | 8 | 12 | 18 | 14 | E | E | E | | E | |
| V. Monocyclanes, Cyclenes, and Cyclodienes | | | | | | | | | | |
| Cyclopropane | 3 | 6 | 34 | 37 | 12 | 21 | 21 | C | 12 | 12 |
| Cyclobutene | 4 | 6 | 31 | 32 | E | E | E | | | |
| Cyclobutane | 4 | 8 | 36 | 34 | 12 | | 22 | C | 12 | 22 |
| Methylenecyclobutane | 5 | 8 | 33 | 31 | 38 | | 19 | H | 38 | |
| 1-Methyl cyclobutene | 5 | 8 | 38 | 35 | 38 | | 19+ E | H | 34 | |
| Cyclopentane | 5 | 10 | 41 | 36 | 12 | 12 | 12,22 | C | 12 | 12,22 |
| 1-Methyl cyclobutane | 5 | 10 | | | | | E,23 | C | | |
| 1,4-Cyclohexadiene | 6 | 8 | 32 | 25 | 30 + E | E | E | | 30 | |
| 1-Methyl-1,4-cyclohexadiene | 7 | 10 | 35 | 27 | E | E | E | | E | |
| trans-1,2-Divinylcyclobutane | 8 | 12 | 27 | 30 | 24 + E | E | E | | 24 | |
| VI. Miscellaneous | | | | | | | | | | |
| Ethylene | 2 | 4 | 44 | 46 | 12 | 12 | 12 | | 12 | 12 |
| Allene | 3 | 4 | 30 | 41 | 12 | 12 | 12 | | 12 | 12 |
| 1,3-Butadiene | 4 | 6 | 45 | 45 | 12 | 12 | 12 | | 12 | 12 |
| 1,5-Hexadiene | 6 | 10 | 43 | 42 | 12 | 12 | | | 12 | 12 |
| Quadricyclene | 7 | 8 | 10 | 6 | E | E | E | | 29 | 31 |
| Bicyclo(2,2,1)heptadiene-2,5 | 7 | 8 | 20 | 10 | 28 | | 26,27,28 | C,H | 28 | 30 |
| 1,3,7-Octatriene | 8 | 12 | 39 | 33 | 32 | E | E | | 32 | |
| SHELLDYNE | 14 | 16 | 6 | 4 | 25 | | 25 | C | 25 | 25 |

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Table A2-2 (Contd). REFERENCES FOR TABLE A2-1 ONLY


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38. W. Shand, V. Schomaker, J. R. Fischer, J. Am. Chem. Soc. 66, 636 (1944).

and Doraiswamy.[3] The contributions of various structural features to $\Delta H_f(g, 25°C)$, as assigned by these authors, are listed in Table A2-3 together with literature references. We have made independent estimates of group contributions from data assembled in the reports of API Research Project 44. Our values are also listed in Table A2-3; the various estimates are not grossly different. The group contribution for cyclopropyl was obtained from our estimate of the heat of formation of methylcyclopropane by methods given later in this section. It will be noticed that our estimate is higher than that given by other authors by 3 kcal/mole or more; this difference affects the heats of formation estimated for compounds like dicyclopropyl and cyclopropylacetylene.

For some hydrocarbons, the sum of the group contributions must be corrected for strain or for conjugation. The corrections proposed by the various authors are listed in Table A2-4. None of the published systems proposes a correction for conjugation between a double bond and a triple bond; for this correction we have chosen to use the same value as for the conjugation between two double bonds. This was done on the basis of the notion that when the pi electron wave function on a double bound interacts completely with one of the pi electron wave functions of a triple bond it will be orthogonal to the other.

Heat of Vaporization of Liquid at 25°C

A value of $\Delta H_f(\ell)$ rather than $\Delta H_f(g)$ is needed for an estimate of the enthalpy available for thrust generation from the combustion of a liquid fuel; an estimate of $\Delta H_v$, the enthalpy of vaporization at the temperature assigned to the liquid fuel initially (usually 25°C) is needed for this purpose. The energy of vaporization, approximately equal to $\Delta H_v$-RT, is likely to be better approximated by a sum of group contributions than is $\Delta H_v$ itself; even this quantity, however, is sensitive to details of molecular packing so that its representation as a sum of group contributions is not very precise. If only hydrocarbons are to be considered, however, the error in this approximation is not large. We have therefore used the data assembled in the reports of API Research Project 44 to estimate group contributions to $\Delta H_v(25°C)$-0.596 kcal/mole. The basis used for this estimate is the high-temperature asymptote approached by the average increment in $\Delta H_v(25°C)$ per $CH_2$ group with increasing boiling point among the normal paraffins; this value was used to derive an average value for the $CH_3$ group, again for the normal paraffins. These values were used to obtain estimates for the other groups. For the acetylenes, use was made of some scanty data assembled in Timmerman's compilation. The values obtained by this procedure are listed in column 6 of Table A2-3.

This estimate of $\Delta H_v$ has been checked by an alternative procedure for those compounds whose boiling points are known. For a number of simple cyclic compounds it has been observed that the Trouton constant varies between the limits 20.2 and 20.9 entropy units, with an average value of 20.5 e.u. For these same compounds, on the basis of data given in the reports of API Project 44, we have observed that the ratio $\Delta H_v(T_B)/\Delta H_v(25°C)$ increases with boiling point nearly linearly from 1.00 at a boiling point of 25°C to 1.14 at 110°C. The heat of vaporization at the boiling point obtained from a Trouton

Table A2-3. GROUP CONTRIBUTIONS TO STANDARD HEAT OF FORMATION OF VAPOR AND TO ENERGY OF VAPORIZATION OF LIQUID HYDROCARBONS AT 25°C (KCAL/MOLE)

(1) This work.
(2) J. L. Franklin, Ind. Eng. Chem. 41, 1070 (1949).
(3) M. Souders, C. S. Matthews and C. O. Hurd, ibid. 41, 1048 (1949).
(4) K. K. Verma and L. K. Doraiswamy, Ind. Eng. Chem. Fundamentals 4, 389 (1965).

| Group | $\Delta H_f(g)$ (298°K) | | | | $\Delta H_v$-RT |
|---|---|---|---|---|---|
| | (1) | (2) | (3) | (4) | (1) |
| $-CH_3$ | -10.13 | -10.12 | -10.05 | -10.25 | 1.11(3) |
| $-CH_2-$ | -4.93 | -4.929 | -4.95 | -4.95 | 1.18(2) |
| $-\overset{\mid}{\underset{\mid}{C}}H$ | -1.5 | -1.09 | -1.57[a)]<br>-0.88[b)] | -1.85 | 0.87 (chain)<br>1.1-1.3 ("unshielded"[d)]) |
| $-\overset{\mid}{\underset{\mid}{C}}-$ | 1.3 | 0.80 | 0.85[a)]<br>2.45[b)] | 0.62 | 0.40 |
| $-CH=CH_2$ | 15.0 | 15.0 | | 15.02 | 2.03 |
| $-\overset{\mid}{C}=CH_2$ | -3.7 | -3.35 | -3.46 | -4.22 | 2.01 |
| $H\overset{\mid}{C}=\overset{\mid}{C}H$ cis | 18.5 | 18.88 | 18.56<br>18.40[c)] | 17.96 | 2.31 |
| $H\overset{\mid}{C}=\overset{\mid}{C}H$ trans | 17.6 | 17.83 | 17.40 | 17.83 | 2.35 |
| $\overset{\mid}{C}=\underset{\mid}{C}H$ | 20.1 | 20.19 | 20.12<br>19.95[c)] | 20.10 | 2.34 |
| $HC\equiv C-$ | 54.5 | 54.44 | 54.69 | 54.49 | 2.7 |
| $-C\equiv C-$ | 55.6 | 54.68 | 55.30 | 54.77 | 3.5 |
| $H_2$ $H_2$ H | (16.2) | 13.28 | | 12.38 | |

a) Second carbon from end in chain or carbon in 6-membered aliphatic ring.
b) Third or higher carbon from end in aliphatic chain.
c) In 6-membered aliphatic ring.
d) "Unshielded" $H\overset{\mid}{\underset{\mid}{C}}-$ groups are those protruding from cyclic structures structures, as in cubane, bicyclobutane or bicyclopentane.

