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POSSIBLE PROPELLANTS FOR USE
IN A NUCLEAR ROCKET

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NUCLEAR PROPULSION

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POSSIBLE PROPELLANTS FOR USE
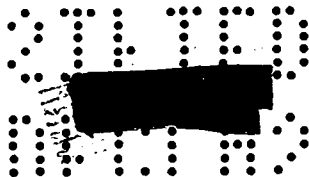## IN A NUCLEAR ROCKET

by

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ABSTRACT

A series of propellants which might be applicable to nuclear-powered rockets have been investigated thermodynamically. These propellants include methane, ethane, propane, mixtures of hydrazine and these hydrocarbons, mixtures of ammonia and these hydrocarbons, hydrazine, ammonia, methanol, ethanol, and propanol. The dissociation products of these compounds and their concentrations have been calculated for the temperature interval 1000 to 3000°K. The mean molecular weights of these various potential propellants were determined from the concentrations of the dissociation products.

The pure hydrocarbons have the lowest mean molecular weights of any of the propellants investigated but are of doubtful use due to the fact that they deposit solid carbon onto the reactor over the entire temperature range studied. Some compositions of ammonia and hydrocarbons and of hydrazine and hydrocarbons do not deposit graphite at reactor operating temperatures but either deposit carbon at certain lower temperatures or corrode the reactor at higher temperatures as well as at temperatures in the range 1000 to 2000°K.

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CONTENTS

1. INTRODUCTION

The nuclear-powered rocket offers a golden opportunity to one interested in obtaining the most efficient propellants for rocket use since it frees him from the complications imposed by the combustion of the propellant in a chemical rocket. Since the nuclear reactor provides the heat source required to raise the propellant to the operating temperature, one can use a monopropellant which dissociates thermally into low-molecular-weight fragments at elevated temperatures.

Liquid hydrogen, the most efficient propellant that we are in a technical position to use at the present time, presents logistical and cryogenic problems to any large-scale rocket endeavor. To circumvent this situation, one would like to find other propellants which are not too inferior to hydrogen in their performance. In addition, these propellants should be available in large supply, should not require cryogeny, and should not be so reactive chemically as to require special materials for containers or special handling procedures for storage.

The maximum theoretical propellant gas exhaust velocity, V_m, is given by the relation

$$V_m = \sqrt{\frac{2gRT}{\overline{M}} \cdot \frac{\gamma}{\gamma-1}} \qquad\qquad 1.1$$

where g = acceleration of gravity at sea level

$\overline{M}$ = mean molecular weight of propellant gases

R = universal gas constant

T = gas temperature within rocket motor prior to expansion

γ = specific-heat ratio of propellant gases = $\Sigma n_i C_{P_i} / \Sigma n_i C_{V_i}$

C_{P_i} = heat capacity at constant pressure for $\underline{i}$th component

C_{V_i} = heat capacity at constant volume for $\underline{i}$th component

The over-all performance of a missile is primarily a function of the exhaust velocity attainable with the propellant considered. It is obvious, therefore, that the mean molecular weight of the propellant gas is the dominant factor in determining the theoretical exhaust velocity of a propellant, since, except for monatomic molecules, γ is in the range 1.22 to 1.40. Although there are no other propellants which have a mean molecular weight near that of hydrogen, there are

many for which the square root of the ratio of molecular weights of the propellant to hydrogen is less than 2. Since all these propellants have densities in the range 0.6 to 0.8 as compared to 0.07 for liquid hydrogen, it is possible to build a rocket with a given exhaust-gas temperature which will be much smaller than the nuclear hydrogen rocket, although it will be somewhat heavier. This statement results from considerations of the impulse of a rocket which are not treated here.

This report covers a study of potential propellants which would be suitable for a nuclear rocket. Materials which have been investigated include methane, ethane, propane, hydrazine, ammonia, mixtures of hydrazine and these hydrocarbons, mixtures of ammonia and these hydrocarbons, methanol, ethanol, and propanol. Data for the first three homologous aliphatic hydrocarbons were extrapolated to such hydrocarbons as hexane and gasoline, which are much easier to handle than the low-molecular-weight members of the series. The methods of calculation used in this study will be discussed in the next two sections. The results will be given in Section 4 and a discussion in Section 5.

2. CALCULATION OF THERMODYNAMIC DATA

2.1 Rigid Rotator-Harmonic Oscillator Method

Thermodynamic data were calculated by the rigid rotator-harmonic oscillator treatment for those molecules for which data in the temperature range above $1500^{\circ}K$ do not exist in the literature. Molecules treated by this method include the hydrocarbons through C_3, both saturated and unsaturated, ammonia, hydrazine, hydrogen cyanide, methanol, and ethanol.

These calculations were carried out originally on a desk calculator and later checked against calculations made on an IBM 701 electronic computer. No large differences were observed between the two methods, although there were small differences of 0.01 to 0.10 per cent due to the different numbers of significant figures carried in the desk calculator and in the 701 and due to small arithmetical errors which arose in the manual calculation. The practical importance of these small differences is essentially zero, however, since they serve only to decrease the number of significant figures which should be considered in the equilibrium calculations.