Table A2-4. CORRECTIONS TO $\Delta H_f(g)$ FROM SUM OF GROUP CONTRIBUTIONS

kcal/g mole

| Configuration | Correction to $\Delta H_f(g)$ [a] | | |
|---|---|---|---|
| | 2 | 3 | 4 |
| $C_3$ saturated ring | +24.22 | | +24.13 |
| $C_4$ saturated ring | ca 18.4 | | 18.45 |
| $C_5$ saturated ring | -5.68 | | 5.44 |
| $C_6$ saturated ring | -0.45 | | -0.76 |
| Two $-\overset{|}{\underset{|}{C}}H$ groups adjacent | | 0.75 | |
| CH and $-\overset{|}{\underset{|}{C}}-$ adjacent | 2.5 | 2.39 | |
| Three -CH groups adjacent | 1.9 | 2.30 | -1.20 |
| Conjugation $\overset{H}{=}C-\overset{H}{C}=$ | | -3.38 | |
| $=\overset{|}{C}-\overset{H}{C}=$ | | -4.45 | |
| $=\overset{|}{C}-\overset{|}{C}=$ | | -2.10 | |
| In 6-ring, $\overset{H}{=}C-\overset{H}{C}=$ | | -1.76 | |

a) Column (2) refers to Franklin (loc cit); column (3) to Souders, Matthews and Hurd (loc cit); column (4) refers to Verma and Doraiswamy (loc cit).

constant of 20.5 e.u. was corrected to 25°C on the basis of this rough rule. In most cases the two independent estimates of $\Delta H_V$ agreed within the precision expected for the estimation of $\Delta H_f(g)$.

Heat of Formation of Vapor in Cyclic Systems

We have used the group additivity method primarily for molecules that do not contain small strained rings (an exception was made for cyclopropyl substituents). For the ring systems we have used a formalism proposed originally by Allen[4] and extended by Skinner.[5] This formalism leads to a value for the heat of formation of the "unstrained" molecule; corrections for strain are added to this value.

The advantage of the Allen scheme is that it takes specific account of the so-called nonbonded interactions in a molecule by introducing two parameters which we shall call $E_2$ and $E_3$. These parameters describe the resultant effect of nonbonded interactions between pairs of bonds radiating from a given carbon atom ($E_2$) or among groups of three bonds radiating from a given carbon atom ($E_3$); their detailed significance has been discussed by Skinner.[5] In the expression for the heat of formation, the parameter $E_2$ occurs $N_2$ times: once for each carbon atom in an unbranched cyclane, i.e., for each $-CH_2-$ group, three times for each tertiary carbon atom and six times for each quaternary carbon atom. The parameter $E_3$ occurs $N_3$ times: once for each tertiary carbon atom and four times for each quaternary carbon atom. The unstrained heat of formation of a hydrocarbon of given structure type containing n carbon atoms then depends on the number of C-C bonds, the number of CH bonds, etc. and the nonbonded interactions, and can be written in terms of n and the heats of formation of methane and ethane. The value assigned to the parameter $E_2$ by Skinner is +2.58 kcal/mole; Allen originally proposed -0.65 kcal/mole for $E_3$; we have preferred to use the value -0.55 kcal/mole subsequently recommended by Skinner.

Let C and H, respectively, represent the heat of formation of atomic carbon and hydrogen in their ground states from the elements in their standard states, and let CC, CH, respectively, represent the carbon-carbon and carbon-hydrogen single bond enthalpies. Then for a saturated hydrocarbon containing n carbon atoms, (2n-a) hydrogen atoms and (n+b) carbon-carbon single bonds, the heat of formation is

$$\Delta H_f = nC + (2n-a)H - (n+b)CC - (2n-a)CH - I + S$$

where $I = N_2E_2 + N_3E_3$ terms and S represents the strain enthalpy. Then

$$\Delta H_f = n[(C-CC) + 2(H-CH)] - bCC - a(H-CH) - I + S.$$

Applying this expression to the heat of formation of methane and ethane, we obtain

$$(C-CC) + 2(H-CH) = \Delta H_f(C_2H_6,g) - \Delta H_f(CH_4,g) = -2.347$$

and

$$CC + 2(H-CH) = 2\Delta H_f(CH_4,g) - \Delta H_f(C_2H_6,g) = -15.542.$$

These expressions are used to express the heat of formation in terms of the very well known heats of formation of methane and ethane, together with values for I and S.

With this approach, we derive the following expressions in kcal/g mole for different kinds of saturated cyclic hydrocarbon structures at 25°C:

Unicyclanes

$$\Delta H_f(g) = -2.347n - 2.580\ N_2 + 0.55\ N_3 + \text{strain}.$$

Unsubstituted Unicyclanes

$$\Delta H_f = -4.927n + \text{strain}.$$

Here the parameter $E_2$ has been assigned the value 2.580 rather than simply 2.58 for numerical consistency.

Bicyclanes and Spiranes

A hydrocarbon of n carbon atoms having either of these structures carries n + 1 CC bonds and 2(n - 1) CH bonds. The heat of formation for either type can thus be written, in kcal/mole,

$$\Delta H_f(g) = (n + 1)\ \Delta H_f(C_2H_6,g) - (n + 2)\ \Delta H_f(CH_4,g) - N_2E_2 - N_3E_3 + \text{strain} = 15.542 - 2.347n - 2.580\ N_2 + 0.55\ N_3 + \text{strain}.$$

Unsubstituted Spiranes

Here $N_2 = n + 5$; $N_3 = 4$.

$$\Delta H_f = 4.79 - 4.927n + \text{strain}$$

Unsubstituted Bicyclanes

Here $N_2 = n + 4$; $N_3 = 2$.

$$\Delta H_f = 6.32 - 4.927n + \text{strain}.$$

Dispiranes and Tricyclanes

A hydrocarbon with either of these structures having n carbon atoms carries (n + 2) CC bonds and (2n - 4) CH bonds. Then

$$\Delta H_f(g) = (n + 2)\ \Delta H_f(C_2H_6,g) - (n + 4)\ \Delta H_f(CH_4,g) - N_2E_2 - N_3E_3 + \text{strain energy} = 31.084 - 2.347n - 2.580\ N_2 + 0.55\ N_3 + \text{strain in kcal/mole}.$$

Unsubstituted Dispiranes

Here $N_2 = n + 10$ and $N_3 = 8$.

$$\Delta H_f = 9.68 - 4.927n \text{ kcal/mole} + \text{strain enthalpy.}$$

Unsubstituted Tricyclanes

Here $N_2 = n + 8$ and $N_3 = 4$.

$$\Delta H_f = 12.64 - 4.927n \text{ kcal/mole} + \text{strain enthalpy.}$$

Strain Enthalpy

We have computed the strain enthalpy in hydrocarbons containing small rings as a sum of contributions from several specific effects. In the following discussion we will use the terms strain energy and strain enthalpy interchangeably, though it is not precise to do so.[6] We also have not attempted to estimate the deviations of HCH and HCC bond angles in strained hydrocarbons from their normal values. A consideration of these matters would have lengthened the calculations considerably. The discussion given here should therefore be taken as approximate.

We have considered the following contributions to the strain energy:

1) Intrinsic ring strain. This is the strain resulting from non-bonded interactions and angular deformation in the carbon framework of a small ring. It is derived by correcting the heats of formation of the unsubstituted cyclanes for other identifiable effects, enumerated below.

2) H-H eclipse. This is the strain (destabilization) resulting from the eclipsed conformation of a pair of C-H bonds separated from each other by one carbon-carbon single bond. In the eclipsed conformation of ethane, there are three such interactions. The strain-energy contributed by each eclipsed pair is thus taken to be one third of the rotational barrier in ethane, or 0.95 kcal/mole. In the case of partial eclipse, the energy is taken to be

$$V_{HH} = 0.95\ (1 - \cos 3\varphi)/2 \text{ kcal/mole}$$

where $\varphi$ is the angle through which one of the CH bonds in question has been rotated from the staggered conformation around the connecting C-C bond as axis. In the eclipsed conformation, $\varphi = 60°$.

3) H-C eclipse. This is a similar effect to H-H eclipse, but the pair of bonds involves one C-H and one C-C at opposite ends of the connecting carbon carbon bond. The strain energy resulting from H-C eclipse is known with much less certainty than that for H-H eclipse. We have taken it to be 1.50 kcal/mole per eclipsed pair; for partial eclipse the strain energy has been taken to be

$$V_{HC} = 1.50\ (1 - \cos 3\varphi)/2 \text{ kcal/mole.}$$

This choice was made on the basis of barrier heights opposing free rotation in propane, ethyl cyanide and isobutane.[28] This effect makes a significant contribution to strain energy in the spiranes; the uncertainty concerning its magnitude is therefore unfortunate.

4) C-C eclipse. Here the eclipsed C-C bonds are at opposite ends of a connecting C-C bond. A simple example occurs in cis-1,2-dimethylcyclopropane. The enthalpy of this compound has been shown by Flowers and Frey[8] to be higher than that of the corresponding trans compound by 1.1 kcal/mole. Whether this effect is similar in kind to H-H overlap is far from clear; it is possible that the repulsion between eclipsed $C-CH_3$ bonds is different from that between eclipsed $C-CH_2$ bonds in ring systems. Ignoring this possibility, we derive from the result reported above

$$HH + CC - 2HC = 1.1 \text{ kcal/mole.}$$

Assuming the values for HH and HC eclipse from (2) and (3) above, we obtain a contribution of 3.1 kcal for each pair of eclipsed neighboring C-C bonds. The uncertainty in this estimate would be resolved by an accurate heat of combustion or hydrogenation for dimethylcyclopropane. Note that a contribution to the strain energy is not counted for those C-C bond eclipses that occur within the framework of a single $C_3$ or $C_4$ ring, since these contributions are taken to be a part of the intrinsic ring strain.

5) Apical Spirane Angular Strain. When a small cyclane is formed, the external HCH bond angles are free to adjust to the abnormally small CCC bond angles. In general they are believed to expand to around 112° in cyclobutane and according to recent electron diffraction data, to 115 ± 1° in cyclopropane.[9] In a small-ring spirane, however, the two C-C-C bond angles sharing a common vertex are both constrained to be abnormally small. It seems reasonable to attribute an additional angular strain energy to this effect.

Results for Various Molecular Structures in Cyclic Systems

(1) Cyclanes

| | kcal/mole |
|---|---|
| **Cyclopropane:** | |
| $\Delta H_f(g)$, experimental (25°C) | 11.9 |
| Strainless $\Delta H_f(g)$, calculated | -14.79 |
| Total strain energy | 26.7 |
| Conformational strain, H-H eclipse | 5.7 |
| Intrinsic $C_3$ ring strain | 21.0 |
| Cyclobutane: | |
| $\Delta H_f(g)$, experimental | 6.39 |
| Strainless $\Delta H_f$, calculated | -19.71 |
| Total strain energy | 26.10 |
| H-H eclipse (x8) | 7.6 |
| Intrinsic $C_4$ ring strain | 18.5 |

| Methylcyclobutane: | kcal/mole |
|---|---|
| $\Delta H_f(g)$, experimental | $-4.0 \pm 3.5$ |
| Unstrained $\Delta H_f$, calculated | -26.7 |
| Total strain energy | $22.7 \pm 3.5$ |
| H-H eclipse (6) | 5.7 |
| H-C eclipse (2) | 3.0 |
| Total conformational strain | 8.7 |
| Intrinsic $C_4$ ring strain | $14.0 \pm 3.5$ |

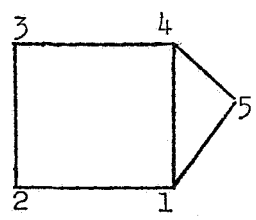
The high uncertainty attached to the experimental value in this case was assigned because of the discrepancy of 3.5 kcal/mole between the heat of formation obtained by the same authors for spiropentane and more recent and precise data. In view of this suggested experimental uncertainty, we have taken the intrinsic $C_4$ ring strain to be 18.0 kcal/mole.

(2) Bi and Tricyclanes

Bicyclo(2,1,0)pentane

The heat of hydrogenation to cyclopentane has been measured by Turner (Table A2-2, Reference 19) as 55.1 kcal/mole in solution. From this result we estimate $\Delta H_f(g)$ to be 36.7 kcal/mole, and the total strain energy to be 55.0 kcal/mole. In order to estimate the contribution of H-C eclipse we have estimated the relevant bond angles by the following approximation:

Two neighboring H atoms on the same side of a cyclobutane ring, together with the C atoms to which they are bonded, define a plane. When these two H atoms are replaced by a $CH_2$ group, assume that the added C atom lies in this plane, and forms an equilateral triangle with the two C atoms to which it is bonded. The remaining bond angles are assumed to be as in cyclobutane and cyclopropane. This model can be only an approximation to the truth. Representing the structure of bicyclopentane by the projection below




we conclude that the eclipse interaction between the CH bond at 2 and the CC bond 1-5 is negligible; the interaction between the CH bond at 5 and each of the CC bonds 1-2 and 4-3, however, is estimated to be 0.7 kcal/mole. The total contribution of eclipse interactions is thus estimated to be 8.0 kcal/mole, leaving a balance of 47.0 kcal for ring strain. This is larger than the sum of the ring strains in cyclopropane and cyclobutane by 8.0 kcal/mole.

## Tricyclo(3,1,0,$0^{2,4}$)hexane

This molecule is constructed by adding a carbon atom to bicyclopentane to form a second cyclopropane ring directly across the cyclobutane ring from the first. The two cyclopropane rings can have a conformation that is either cis or trans with respect to the cyclobutane ring. In the cis conformation there will be 8 H-H, 2 C-C and 4 partial H-C eclipse interactions for a total contribution of 16.6 kcal/mole if the high value chosen for the C-C eclipse interaction is valid (it may well be too high) or around 13.5 kcal if a lower value is used. In the trans conformation, there will be only 6 HH and 4 partial HC eclipse interactions for a total contribution of 8.5 kcal/mole. This should therefore be the stable conformation.

To estimate the ring strain, we apportion the ring strain in bicyclopentane as follows: 1/3 of the ring strain in cyclopropane to position 5 and half of the ring strain in cyclobutane to positions 2 + 3, for a total of 16.0 kcal. This leaves a balance of 31.0 kcal/mole for the configuration around positions 1 and 4. This configuration occurs twice in the bicyclohexane. Hence we assign a ring strain of 62. + 14.0 or 76.0 kcal/mole to the $C_6$ compound.

The estimated total strain energy in trans tricyclo(3,1,0,0)hexane is thus 84.5 kcal/mole, and the heat of formation in the gas phase is estimated to be 67.6 kcal/mole. We estimate the heat of vaporization of bicyclobutane (q.v.) at 25°C to be about 5.60 kcal/mole. If we allow a contribution of 1.18 kcal per $CH_2$ group to ($\Delta H_V$-RT) from Table A2-3 we obtain a contribution of 2.6(4) kcal per pair of ring CH groups in a polycyclane. Thus we estimate the heat of vaporization of the tricyclohexane to be about 8.2 kcal/mole. The final estimated heat of formation in the liquid phase for the trans tricyclohexane is 60.0 kcal/mole. The reliability of this estimate is quite uncertain.

## Bicyclobutane

The heat of hydrogenation of 1,3-dimethylbicyclobutane in solution to form an analyzed mixture of 1,3-dimethylcyclobutane (0.15 to 0.21 mole/mole) and 2-methylpentane (0.85 to 0.79 mole/mole) has been measured by R. B. Turner et al.[10] From their results they derive for 1,3-dimethylbicyclobutane a value $\Delta H_f(g)$ = +38.5 ± 1 kcal/mole. By an independent analysis of their data we derive from their two experiments $\Delta H_f(\ell)$ = +32.10 and +30.42 kcal/mole for a mean of 31.3 ± 1 kcal/mole.

From vapor pressure measurements in the temperature range -21 to 8°C (details not given) K. B. Wiberg et al (see Table A2-2, ref 17) derive an average heat of vaporization for unsubstituted bicyclobutane of 6.04 kcal/mole. From this and the $\Delta H_V$ vs T curve estimated by C. V. Sternling at these laboratories we obtain a heat of vaporation at 25°C of 5.6 kcal/mole.

The difference in heat of vaporization at 25°C between 1,3-dimethylcyclopentane (average of cis and trans) and cyclopentane is 1.41 kcal/mole from the API 44 Tables. The corresponding difference in the cyclohexanes is 1.36 kcal/mole. We therefore estimate the heat of vaporization of 1,3-dimethylbicyclobutane as 6.9 kcal/mole at 25°C. This leads to $\Delta H_f^{298}(g)$ equal to +38.2 ± 1 kcal/mole in good agreement with the estimate of 38.5 by Turner et al.

From this point we can proceed in several ways to estimate $\Delta H_f$ for bicyclobutane. The most straightforward is to observe that the difference in $\Delta H_f$(g, 25°C) between cyclopentane and 1,3-dimethylcyclopentane (average of cis and trans) is 13.7 kcal/mole. This leads to $\Delta H_f$(g) (bicyclobutane, 25°C) of 51.9 ± 3 kcal/mole where the uncertainty is a guess.

We choose as the values to use for bicyclobutane

$$\Delta H_f(g) = 52 \pm 3 \text{ kcal/mole}$$
$$\Delta H_f(\ell) = 46 \pm 3 \text{ kcal/mole.}$$

The strain enthalpy of bicyclobutane on this basis is 65.(3) kcal/mole; of this 6 or 7 kcal can be attributed to eclipse interactions. The balance of 58-59 kcal is more than twice the intrinsic ring strain in cyclopropane by 16-17 kcal/mole. This is, not surprisingly, an even larger departure from additivity than was observed in the case of bicyclopentane.

(3) Spiranes and Dispiranes

Spiropentane(2,2)

| | |
|---|---|
| Experimental $\Delta H_f$(g), kcal/mole | 44.9 |
| Total strain energy, kcal/mole | 63.7 |
| H-H eclipse, 4 x 0.95 kcal | 3.8 |
| H-C eclipse, estd, 8 x 1.02 kcal | 8.2 |
| Ring strain (balance) | 51.7 |

Thus the ring strain is greater than twice the ring strain in cyclopropane by a margin of 9.7 kcal/mole on this basis. Indeed, the total strain energy is greater than twice that in cyclopropane by a margin of 10.3 kcal/mole.