The rigid rotator-harmonic oscillator treatment assumes that the molecules concerned are rigid rotators and harmonic oscillators, with no interaction between the rotation and vibration. Although none of these assumptions is strictly true, only the anharmonicity of the molecules at high temperatures introduces any appreciable error into the thermodynamic data obtained. However, even this error tends to cancel out in the equilibrium calculations, since the anharmonicity always shifts the free-energy function in the same direction; hence, for any

given equilibrium approximately the same error is added to both the reactant and product free-energy functions.

The thermodynamic behavior of a molecule can be conveniently treated in terms of the partition function, which is defined as follows in terms of the energy, ϵ_n, per molecule in the nth state and the a priori probability, g_n, of that state:

$$Q = \sum_{n=0}^{\infty} g_n e^{-\epsilon_n/kT} \qquad\qquad 2.1$$

Here k is the Boltzmann constant and T the absolute temperature in $^\circ$K.

The total energy of the molecule can then be broken down into a translation energy, ϵ_{tr}, and an internal energy, ϵ_{int}. The internal energy, however, is composed of a rotational portion, ϵ_{rot}, a vibrational portion, ϵ_{vib}, and an electronic portion, ϵ_{el}. For polyatomic molecules considered in this study, the degeneracy of the ground electronic state is unity, and the contribution of higher electronic states is negligible; the electronic contribution to the total partition function is, therefore, zero. If there are n atoms in a given molecule, there are 3n degrees of freedom in the molecule. Three of these degrees of freedom are assigned to translational motion. Two degrees of freedom are used by rotation in diatomic molecules and linear polyatomic molecules, whereas three degrees of freedom are necessary to describe the rotation in non-linear polyatomic molecules. This leaves (3n-5) degrees of vibrational freedom in diatomic and linear polyatomic molecules and (3n-6) degrees in non-linear polyatomic molecules. This number of vibrational frequencies will be designated as i (running index in the vibrational partition function).

In accordance with the above energy breakdown, one may now write the partition function as:

$$Q = Q_{tr} \cdot Q_{rot} \cdot Q_{vib} \qquad\qquad 2.2$$

The translational, rotational, and vibrational partition functions are derived in any good text on statistical mechanics or chemical thermodynamics.[1] Making use of these derivations, one

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1. G. Herzberg, Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules, pp. 501-530, D. Van Nostrand Company, Inc., New York, 1945.

    S. Glasstone, Theoretical Chemistry, pp. 347-422, D. Van Nostrand Company, Inc., New York, 1945.

    J. E. Mayer and M. G. Mayer, Statistical Mechanics, pp. 149-217, John Wiley & Sons, Inc., New York, 1940.

obtains for the respective partition functions

$$Q_{tr} = \left(\frac{2\pi M}{h^2 N}\right)^{3/2} (RT)^{5/2} P^{-1}$$

2.3

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} \qquad \text{(linear molecules)}$$

2.4

$$Q_{rot} = \sqrt{8\pi^3 I_A I_B I_C} \left(\frac{8\pi^2}{\sigma h^3}\right)(kT)^{3/2} \qquad \text{(non-linear molecules)}$$

2.4'

$$Q_{vib} = \prod_{i=o}^{i} \left(1 - e^{-hc\nu_i/kT}\right)^{-1}$$

2.5

where c = velocity of light = 2.99776×10^{10} cm/sec

h = Planck's constant = 6.62377×10^{-27} erg sec

I = moment of inertia of molecule

I_A, I_B, I_C = moment of inertia around X, Y, or Z axis

k = Boltzmann's constant = 1.38026×10^{-16} erg/molecule/deg

M = molecular weight of the molecule

N = Avogadro's number = 6.02544×10^{23}

P = pressure in dynes/cm^2 = 1.01332×10^6/atm

R = gas constant = 1.98718 cal/deg/mole

T = temperature in °K

σ = symmetry number (number of equivalent orientations in space as the result of simple rotation)

ν = vibrational frequency in cm^{-1}

Although all of the thermodynamic functions can be calculated with the partition function, only the free-energy function is of use in making the equilibrium calculations. The translational, rotational, and vibrational contributions to the free-energy function, $-\left(\frac{F^O - E_0^0}{T}\right)$, are listed below.

$$-\left(\frac{F^O - E_0^0}{T}\right)_{tr} = 5/2 R \ln T + 3/2 R \ln M + R \ln\left[\left(\frac{2\pi}{N}\right)^{3/2} \frac{k^{5/2}}{h^3}\right] - R \ln P$$