This discrepancy may be attributed to abnormal C-C-C bond angles between the two rings. In cyclopropane, the HCH bond angles are about 116°, which corresponds to a C-C-H angle of 125.3°. In spiropentane we estimate that the corresponding inter-ring C-C-C bond angle has been enlarged to 138.5°. The deformation is then 13.2° or 0.392 radians. The excess strain energy can be described as

$$E = 1/2\ k'(\Delta\theta)^2 .$$

The excess of 9.7 kcal/mole distributed over four bond angles corresponds to a value for the force constant k' of 91 kcal/mole radian$^2$, which is reasonable in order of magnitude though a little high. We therefore choose as an expression for the total apical angle strain enthalpy in a spirane

$$\Delta H = 5.56 \times 10^{-2}\ (\Delta\theta, \text{deg})^2 \text{ kcal/mole}$$

where $\Delta\theta$ is the deformation in degrees of a single apical C-C-C bond angle from its unconstrained value.

Spirononane(4,4)

| | |
|---|---|
| Experimental $\Delta H_f$(g), kcal/mole | -24.4 |
| Strain energy, kcal/mole | 15.1 |

This is greater than twice the strain energy in cyclopentane by 2.7 kcal/mole. Most of the strain in cyclopentane comes from H-H eclipse. In spirononane, 4 of the H-H eclipse interactions are replaced by H-C interactions; this is expected to increase the strain energy by 2.2 kcal/mole, in agreement with observation within the accuracy of the model.

Bond angles in this molecule should be approximately normal. One therefore expects no additional strain from abnormal bond angles at the apical carbon atom. Similar conclusions are reached from a consideration of the experimental heats of formation in the spiro(4,5)decane, where a 5-carbon and 6-carbon ring share a common carbon atom, and in spiro(5,5)undecane. These observations support the idea that the extra strain energy in spiro(2,2)pentane is to be attributed to the abnormal C-C-C bond angles between carbon atoms on two different rings through the central carbon atom.

Spiro(3,3)heptane

If we take the cyclobutane rings in this compound to be planar, and the C-C-C bond angles within the cyclobutane rings to be 90°, neither of which is strictly true, the apical C-C-C bond angle is 120°. The HCH bond angle in cyclobutane is 112° corresponding to a CCH bond angle of 113.3°. Then the apical angle strain is 6.7°, and the corresponding strain enthalpy is 2.5 kcal/mole. The H-C eclipse enthalpy is estimated to be 1.4 kcal per interacting pair of bonds. We then estimate the heat of formation as follows:

| | kcal/mole |
|---|---|
| Strainless $\Delta H_f(g)$ | -29.2 |
| Ring strain, 2 x 18.0 | 36.0 |
| H-H eclipse, 8 x 0.95 | 7.6 |
| H-C eclipse, 8 x 1.4 | 11.2 |
| Apical angle strain | 2.5 |
| Net $\Delta H_f(g)$ | 28.1 |

The heat of vaporization at 25°C from additive contributions is about 8.1 kcal/mole. From Trouton's rule and the boiling point it is estimated to be about 7.7 kcal/mole at 95°C; an increase to about 8.5 at 25°C is not unreasonable. We choose a value of 8.3 kcal/mole for $\Delta H_v$ and finally obtain 19.8 kcal/mole for $\Delta H_f(\ell)$, with an uncertainty of 3 or 4 kcal/mole

Spiro(2,3)hexane

Again assuming the cyclobutane ring to be planar with 90° C-C-C bond angles, we obtain

| | kcal/mole |
|---|---|
| Unstrained $\Delta H_f(g)$ | -24.3 |
| Ring strain, 21.0 + 18.0 | 39.0 |
| H-H eclipse, 6 x 0.95 | 5.7 |
| H-C eclipse: | |
| C on 3-ring, H on 4-ring | 5.0 |
| C on 4-ring, H on 3-ring | 4.8 |
| Net $\Delta H_f(g)$ | 36.2 |
| Net $\Delta H_f(\ell)$ | 29.3 |

In this case the apical angle strain was calculated as the mean of the strain energies corresponding to the difference between the apical C-C-C bond angle and the C-C-H bond angles in cyclobutane and cyclopropane.

The results obtained for spirohexane and spiroheptane were used to estimate strain energies for dispiro(2,2,2)octane and dispiro(3,2,3)decane.

## Sources of Uncertainty in Spirane Estimates

The bond angles in the spiranes and dispiranes have been estimated only very roughly, and these affect the estimates of the strain energy associated with both apical angle strain and H-C eclipse interactions. In addition, the magnitude of the H-C eclipse interaction, as remarked earlier, is quite uncertain. It is therefore possible that the estimated heats of formation of these compounds are too high. To be conservative, we therefore assigned a range of values to these heats of formation; the lower value indicated for each compound on the basis of a rough guess is probably too low, and the higher value is quite possibly too high.

RANGE OF ESTIMATES FOR $H_f(\ell)$

| | |
|---|---|
| Spiro(2,3)hexane | 29.3 - 26.0 |
| Spiro(3,3)heptane | 19.8 - 16.2 |
| Dispiro(2,2,2)octane | 56.7 - 50.0 |
| Dispiro(3,2,3)decane | 35.3 - 29.3 |
| Spiro(3,4)octane | -6.6 - 8.0 |

## Tetrahedrane and the Cubanes

An experimental heat of combustion and an average heat of sublimation from the temperature dependence of the vapor pressure have recently become available for cubane.[11] The strain energy, then, is 161 kcal/mole on the basis of our table of group equivalents and 162 kcal/mole on the basis of the Allen scheme.

The strain energy attributable to "H-H eclipse" interactions is about 11 kcal/mole. Thus the "intrinsic strain" enthalpy associated with the carbon skeleton of cubane is about 150 kcal/mole. This is larger by 51-54 kcal/mole than 6 times the intrinsic ring strain associated with each cyclobutane face of the cube; the enhancement is similar in kind to that encountered in bicyclobutane and bicyclopentane.

From the vapor pressure data the average heat of sublimation is 19.2 kcal/mole and the boiling point is 95 to 140°C; a value around 125° seems not unlikely; the melting point (130°C) is slightly higher. From Trouton's rule, the heat of vaporization of the liquid would be about 8.3 kcal/mole at the boiling point or 9.6 kcal/mole at 25°C; our rough method of group equivalents leads to a value in the range 9.4 to 11.0 for the latter quantity. This implies that the heat of fusion at the melting point is 10 or 11 kcal/mole, with a corresponding entropy change of 25 to 27 eu. This high value implies that cubane does not rotate freely in the solid; the potential entropy gain on solution may make it appreciably soluble in suitable hydrocarbons at room temperature.

In methylcubane the heat of formation should be lowered by replacement of a CH bond by a $C-CH_3$ bond and raised by replacement of 3 "H-H eclipse" interactions by 3 C-H eclipse interactions. The net effect is estimated to be a change of -5.8 kcal/mole in $\Delta H_f(g)$. The heat of vaporization at 25° will correspondingly be increased by about 0.2-0.5 kcal/mole.

The estimate of $\Delta H_f(g)$ in Table 3 for tetrahedrane (tricyclo-[1,1,0,$0^{2,4}$]butane) is based on an estimate of the strain energy published by Weltner[12] on the basis of semi-empirical quantum mechanical calculations. It should be noted that the definition of strain energy used by him is not identical with that used here. The reliability of this estimate is not known; his calculated value of $\Delta H_f(g)$ for cubane was 150-160 kcal/mole, however, as compared to the experimental value 149.

## Methods to Estimate the Density of Liquid Hydrocarbons (by A. A. Bondi)

### Purpose and Scope

The liquid density data required in the present program are only rarely available and must therefore be estimated, if possible, from molecular structure data alone, or from whatever other physical property data may be available. The problem is aggravated by two phenomena, the absence of a theory able to provide quantitative liquid property estimates, and the general availability of NMR spectroscopy which has tended to replace all other means of characterizing organic - especially hydrocarbon - compounds. Recent reports on novel compounds therefore often lack the previously common density, refractive index, or boiling point information.

Three methods have been employed to estimate the density of liquid pure hydrocarbons:

1. From molar refractivity correlations (when refractive index data are available).
2. A group increment scheme for molal volume.
3. A packing density correlation.

### Density From Refractivity Correlations

If one assumes reliable group increment additivity of the molar refractivity [R], where

$$[R]_\omega = \frac{n_\omega^2 - 1}{n_\omega^2 + 2} \frac{M}{\rho} \qquad \text{(A2-1)}$$

the density ($\rho$) of a compound at temperature T can obviously be estimated from its refractive index $n_\omega$ - obtained at frequency $\omega$ and at the same temperature T via

$$\rho = \frac{n_\omega^2 - 1}{n_\omega^2 - 2} \frac{M}{[R]_\omega} \qquad \text{(A2-2)}$$

where M = molal weight.

The literature is replete with atom and bond refraction increments.[15)19)23)] The user should remember, however, that the various schemes are not entirely consistent with each other, so that increments are not transferable. The scheme he selects he must stick with. No existing scheme contains provision for highly strained three dimensional ring systems.

Inspection of the available information assembled in Table A2-5, shows that the ring increments proposed by Vogel[a)] are not entirely correct and that the deviations from them are systematic. In the compounds of interest to us, which may contain several cyclopropyl and/or cyclobutyl rings large errors can be produced by incorrect ring increments. For quadricyclene one estimates with Vogel's ring increments $\rho^{25} = .912$, whereas the increments suggested by the data of Table A2-5 and collected on Table A2-6 lead to $\rho^{25} = .835$, very close to the estimate obtained by the volume method discussed further on.

The cause of the exaltations in Table A2-5 must, of course, be found in the electronic structure of the molecule. For cyclopropane it is commonly assumed[24)] that the carbon-carbon bonds have more $\pi$-character than in other alkanes, hence their electron cloud would be more extended, accounting for the increase in polarizability, magnetic susceptibility,[14)] as well as volume.

A Molal Volume Increment Method

Cyclization changes the molal volume by three routes: a) Loss of hydrogen, b) change of a long intermolecular contact into a short intramolecular contact, and c) rigidification of the molecule. Before demonstrating these three effects in detail "ground rules" must be formulated for making valid comparisons, and thus for producing valid prediction methods. A basic rule should be that all comparisons be made at the same reduced temperature $T/T_c$. In the absence of $T_c$ data, a constant ratio $T/T_b$ would be a fair approximation. Even that is not always enforceable because of lack of $T_b$ data. As a zeroth approximation we shall employ at minimum the rule of comparison at a fixed temperature at constant carbon number, ($N_c$). The change $d\Delta_c/dN_c$ for each type of cyclization increment $\Delta_c$ must therefore be known before one can transfer the information across carbon number lines.

Case (a), hydrogen loss, is too obvious to require any further discussion and its magnitude has been fully described elsewhere[20)22)] as essentially independent of hydrocarbon type, ca 3 $cm^3$/mole/H atom (at 25°C). This decrement size is confirmed for most cyclic hydrocarbons on Table A2-7, where a few systematic exceptions are noted. The cause of these exceptions is the well known,[13)21)] but still unquantified, effect of conformation on molal volume.

In ordinary chemistry cause (b), change from nonbonded to bond distance, and (c), rigidification, occur together. For example, the volume contraction accompanying formation of an addition compound from the liquid reactants is as much due to the conversion of an intermolecular to an

a) The ring increments suggested by Batsanov[15)] for the Eisenlohr system also appear to be too large.

Table A2-5. EXALTATION[a] OF MOLAR REFRACTIVITY FOR VARIOUS CYCLOALKANE SYSTEMS (IN $CM^3$/MOLE)

| Ring | Single Ring Systems[b] | | | |
|---|---|---|---|---|
| | Cyclohexane | Cyclopentane | Cyclobutane | Cyclopropane |
| Alkyl Group(s): None[c] | -.17(+.24) | -.10(+.23) | [-.43(-.26)][d] | .26(+.46)[e] |
| Vogel's ring increments | -.15 | -.19 | +.32 | +.61 |
| Methyl | -.03 | -.05 | +.40 | - |
| Ethyl | -.16 | -.13 | +.27 | +.43 |
| Propyl | -.14 | -.13 | - | +.36 |
| 1,1-Dimethyl | -.14 | -.04 | +.52 | +.60 |
| 1,cis-2-Dimethyl | -.33 | -.32; -.23 | +.12 | +.33; +.43; +.34 |
| 1,trans-2-Dimethyl | -.06 | -.02 | - | +.60; +.60; +.45 |
| 1,cis-3-Dimethyl | +.12 | +.07 | +.40 | |
| 1,trans-3-Dimethyl | -.16 | 0 | +.53 | +.60 |
| 1,trans-4-Dimethyl | +.13 | | | |

| | Multiple Ring Systems | |
|---|---|---|
| | $\delta[R]_D$ | $\delta[R]_D$/Ring |
| Spiropentane[f] | 1.23 | 0.62 |
| 3,3-Spiroheptane[g] | 0.83 | 0.42 |
| 3,1,3,1-Dispirodecane[h] | 1.14 | 0.38 |
| 5,5-Spiroundecane[h] | -0.5 | -0.25 |
| Dicyclopropyl[i] | 0.70 | 0.35 |
| 2,1,0-Bicyclopentane[j] | 0.62 | 0.31 |
| 2,2,0-Bicyclohexane[k] | 0.78 | 0.39 |
| 4,1,0-Bicycloheptane[k] | 0.58 | 0.29 |

a) Relative to Vogel's Molar Refraction $[R]_D$ increments for carbon and hydrogen only.
b) From tables of API Project 44.
c) The values in parentheses are relative to $[R]_D(CH_2) = 4.579$, obtained from the cycloalkane data of reference (b) above cycloheptane.
d) The experimental cyclobutane datum is obviously faulty.
e) A. V. Grosse and C. B. Linn, J. Am. Chem. Soc. 61, 751 (1939).
f) V. A. Slabey, ibid. 68, 1335 (1946).
g) E. R. Buchman et al, N6-onr-244/XI, Cal. Tech. Oct. 1951.
h) P. A. Naro, J. Chem. Eng. Data 10, 86 (1965).
i) V. A. Slabey, J. Am. Chem. Soc. 74, 4928 (1952).
j) R. Criegee and A. Rimmelin, Chem. Ber. 90, 414 (1957).
k) S. W. Ferris, "Handbook of Hydrocarbons", Academic Press, 1955.

Table A2-6. RECOMMENDED RING INCREMENTS FOR MOLAL REFRACTIVITY RELATIVE TO VOGEL'S C AND H INCREMENTS[a] IN $[R]_D$ = $CM^3$/MOLE PER RING

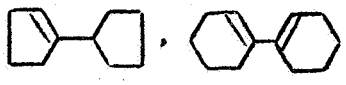
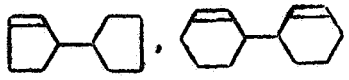
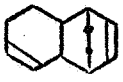
| Correction | Ring Size | | | |
|---|---|---|---|---|
| | 3 | 4 | 5 | 6[c] |
| $CH_2$ | +.40 | +.27 | -.13 | -.15 |
| 1,cis-2-Dimethyl | +.37 | +.13 | -.28 | -.33 |
| 1,cis-3 | - | +.40 | +.07 | +.12 |
| 1,trans-2-Dimethyl | +.60 | +.38 | 0 | -.06 |
| 1,cis-4 | | | | -.17 |
| 1,1-Dimethyl | +.60 | +.50 | -.04 | -.14 |
| Spiroalkane | +.62 | +.40 | +.15[b] | -.30 |
| Condensed Cycloalkanes | | | | |
| 01X | +.35 | +.25 | +.2 | +.2 |
| 02X | +.35 | +.3 | -.2 | (-.25) |
| 03X | | | -.15 | cis -.25<br>trans 0 |
| 04X | | | -.15 | cis -.25<br>trans -.05 |

a) $[R]_D(C) = 2.591$; $[R]_D(H) = 1.028$; based largely but not entirely on the data of Table A2-5.

b) In spiroalkanes where the adjacent ring is large the increment is more nearly (-.1) in keeping with expectations from the 1,1-dimethyl derivative.

c) For 7- and 8-membered rings, deduct a further 0.068 ($n_R$-6) from the datum in the cyclohexane columns, where $n_R$ = numbers carbon atoms in the large ring.