2.6

$$= 11.4392 \log T + 6.86349 \log M - 7.2795$$

2.6'

$$-\left(\frac{F^O-E^O_0}{T}\right)_{rot} = R \ln Q_{rot} \qquad\qquad 2.7$$

$$= R \ln \left(\frac{8\pi^2 IkT}{\sigma h^2}\right) \qquad \text{(linear molecules)} \qquad 2.7'$$

$$= R \ln \left[(8\pi^3 I_A I_B I_C)^{1/2}\left(\frac{8\pi^2}{h^3}\right)(kT)^{3/2}\right] \qquad \text{(non-linear molecules)} \qquad 2.7''$$

$$-\left(\frac{F^O-E^O_0}{T}\right)_{vib} = R \ln Q_{vib} \qquad\qquad 2.8$$

$$= R \ln \left[\prod_{i=o}^{i}\left(1-e^{-hc\nu_i/kT}\right)^{-1}\right] \qquad 2.8'$$

$$= -R \sum_{i=o}^{i} \ln\left(1-e^{-hc\nu_i/kT}\right) \qquad 2.8''$$

2.2 Hindered Internal Rotation

Some molecules, namely saturated hydrocarbons with more than two carbon atoms and alcohols, have potential barriers which restrict the internal rotation of the different hydrocarbon groups with respect to one another or to the hydroxyl group of the alcohol. Hydrazine has a barrier hindering the rotation of the two NH_2 groups with respect to each other. Although the exact nature of this potential barrier is not known, it is known that the barrier is a threefold symmetry type for all these cases. That is,

$$V = \frac{V_o}{2}(1-\cos 3\varphi) \qquad\qquad 2.9$$

where V_o = the maximum height of the barrier

φ = angle of rotation

Pitzer and Gwinn[2] have worked out a method of calculating the contributions to the various thermodynamic quantities of a molecule with one or more degrees of hindered internal rotation. For each degree of hindered internal rotation of threefold symmetry

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2. K. S. Pitzer and W. D. Gwinn, "Energy Levels and Thermodynamic Functions for Molecules with Internal Rotation, I. Rigid Frame with Attached Tops," J. Chem. Phys. 10, 428 (1942).

$$Q_{h.i.r.} = \left(\frac{2\pi IkT}{h^2}\right)^{1/2} \int_0^{2\pi/3} e^{-(V_0/2kT)(1-\cos 3\phi)} d\phi \qquad 2.10$$

and

$$-\left(\frac{F-E_0^0}{T}\right)_{h.i.r.} = R\left[\ln \frac{2\pi IkT}{h^2}^{1/2} - \frac{V_0}{2RT} + \ln J_0(iV_0/2RT)\right] \qquad 2.11$$

where $J_0(iV_0/2RT)$ is a Bessel function of zero order. It can be evaluated by a series expansion as

$$J_0(iV_0/2RT) = J_0(ix) = 1 + \frac{x^2}{2^2} + \frac{x^4}{2^4(2!)^2} + \frac{x^6}{2^6(3!)^2} + \ldots + \frac{x^{2k}}{2^{2k}(k!)^2} \qquad 2.12$$

For calculations involving a desk calculator, Pitzer and Gwinn have a two-entry table by which $-\left(\frac{F-E_0^0}{T}\right)_{h.i.r.}$ can be evaluated as a function of V_0/RT and of $1/Q_f$, where Q_f, the partition function for free internal rotation, is defined as

$$Q_f = \left(\frac{8\pi^3 IkT}{h^2}\right)^{1/2} \qquad 2.13$$

For calculations on an IBM 701 computer, $J_0(ix)$ is evaluated directly and the free-energy function for hindered internal rotation is then calculated by equation 2.11.

The total free-energy function for a molecule with hindered internal rotation is the sum of the rigid rotator-harmonic oscillator, translational, and hindered-rotation free-energy functions. Here the vibrational partition function has one vibrational mode removed for every degree of internal rotation so that the total number of degrees of freedom of the molecule is still 3n.

3. EQUILIBRIUM CALCULATIONS

The equilibrium constant of the gas reaction

$$aA + bB + \cdots \rightleftharpoons mM + nN + \cdots \qquad 3.1$$

can be written as

$$K_p = \frac{P_M{}^m P_N{}^n \cdots}{P_A{}^a P_B{}^b \cdots} \qquad\qquad 3.2$$

where P_M, P_N, $\cdots$, P_A, P_B, $\cdots$ are the partial pressures of M, N, $\cdots$, A, B, $\cdots$.

A well-known theorem of thermodynamics states that

$$-R \ln K_p = \Delta F / T = \Delta E_0^O + \sum \left(\frac{F^O - E_0^O}{T}\right)_{products} - \sum \left(\frac{F^O - E_0^O}{T}\right)_{reactants} \qquad 3.3$$

Here ΔF is the total standard free-energy change and ΔE_0^O is the total standard zero-point energy change for the reaction. Since E_0^O is known for all atoms and molecules involved in any possible reaction of interest in this propellant study, ΔE_0^O for the reaction can be calculated quite simply. The various free-energy functions, $-\left(\frac{F^O - E_0^O}{T}\right)$, for substances participating in the reactions can be calculated by the methods of sections 2.1 and 2.2. One is thus in a position to calculate the equilibrium constants for any reaction and the equilibrium compositions of the several possible species existing in a multicomponent gaseous system.