Table A2-7. DOUBLE BOND INCREMENT OF THE MOLAL VOLUME AT 20°C FOR CYCLOALKENES RELATIVE TO THE EQUISTRUCTURE CYCLOALKANE IN $-CM^3$/MOLE PER DOUBLE BOND

| Type of Double Bond | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|
| cis-Mono-ene | | | | 4.6[d] | 5.3[d] | 5.9[e] | | | |
| trans-Mono-ene | 5.9[a] | 6.8[a] | 4.7[b] | 4.7[c] | 4.3[d] | 4.4[e] | | | |
| 1,3-Diene | | 6.4[f] | 7.3[f] | 5.1[f] | | | | | |
| 1,4-Diene | | 7.3[f] | | 5.4[f] | | | | | |
| 1,5-Diene | | | | 4.4[f] | | | | | |
| 1,2-Diene | | | 5.5[f] | | | | | | |
| 1,3,5-Triene ñ,ñ,ñ | | | 5.9[f] | | | | | 3.4[g] | |
| c,ñ,ñ | | | | | | | | 4.3[g] | |
| c,c,ñ | | | | | | | | 5.0[g] | |
| c,c,c | | | | 5.8[f] | | | | | |
| 1,3,5,7-Tetrane | | | | 5.3[h] | | | | | |
| Dicycloalkylidene ( ) | | | | | | 7.8[i] | | | 6.0[i] |
|  | | | | | | 6.7[i] | | 8.3[i] | |
|  | | | | | | 5.8[i] | | 7.5[i] | |
|  | | | | | | | | 4.5[i] | |
| vs | | | | | | 4.3[i] | | | |
| 2,5 vs 3,7 diene | | | | | | 2.0[i] | | | |

a) API Res. Project 44 tables.
b) Beilstein.
c) A. C. Cope et al, J. Am. Chem. Soc. 75, 3212 (1953).
d) A. T. Blomquist et al, ibid. 74, 3643 (1952).
e) A. T. Blomquist et al, ibid. p. 3636.
f) M. P. Doss, Phys. Constants of the Principal Hydrocarbons, Texas Co., 1943.
g) G. Wilke et al, Makromol. Chemie 68, 18 (1963 in combination with L. I. Zakharkin and V. V. Korneva, C. A. 62, 6389e.
h) E. Kuss, Z. angew. Physik 8, 373 (1955).
i) WADC, TR 59-327.

intramolecular constant as it is due to the loss of the loss of the external degrees of freedom of one molecule. Since a rigid ring compound cannot have less than 6 external degrees of freedom, its further cyclization provides a direct measure of the effects of cause (b). Examples are shown in Table A2-8.

A special form of case (b) is observed with spirohydrocarbons, Table A2-9, where the inaccessibility of the central C-C bonds to intermolecular interactions causes a sharp drop in the interaction energy manifest in the energy of vaporization as well as boiling point. Hence at a fixed temperature the liquid is considerably more expanded than is that composed of nonspiro cyclics.

Cause (c), the loss of molecular flexibility, reduces volume because the extra degrees of freedom associated with internal rotation are additive to the usual external degrees of freedom per molecule and contribute correspondingly to its kinetic energy. A striking illustration of this point is the change in molal volume accompanying conversion of hexene-1 to cyclohexane, etc., shown on Table A2-10. The number of external degrees of freedom per molecule given on Table A2-10 has been derived from density and energy of vaporization data by a method described elsewhere.[16][17]

The effects of ring-conformation on molal volume have already been noted in connection with the cyclo-olefins. They are even more pronounced with condensed cycloparaffins, as evident from the data of Table A2-11. One notes that the ring closure decrement for the denser cis-isomer generally approaches the "typical" ring closure decrement in magnitude, while that for the trans-isomer is appreciably smaller. The high density of the cis-isomer appears to be connected with their greater east of packing (stacking). Allinger's explanation of the high density due to crowding of the hydrogens is not borne out by calculation.

Isomerization of cycloalkanes to alkylcycloalkanes is accompanied by an appreciable volume expansion (Table A2-12) because of the low energy of methyl/methyl interaction and the concurrent rise in kinetic energy due to the mobility of the alkyl groups. The large effects of cis-trans isomerization (and ring conformation) on the volume of the different dialkyl cycloalkanes seems to be largely a function of the space requirement for rotation as is indicated by the excellent correlation of the molal volume of the isomeric dimethylcyclohexanes and decalins with the mean-square radius of gyration of the molecules on Figure A2-1. Were it not that the volume of 1,1-dimethylcyclohexane is a maverick also in other correlations,[13] its excursion on Figure A2-1 might throw the entire correlation into question.[a] In the absence of numerical estimates of Allinger's suggestion of volume loss per molecule due to intramolecular crowding, one cannot assess which of these two causes should be considered as of primary importance.

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a) Comparison at constant $T/T_b$ also should not reduce $\delta V$ of 1,1-dimethylcyclohexane below that of the cis-1,2-isomer, as required by the radius of gyration.

Table A2-8. VOLUME CHANGE ACCOMPANYING ADDITIONAL RING CLOSURE OF CYCLOALKANES OR CYCLOALKENES (-$CM^3$/MOLE PER ADDITIONAL RING CLOSURE) AT 20°C

| Type of Closure[d] | $N_c$ | 5 | 6[c] | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|
| 01 ($N_c$-3) | $\delta_c$[b]<br>$\delta_e$[b] | 8.1<br>2.2 | 8.0<br>(1.2) | 6.6<br>1.8 | | | 7.9<br>(2.0) | | |
| 02 ($N_c$-4) | $\delta_c$<br>$\delta_e$ | | 8.6<br>1.8 | 8.1<br>3.3 | 6.0<br>1.8 | 5.5<br>(0.2) | | | |
| 03 ($N_c$-5)[a] | $\delta_c$<br>$\delta_e$ | | | | 7.6<br>3.4 | 8<br>2.7 | | | |
| 04 ($N_c$-6)[a] | $\delta_c$<br>$\delta_e$ | | | | | | 9.2<br>3.3 | | 6.8 |
| 12 ($N_c$-5) | $\delta_c$<br>$\delta_e$ | | | 10<br>4 | (10) | 10.6<br>(4) | (12-13) | | 10.5 (13)<br>3.5 to 6 |
| 22 ($N_c$-6) | $\delta_c$<br>$\delta_e$ | | | | 9-10 | | | | 15<br>8 |

a) Nearly all references are from reference (b) of Table A2-7.
b) $\delta_c$ = decrement relative to cycloalkane, $\delta_e$ = decrement relative to cycloalkene, i.e., the isomerization of the double bond to a ring closure.
c) Only the cis isomer is referred to here.
d) The symbol 01 ($N_c$-3) specifies that the shortest path across the bridgehead contains 0 carbon atoms (direct bonding); the next longest path contains 1 carbon atom; the longest path contains ($N_c$-3) where $N_c$ is the number of carbon atoms in the ring prior to closure.

Table A2-9. VOLUME CHANGE ACCOMPANYING RING CLOSURE OF CYCLOALKANES[a] OR CYCLOALKENES TO SPIROALKANES (-CM³/MOLE PER ADDITIONAL RING CLOSURE) AT 20°C

| Type of Closure[e] | $N_c$ | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2, $(N_c-3)$ | $\delta_c$[b] | 4 | 4 | | -1.4 | | | | | | |
| | $\delta_e$[b] | -1.9 | -3 | | -2.8 | | | | | | |
| 3, $(N_c-4)$ | $\delta_c$ | | | 1.5 | | 2.7 | 1.8[c] | | | | (4.3)[d] |
| | $\delta_e$ | | | -3.3 | -3 | -2.5 | -4[c] | | | | |
| 4, $(N_c-5)$ | $\delta_c$ | | | | | | 6.2 | | | | |
| | $\delta_e$ | | | | | | 1.8 | | | | |
| 5, $(N_c-6)$ | $\delta_c$ | | | | | | | 7.7 | 10.9 | | |
| | $\delta_e$ | | | | | | | 1.8 | 4 | | |

a) All from the spiro reference of Table A2-5 and reference (b) of Table Table A2-6.
b) See definition on Table A2-8.
c) For the dispiro decane.
d) 5,3,5-Dispiro tetradecane.
e) The symbol specifies the number of carbon atoms other than the apical one one in each of the connected rings. $N_c$ is the number of carbon atoms in the ring prior to closure.

Table A2-10. VOLUME CHANGE ACCOMPANYING RING CLOSURE OF 1-ALKENES TO CYCLOALKANES COMPARED AS TO THE NUMBER OF EXTERNAL DEGREES OF FREEDOM (3c) OF THE 1-ALKENES[a)]

| $N_c$ | $-\Delta V_{20}$, $cm^3$/mole | (3c-6) of 1-Alkene |
|---|---|---|
| 3 | 7.0[b)] | 0 |
| 4 | 9.7[b)] | 0.3 |
| 5 | 13.3[b)]<br>15.4 | 0.5 |
| 6 | 16.9 | 0.9 |
| 8 | 22.8 | 1.8 |
| 9 | 24.6 | 2.2 |
| 10 | 25.7 | 2.7 |
| 12 | 26.9 | 3.6 |
| 20 | (22.5)[c)] | 7.1 |

a) For the cycloalkanes $N_c \leq 12$ one finds $3c \approx 6$.
b) At the atmospheric boiling point.
c) From extrapolated density data. For cycloalkanes of this size $3c > 6$, hence $\Delta V$ is indeed likely to decrease at $N_c > 12$.

Table A2-11. VOLUME CHANGE ON cis-trans ISOMERIZATION OF CONDENSED CYCLOALKANES

| Compound | $V_{20}$(trans)-$V_{20}$(cis), $cm^3$/mole | $-\delta V_R$ for cis Cpd, $cm^3$/mole |
|---|---|---|
| 033 Bicyclooctane | 1.2 | 7.6 |
| 034 Bicyclononane | 3.4 | 7.5 |
| 025 Bicyclononane[a)] | 0.15 | 5.6 |
| 035 Bicyclodecane | -2.5 | |
| 044 Bicyclodecane | 4.8 | 9.4 |

a) N. A. Allinger, J. Am. Chem. Soc. 81, 4074 (1959) all other references previously cited.