Let one suppose that methane is passed through a nuclear reactor under such conditions that the methane decomposes to the following products:

1)	C solid	6)	CH
2)	C gas	7)	C_2H_4
3)	H_2	8)	C_2H_6
4)	H	9)	C_3H_8
5)	C_2H_2		

The following equilibria can be written:

1) $C_{(s)} \rightleftharpoons C_{(g)}$ $\qquad\qquad K_1 = n_{C_{(g)}} (RT/V)$ $\qquad\qquad 3.4.1$
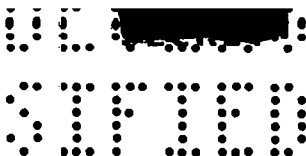
2) $1/2\ H_2 \rightleftharpoons H$ $\qquad\qquad K_2 = \dfrac{n_H}{n_{H_2}^{1/2}} (RT/V)^{1/2}$ $\qquad\qquad 3.4.2$

3) $C_{(s)} + 1/2\ H_2 \rightleftharpoons 1/2\ C_2H_2$ $\qquad\qquad K_3 = \dfrac{n_{C_2H_2}^{1/2}}{n_{H_2}^{1/2}}$ $\qquad\qquad 3.4.3$

4) $C_{(s)} + 1/2\ H_2 \rightleftharpoons CH$ $\qquad K_4 = \dfrac{n_{CH}}{n_{H_2}^{1/2}}(RT/V)^{1/2}$ $\qquad$ 3.4.4

5) $C_{(s)} + H_2 \rightleftharpoons 1/2\ C_2H_4$ $\qquad K_5 = \dfrac{n_{C_2H_4}^{1/2}}{n_{H_2}}(RT/V)^{-1/2}$ $\qquad$ 3.4.5
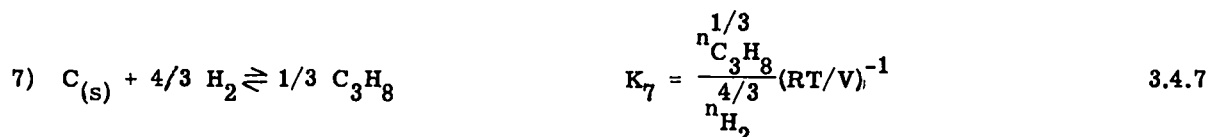
6) $C_{(s)} + 3/2\ H_2 \rightleftharpoons 1/2\ C_2H_6$ $\qquad K_6 = \dfrac{n_{C_2H_6}^{1/2}}{n_{H_2}^{3/2}}(RT/V)^{-1}$ $\qquad$ 3.4.6

7) $C_{(s)} + 4/3\ H_2 \rightleftharpoons 1/3\ C_3H_8$ $\qquad K_7 = \dfrac{n_{C_3H_8}^{1/3}}{n_{H_2}^{4/3}}(RT/V)^{-1}$ $\qquad$ 3.4.7
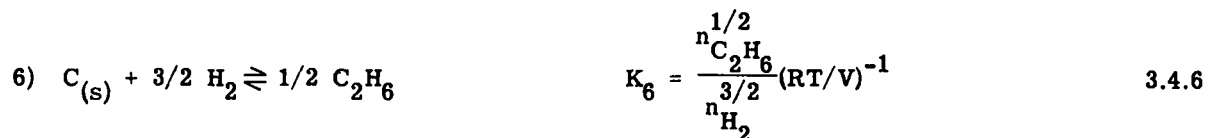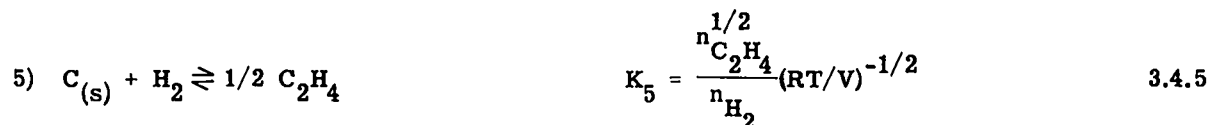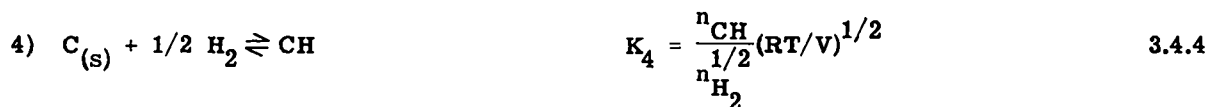
It is assumed that the partial pressure of any component can be replaced by the product of the number of moles of that component and the total pressure. Let n_i represent the number of moles of component i per gram of total material. Assuming that the gas law
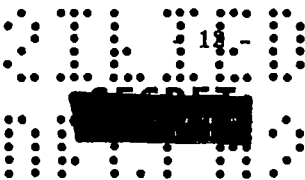
$$PV = nRT \qquad\qquad 3.5$$

holds, one can substitute $\dfrac{nRT}{V}$ for the pressure, P. If these substitutions are made in equation 3.3, it is transformed into equations of the type 3.4.

There are now seven equations in nine unknowns. One can obtain two more equations by setting up mass balances for the carbon and hydrogen. These are

$$\Sigma C = n_{C_{(s)}} + n_{C_{(g)}} + n_{CH} - 2n_{C_2H_2} + 2n_{C_2H_4} + 2n_{C_2H_6} + 3n_{C_3H_8} \qquad 3.6.1$$

$$\Sigma H = n_H + n_{CH} + 2n_{H_2} + 2n_{C_2H_2} + 4n_{C_2H_4} + 6n_{C_2H_6} + 8n_{C_3H_8} \qquad 3.6.2$$

If one replaces each of the n_i in the two mass-balance equations by the corresponding value of n_i in terms of the equilibrium constant, the hydrogen concentration, and (RT/V), he obtains

$$\Sigma C = n_{C_{(s)}} + K_1(RT/V)^{-1} + K_4 n_{H_2}^{1/2}(RT/V)^{-1/2} + 2\left[K_3 n_{H_2}^{1/2}\right]^2$$

$$+ 2\left[K_5 n_{H_2}(RT/V)^{1/2}\right]^2 + 2\left[K_6 n_{H_2}^{3/2}(RT/V)\right]^2 + 3\left[K_7 n_{H_2}^{4/3}(RT/V)\right]^3 \qquad 3.6.3$$

$$\Sigma H = K_2 n_{H_2}^{1/2}(RT/V)^{-1/2} + K_4 n_{H_2}^{1/2}(RT/V)^{-1/2} + 2n_{H_2} + 2\left[K_3 n_{H_2}^{1/2}\right]^2$$

$$+ 4\left[K_5 n_{H_2}(RT/V)^{1/2}\right]^2 + 6\left[K_6 n_{H_2}^{3/2}(RT/V)\right]^2 + 8\left[K_7 n_{H_2}^{4/3}(RT/V)\right]^3 \qquad 3.6.4$$

Let one now pick some definite quantity of methane to exist initially in the calculation; for the sake of simplicity, 1 mole. Then,

$$\Sigma H = \frac{\text{number of H atoms}}{\text{molecular wt. of CH}_4} = \frac{4}{16.042}$$

Also, one can make two guesses as to the number of moles of hydrogen per gram which will exist at the equilibrium conditions. Let one use here

$$^1 n_{H_2} = 0.01$$

$$^2 n_{H_2} = 0.1$$

If one now rewrites equation 3.6.4 as

$$G = (K_2 + K_4)n_{H_2}^{1/2}(RT/V)^{-1/2} + 2n_{H_2}(1 + K_3^2) + 4K_5^2 n_{H_2}^2(RT/V)$$

$$+ 6K_6^2 n_{H_2}^3(RT/V)^2 + 8K_7^3 n_{H_2}^4(RT/V)^3 - \Sigma H \qquad 3.7$$

he can evaluate a G_1 with $n_{H_2} = 0.01$ and a G_2 with $n_{H_2} = 0.1$, where G is simply the difference between the actual ΣH and the ΣH which is calculated by using the appropriate powers of n_{H_2} in equation 3.7. He can then use a standard iteration formula to solve for a new n_{H_2} which will make G_3 equal to zero. By repeating this iteration until G_n converges to within a given criterion (10^{-8} in all these calculations), one obtains a value for the number of moles

of hydrogen which is sufficiently exact to carry out the remainder of the computation.

One now substitutes the value of n_{H_2} obtained from the iteration process above and the various K's derived from thermodynamic free-energy functions into equations of type 3.4 to obtain values for the number of moles of the various components. The number of moles of solid carbon is obtained by subtracting the sum of all the hydrocarbon and gaseous carbon components from ΣC in equation 3.6.1. Here

$$\Sigma C = \frac{\text{number of C atoms}}{16.042} = \frac{1}{16.042}$$

In setting up the conditions for the problem so that the 701 computer has sufficient information to complete the calculation, one must specify a volume, a pressure, and a total number of moles per gram at an elevated temperature, T, to be used in the calculation. When one adds up the total number of moles calculated by using the equilibrium constants and the number of moles of hydrogen obtained from the iteration process, one undoubtedly will get a different value for the total number of moles. By adding half the difference between the original number of moles stipulated in the initial data input and the calculated number of moles with the appropriate sign to the original number of moles, one can obtain a new guess for the total number of moles.

One now calculates a new volume, using the pressure and temperature data-input for the elevated temperatures, Thus,

$$V = \frac{RT \cdot \Sigma n_i}{P} \qquad\qquad 3.8$$

A new (RT/V) is calculated and the evaluation of a new n_{H_2} is made using the same two initial guesses for $^1n_{H_2}$ and $^2n_{H_2}$. When the desired value for the number of moles of hydrogen at equilibrium is obtained, the number of moles of each component is again computed and a total number of moles calculated. Half the difference between this new number of moles and the previous Σn_i is added with the correct sign to the previous Σn_i and a new (RT/V) is calculated. A new number of moles of hydrogen at equilibrium is obtained and the iteration of n_{H_2} and Σn_i is continued until half the difference of the Σn_i used in that cycle and the Σn_i computed at the end of that cycle is less than some specified value (usually about 1 to 5×10^{-5}).