Table A2-12. VOLUME CHANGE ON ISOMERIZATION OF CYCLOALKANE TO ALKYLCYCLOALKANES (CYCLO $C_n \rightarrow$ Me CYCLO $C_{n-1}$ AND CYCLO $C_n \rightarrow Me_2$ CYCLO $C_{n-2}$)

All in $cm^3$/mole per alkyl group.

| Alkyl Cycloalkane | Ring Size, Cycloalkane | | | | | | |
|---|---|---|---|---|---|---|---|
| | 4 | 5 | 6 | 7 | 8 | 8[b)] | 9 |
| Methyl cycloalkane | 4[a)] | 7 | 4.3 | 6.5 | 4.8 | | 2.6 |
| 1,1-Dimethyl | | 6.0 | 5.0 | 4.5 | 4.8 | 3.0 | |
| cis-1,2-Dimethyl | | 3.5 | 3.1 | | 3.4 | 2.3 | |
| trans-1,2-Dimethyl | | 5.3 | 5.0 | | 5.2 | 3.8 | |
| cis-1,3-Dimethyl | | | 5.2 | 5.4 | 6.2 | 4.4 | |
| trans-1,3-Dimethyl | | | 6.0 | | 4.4 | 3.0 | |
| cis-1,4-Dimethyl | | | | | 4.6 | 3.1 | |
| trans-1,4-Dimethyl | | | | | 6.5 | 4.6 | |

a) At atmospheric boiling point, methylcyclopropane datum from Egloff, Physical Constants of Hydrocarbons, Vol. 2, p. 42.

b) All at $T/T_b$ = .701 (the "reduced" temperature for cyclooctane at 25°C). All other data from previous references.

Generalized Density vs Temperature Relation

In principle it would have been more desirable to express the density of the liquids of interest in terms of the generalized coordinates packing density $V_W/V(T) = f(T^X) = f(ZcRT/2E°)$ developed earlier,[17] where $V_W$ is the volume actually occupied by the molecule as estimated from x-ray diffraction data,[18] E° is the energy of vaporization at the standard condition $V(T)/V_W = 1.70$, Z is the number of nearest neighbors per molecule, generally taken as 10, and 3c is the number of internal degrees of freedom per molecule mentioned earlier.

While a generalized function exists which describes the density of a wide range of aliphatic and aromatic substances in the liquid state quite well, with a single value of Z, it does not handle the cyclic compounds of the present investigation without adjustment of either $V_W$ or of Z, or of both. It may, of course, be entirely true that for the more nearly spherically symmetrical compounds of the present investigation Z differs substantially from the value more commonly found. But there is at present no guide for a priori estimation of Z. Hence, it would be just another disposable parameter. For that reason in the present investigation the generalized density has been used just to check the reasonableness of the numbers arrived at by different methods.

Nature and Reliability of the Correlations Developed

The Refractive Correlation is only of limited utility because refractive index data are ever more rarely determined by preparative chemists. A systematic treatment of the Molar Refractivity of (strained) polycycloalkanes is also still wanting. The reliability of the density estimates so obtained is displayed by the examples on Table A2-13. It should be noted that there are no refractivity data for hydrocarbons of high strain concentration.

The Molal Volume Correlation discussed in the body of this report can be scrutinized for reliability on several levels, first by examination of the scatter of the cyclization increment/magnitude, and then by a few applications.

In principle one prefers the reference compound to be as close to the compound under consideration as possible, so that the additional ring closure increments are as few and as small as possible. Instead of considering the single closure of a cycloalkane, involving the loss of $H_2$, one should consider the isomerizing closure of a cycloalkene, etc. Unfortunately, this path is obstructed by the peculiar effect of detailed conformation of the cycloalkenes and higher cyclopolyenes on the molal volume. There is no obvious reason for choosing a particular cycloolefin as reference compound in preference over its isomer(s). A somewhat arbitrary choice may be the one that has a dehydrogenation decrement most nearly like 6 $cm^3/H_2$.

A comparison of the ring-closure decrements obtained by both procedures, on Table A2-14, shows that the fractional scatter of the olefin derived decrements is indeed larger than it is for the cycloalkane derived decrements. But the absolute scatter, in $cm^3$/mole, is generally smaller.

Table A2-13. COMPARISON OF DENSITY ESTIMATES FROM REFRACTIVE INDEX DATA WITH OBSERVED DENSITY

| | $\rho^t$ calc | $\rho^t$ obs |
|---|---|---|
| Bicyclo[2,2,0]hexane | .830 | .825 |
| 2,2-Dimethyltricyclo[3,1,0]-[2,2,1]heptane[a)] | .873 | .873 |
| Bicyclo[5,2,0]nonane | .866 | .864 |

a)

Table A2-14. RECOMMENDED VOLUME INCREMENTS $\delta_c V_R$ PER ADDITIONAL RING CLOSURE OF CYCLOALKANES AND $\delta_e V_R$ PER ISOMERIZING RING CLOSURE OF CYCLOALKENES (IN -CM³/MOLE PER ADDITIONAL RING CLOSURE) AT 20°C

All for $N_c \leq 10$.[a)]

| Type of Ring Closure | cm³/Mole Per Additional Ring Closure[b)] | |
|---|---|---|
| | $-\delta_c V_R$ | $-\delta_e V_R$ |
| Condensed Rings[c)] | | |
| 01X | 7.4 ± 0.7 | 1.9 ± .3 |
| 02X | 7.1 ± 1.3 | 1.8 ± 1.1 |
| 03X | 7.5 ± 0.2 | 2.7 ± .5 |
| 04X | 10 | |
| 12X | 10 | (4) |
| 22X | 10 | (4) |
| Spiroalkanes[d)] | | |
| 2, ($N_c$-3) | (e) | -2.6 ± .5 |
| 3, ($N_c$-4) | 2.0 ± .5 | -3.3 ± .6 |
| 4, ($N_c$-5) | 6 | 1.8 |

a) The rise of increments with carbon number at $N_c > 10$ has yet to be worked out.
b) Beyond the simple cycloalkane.
c) Based largely, but not entirely on the data of Table A2-8.
d) Based largely, but not entirely on the data of Table A2-9.
e) Too irregular to permit averaging.

Systematic trends of the ring closure decrements with the total size of the molecule are difficult to find at $N_c \leq 10$, except for a trend to pass through a shallow minimum at $N_c = 7$ to 8. But the magnitude of nearly all decrements increases sharply at $N_c > 10$. So far it has not been established whether this is a real effect or an artifact, inherent in the use of extrapolated rather than experimental values of the reference volumes of the cycloalkanes, a list of which is attached as Table A2-15.

Examples

A number of pertinent cases has been calculated by the methods discussed. The results are shown on Table A2-16. Discrepancies between the results are a measure of the remaining uncertainties of the method. When expressed as uncertainty in density impulse these data could be used to pinpoint the economic value of experimental determination (preceded by the synthesis of requisite amounts of material) of the necessary information.

Table A2-15. MOLECULAR VOLUME AND MOLECULAR REFRACTION OF CYCLOALKANES

| Compound | Formula | Molecular Volume $V = M/d$ | | Molecular Refraction $V(n_D^2 - 1)/(n_D^2 + 2)$ | |
|---|---|---|---|---|---|
| | | 20°C | 25°C | 20°C | 25°C |
| | | ml/mole | | ml/mole | |
| Cyclopropane | $C_3H_6$ | - | - | - | - |
| Cyclobutane | $C_4H_8$ | 80.81[a)] | 81.43[a)] | 18.06[a)] | 18.06[a)] |
| Cyclopentane | $C_5H_{10}$ | 94.086 | 94.713 | 23.133 | 23.144 |
| Cyclohexane | $C_6H_{12}$ | 108.093 | 108.744 | 27.709 | 27.722 |
| Cycloheptane | $C_7H_{14}$ | 121.06 | 121.72 | 32.21 | 32.23 |
| Cyclooctane | $C_8H_{16}$ | 134.20 | 134.87 | 36.67 | 36.68 |
| Cyclononane | $C_9H_{18}$ | 148.48 | 149.16 | 41.17 | 41.19 |
| Cyclodecane | $C_{10}H_{20}$ | 163.57 | 164.28 | 45.77 | 45.79 |
| Cycloundecane | $C_{11}H_{22}$ | 179.0 | 179.6 | 50.5 | 50.5 |
| Cyclododecane | $C_{12}H_{24}$ | 195.0[b)] | 195.7[b)] | 55.1[b)] | 55.1[b)] |
| Cyclotridecane | $C_{13}H_{26}$ | 211.5[b)] | 212.3 | 59.8[b)] | 59.8 |
| Cyclotetradecane | $C_{14}H_{28}$ | 288.1[b)] | 228.9[b)] | 64.3[b)] | 64.3[b)] |
| Cyclopentadecane | $C_{15}H_{30}$ | 244.9[b)] | 245.8[b)] | 69.0[b)] | 69.0[b)] |
| Cyclohexadecane | $C_{16}H_{32}$ | 261.9[b)] | 262.8[b)] | 73.5[b)] | 73.5[b)] |
| Cycloheptadecane | $C_{17}H_{34}$ | 278.9[b)] | 279.9[b)] | 78.1[b)] | 78.1[b)] |
| Cyclooctadecane | $C_{18}H_{36}$ | 296.0[b)] | 297.0[b)] | 82.7[b)] | 82.7[b)] |
| Cyclononadecane | $C_{19}H_{38}$ | 313.2[b)] | 314.3[b)] | 87.4[b)] | 87.4[b)] |
| Cycloeicosane | $C_{20}H_{40}$ | 330.4[b)] | 331.6[b)] | 91.8[b)] | 91.8[b)] |

a) At saturation pressure.
b) For the undercooled liquid below the normal freezing point.