The mole fractions of the individual components are then evaluated in the standard way, where

$$X_i = \frac{n_i}{\Sigma n_i} \qquad\qquad 3.9$$

Here

X_i is the mole fraction of component i

n_i is the number of moles of component i per gram

Σn_i is the total number of moles per gram of the system

The mole fractions, as well as the total number of moles, the pressure, the temperature, and the final volumes are then printed out by the 701 computer. The conditions of the problem are changed such that the temperature is increased $100°K$ and the volume is correspondingly corrected. In all the problems studied in this series, the initial temperature was $1000°K$; to correct the volume, therefore, one merely multiplies the final volume by 0.1 and retains this number as a volume increment to be added for each $100°K$ temperature rise. The temperature and volume are increased by the appropriate amounts; the pressure and the total number of moles are held to their values at the previous temperature. The machine goes through the entire sequence of events described previously and arrives at a solution for the increased temperature. This cycle is repeated until the temperature has risen to $3000°K$ and, in a few instances, $4000°K$. At this point the problem has been completed.

The calculations become more complicated if oxygen or nitrogen is introduced into the system either as the element or in the form of some chemical compound. Additional equilibria considering all possible reactions of importance with oxygen or nitrogen as reactants are incorporated into the series of equilibria already existing for carbon and hydrogen. A mass-balance equation for the oxygen or nitrogen is then put into the calculation so that one will still have n simultaneous equations in n unknowns. This mass-balance equation, when expanded in terms of equilibrium constants, hydrogen concentrations, and oxygen or nitrogen concentrations, has always turned out to be a quadratic equation in terms of the oxygen or nitrogen molecular concentration; therefore, a solution is easily obtained.

One proceeds to solve the three-element equilibrium problem in the same manner as the two-element problem. Two guesses are made for the equilibrium hydrogen concentration and the corresponding oxygen or nitrogen concentrations are obtained by means of the quadratic equation referred to in the preceding paragraph. One then substitutes the values of the oxygen or nitrogen concentrations into the places where they occur in the hydrogen mass-balance equation and calculates two G's as was done in the two-element calculation. The new n_{H_2} is next fed back into the quadratic equation for the oxygen or nitrogen concentration and the iteration is continued until G has converged as closely as desired to zero. A criterion of 10^{-8} has

been used for the three-element as well as for the two-element calculation. The molar concentrations per gram are then evaluated for all species and an iteration is performed on Σn_i until the difference between the Σn_i used in the cycle and the Σn_i calculated in that cycle is as small as desired. The mole fractions for all species are computed as before and printed out and the temperature is raised 100^OK.

4. RESULTS

The principal dissociation products formed in the thermal decomposition at 100 atmospheres of methane, ethane, and propane, as well as their mole fractions, are indicated in Figures 1 through 3. Figure 4 shows how the mean molecular weight, $\overline{M}$, of the decomposition products of methane varies with temperature. The other hydrocarbons show a similar behavior. The minimum in $\overline{M}$ at 2400^OK is caused by a decrease in $\overline{M}$ from 1000 to 2400^OK due to the dissociation of the parent hydrocarbon primarily into hydrogen and solid carbon and by an increase in $\overline{M}$ above 2400^OK due to the formation of acetylene from hydrogen and solid carbon. Figure 5 is a plot of log $\overline{M}$ at 2773^OK against C/H for methane, ethane, and propane. Values of $\overline{M}$ for other hydrocarbons through C_8H_{18} (gasoline) are extrapolated.

The data for hydrazine and ammonia are not presented graphically, since the products above 1000^OK are the stoichiometric quantities of hydrogen and nitrogen. At 2773° the mole fraction of hydrogen atoms in both cases becomes significant since it then amounts to 1 per cent of the total hydrogen concentration; at 3000^OK this fraction increases to 3 per cent of the total hydrogen concentration.

The hydrazine-hydrocarbon and ammonia-hydrocarbon mixtures are considered together since their behaviors are so similar. The similarity holds whether the hydrocarbon is methane, ethane, or propane and whether it is mixed with hydrazine or ammonia. As would be expected, the mean molecular weights of the decomposition products for these six systems increase as one goes to higher hydrocarbons or if one replaces ammonia by hydrazine. For any given system, $\overline{M}$ goes through a minimum at about 2200^OK. Figure 6 indicates the major decomposition products and their mole fractions from 1000 to 3000^OK at 100 atmospheres for the system 90 mole % NH_3 - 10 mole % CH_4, whereas Figure 7 gives a more accurate plot of the mole per cent of solid carbon at various temperatures in the temperature interval. An increase in the percentage of ammonia (or hydrazine) decreases the mole fraction of solid carbon at any given temperature, but a decrease in the percentage or a change from methane to ethane or propane at the same percentage of hydrocarbon increases the mole fraction of solid carbon at any given temperature.

The results for ethanol and propanol are also quite similar. The oxygen is tied up almost completely as carbon monoxide over practically the entire temperature range. Figure 8

shows the variation in the mole fraction of the decomposition products of ethanol at 100 atmospheres as a function of temperature. At 2773°K, $\bar{M}$ for ethanol is 9.61 and $\bar{M}$ for propanol is 8.96.