Table A2-16. EXAMPLES OF PREDICTED DENSITIES

| Compound | $\rho^{20}$ From Refractive Index | $\rho^{20}$ From $\delta_c V_R$ | $\rho^{20}$ From $\delta_e V_R$ |
|---|---|---|---|
| Quadricyclene | .935[c)] | .932 | .940[c)] |
| trans-[5,1,0,$0^{3,5}$]Tricyclooctane | .896[a)] | .905[b)] | .903[b)] |
| Tetracyclo[4,1,0,$0^{2,4}$,$1^{3,7}$]octane | .970[d)] | .970 | .972[e)] |
| Bicyclobutane (at 0°C) | – | .750 | .754 |
| Tetrahedrane (at 0°C) | – | .806 | .792 |
| Tricyclo[1,1,1,0]pentane | – | .835 | .848 |
| 1,2-Dimethyltricyclo[3,1,0,$0^{2,4}$]-hexane | | cis .860<br>trans .835 | |
| 1,4-Dimethyltricyclo[3,1,0,$0^{2,4}$]-hexane | | cis .845<br>trans .818 | |
| Tricyclo[4,2,0,$0^{2,5}$]octane | | .90 ± .02 | .91 ± .015 |
| Pentacyclooctane (cubane) | | .98 ± .04 | .990 ± .04[f)] |

a) $n_D^{20}$ from S. Winstein et al, J. Am. Chem. Soc. 86, 3127 (1964).
b) If one assumes a positive volume increment of 3 $cm^3$/mole (see Table A2-11) for the trans conformation one obtains $\rho$ = .885 and .882, respectively, in the last two columns.
c) $n_D^{26.5}$ from G. S. Hammond et al, J. Am. Chem. Soc. 83, 4674 (1961).
d) $n_D^{26}$ from N. A. LeBel and R. N. Liesmann, ibid. 87, 4301 (1965).
e) Starting from the datum for bicycloheptadiene ($\rho_4^{20}$ = .9065) by C. T. Mortimer et al, 1963, 3823.
f) Starting from the datum for cyclooctatetraene (ref. h of Table A2-7).

 Figure A2-1 follows

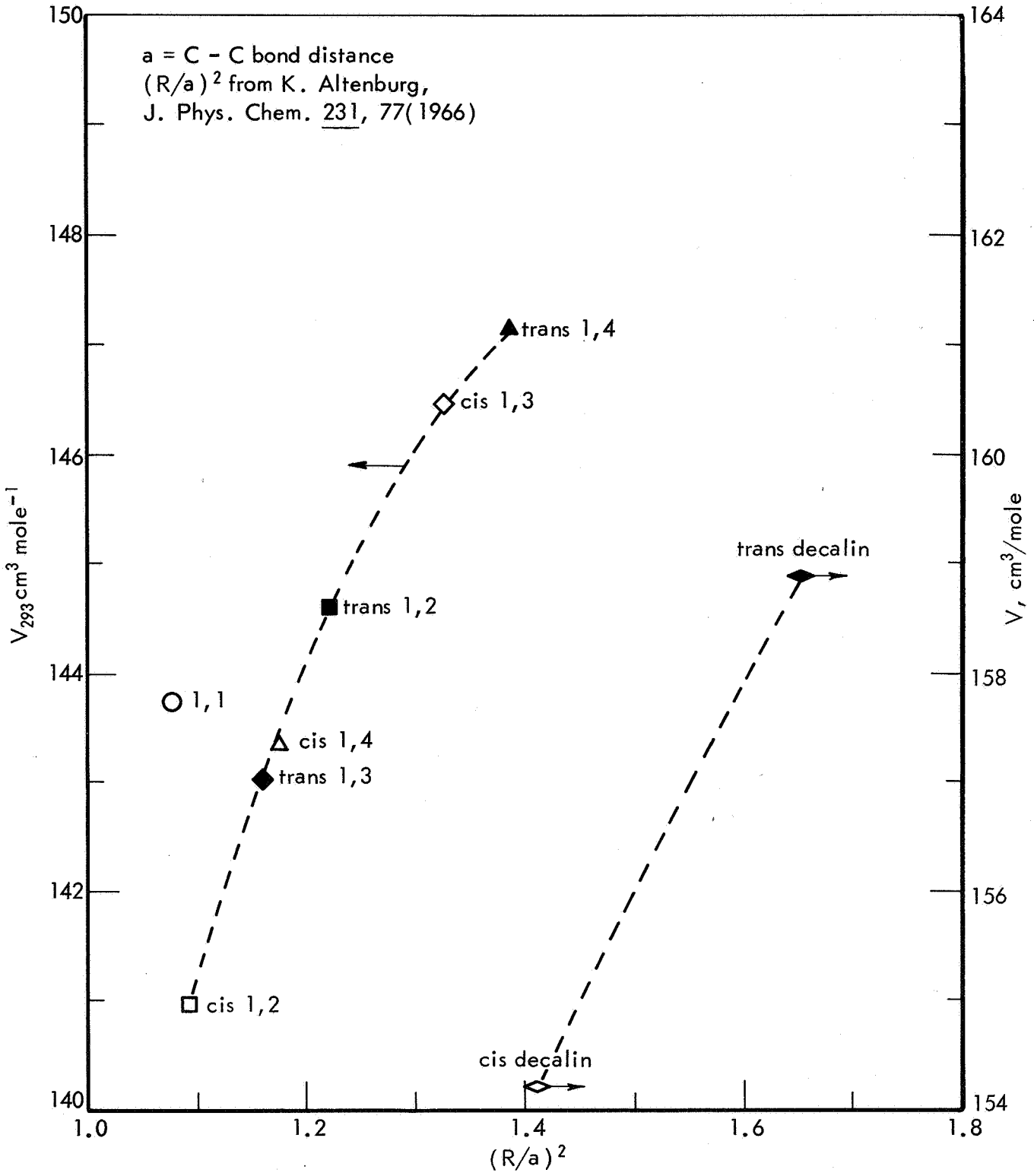


Figure A2-1. RELATION OF THE MOLAL VOLUME OF THE ISOMERIC DIMETHYLCYCLOHEXANES AND OF THE DECALIN ISOMERS TO THE REDUCED RADIUS OF GYRATION R

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13. ABSTRACT

Specific impulse (1000 psia/atm) and flame temperatures in combustion with liquid oxygen have been calculated for over forty strained or unsaturated hydrocarbons whose heats of combustion per unit mass are relatively high. Calculations were made assuming both frozen and shifting equilibria during expansion; the required enthalpies of formation and densities were estimated when experimental values were lacking. The calculated gain in specific impulse over that of the kerosene fuel RP-1 ranged up to 18 seconds or 6% at an oxygen/fuel ratio stoichiometric for combustion to carbon monoxide and water. The results obtained have been correlated with the hydrogen/carbon atom ratio of the hydrocarbon and its enthalpy of formation per gram atom of carbon.

Available information on the thermal stabilities of these types of hydrocarbons has been reviewed. Physical properties and heat-transfer properties have been estimated over a range of temperatures for seven selected hydrocarbons for comparison with those of RP-1. Similar data are presented for a very dense hydrocarbon.

Preliminary and approximate estimates have been made of the cost of large-scale manufacture for two energetic hydrocarbons: 1,7 octadiyne and spiro(2,2)pentane. Synthetic routes to a number of unusual hydrocarbons are reviewed briefly.

Potential problems in the use of such hydrocarbons as replacements for RP-1 in existing rocket engines are discussed. In most cases the major difficulty is posed by a low hydrogen/carbon atom ratio; this requires that the mass-flow rate of the fuel be enhanced at near-stoichiometric conditions to avoid a decrease in the mass-flow of propellant and in available thrust. This problem is aggravated if the density of the hydrocarbon is lower than that of RP-1. If this problem can be overcome, substantial gains in payload are potentially attainable.

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