Since methanol behaves quite differently from the higher alcohols, the decomposition products are shown in Figure 9. It is important to note that carbon is deposited from methanol only at temperatures below 1250°K, whereas it deposits over the entire temperature range for the higher alcohols. Figure 10 shows the deposition and removal of carbon over the temperature interval 1000 to 3000°K.

5. DISCUSSION

If one is interested in choosing the propellant with the lowest mean molecular weight, he will choose hydrogen. However, since the density of hydrogen is so low, he can pick a more dense propellant with a larger $\bar{M}$ and still have a missile that is smaller in over-all size than the hydrogen rocket.

The pure aliphatic hydrocarbons have the lowest mean molecular weights after hydrogen, ranging at 2773°K from 5.61 for methane to 7.2 for gasoline. Mixtures of hydrocarbons and ammonia or hydrazine have $\bar{M}$'s between the $\bar{M}$ of the hydrocarbon and that of the ammonia or hydrazine. At 2773°K the $\bar{M}$ of ammonia is 8.48 and the $\bar{M}$ of hydrazine is 10.64. Methanol has an $\bar{M}$ of 10.66, whereas the $\bar{M}$'s of ethanol and propanol, respectively, are 9.61 and 8.96.

If one also is concerned about the chemical behavior of these propellants in a graphite reactor, then he is faced with another problem. All of them either corrode the graphite or deposit additional carbon onto the reactor when they thermally decompose. It is possible to make a blended propellant which will not attack the reactor chemically or deposit carbon onto it over a limited temperature range but, so far, no mixtures have been investigated which do not affect the reactor over a several hundred degree temperature interval.

Hydrogen, ammonia, hydrazine, and methanol attack graphite over 2000°K. The hydrocarbons, ethanol, and propanol deposit carbon at all temperatures of interest. Mixtures of hydrocarbons and ammonia or hydrazine can be made which will not attack the reactor at operating temperatures but which, unfortunately, corrode the reactor at lower and higher temperatures, as Figure 7 indicates.

An effort will be made to blend multicomponent systems containing carbon, oxygen, nitrogen, and hydrogen which will neither deposit carbon nor corrode the reactor over an appreciable temperature interval around 2500°C. This work will be described in a future report.
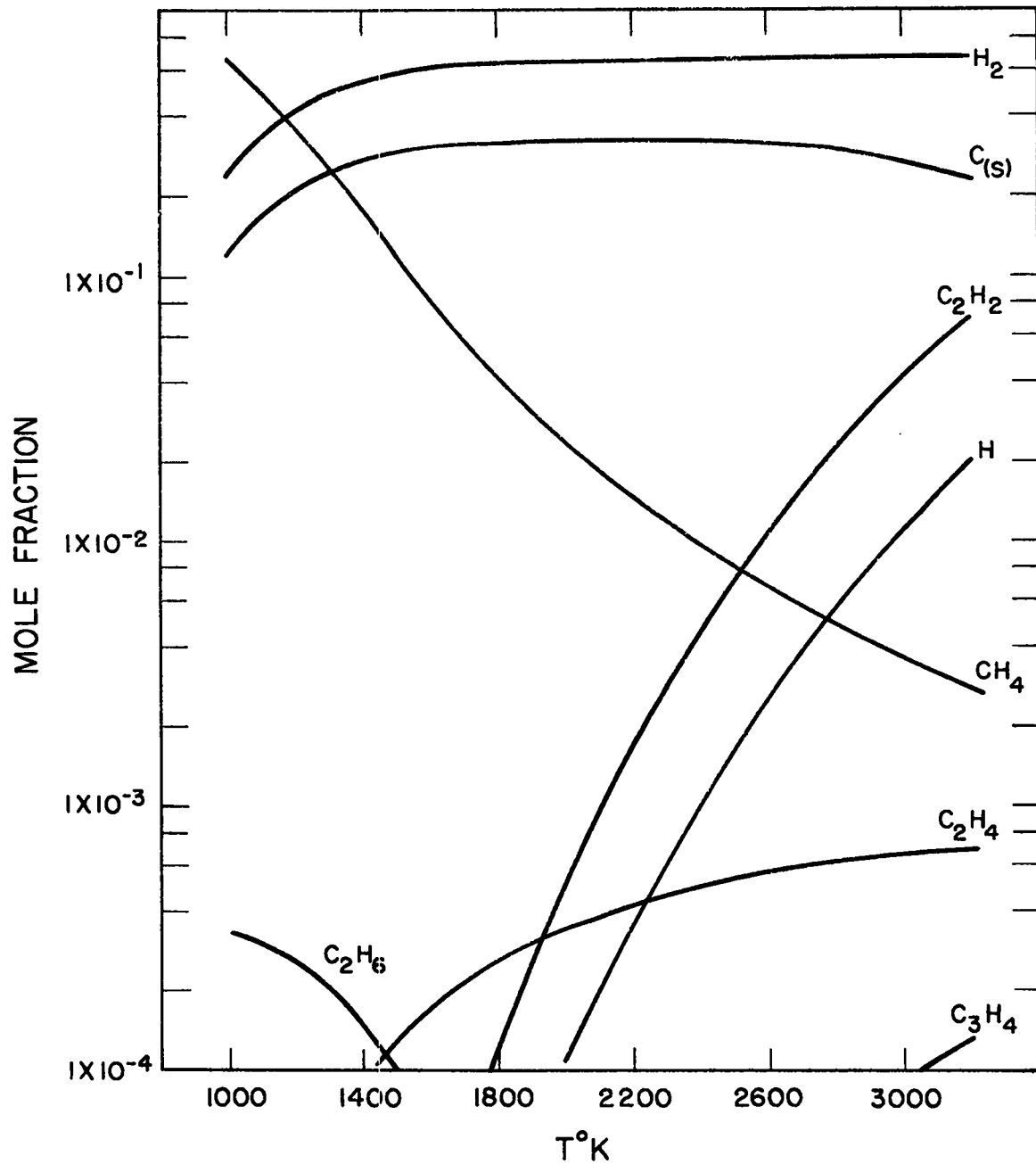
Fig. 1 Principal decomposition products of methane
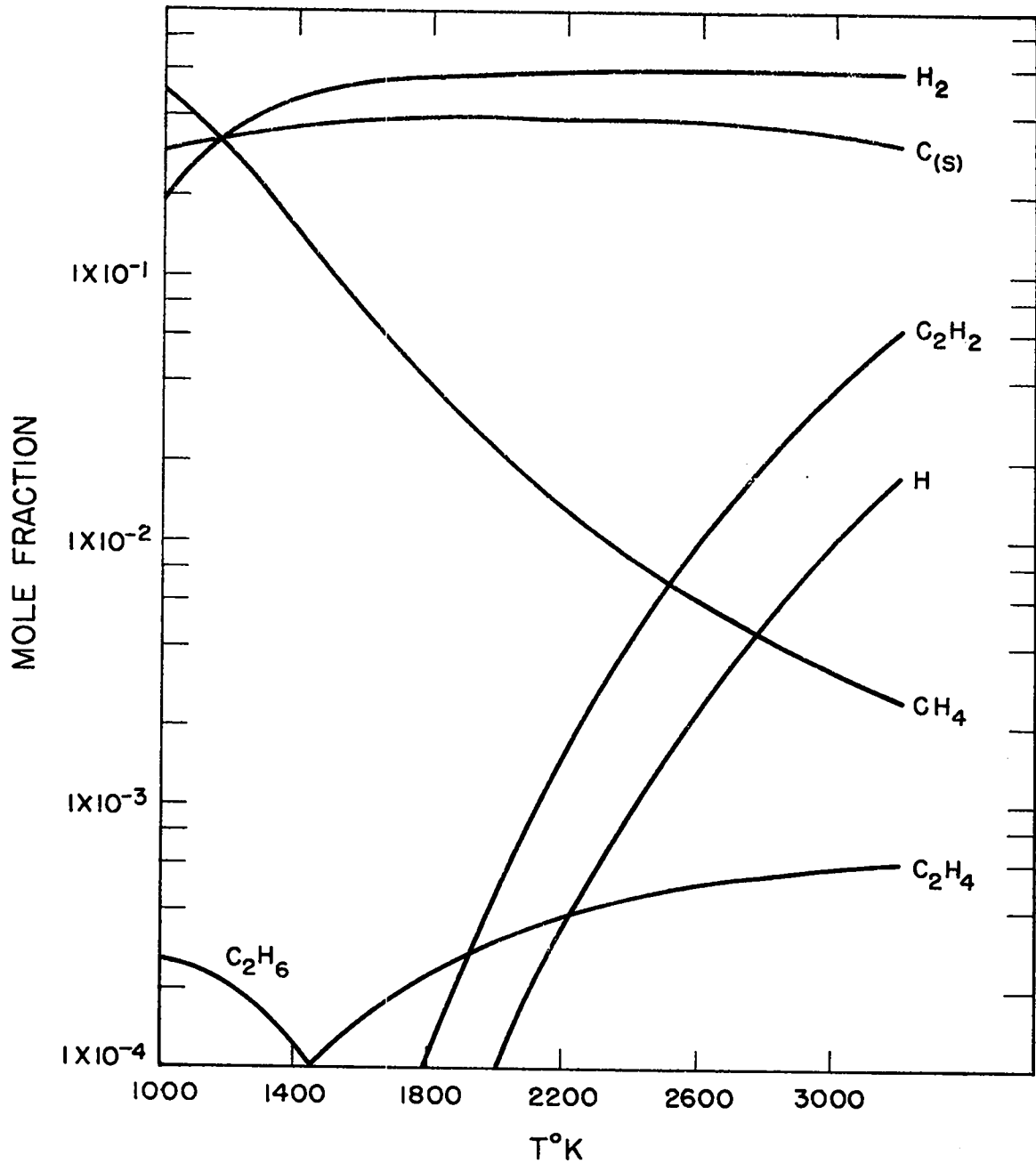
Fig. 2 Principal decomposition products of ethane
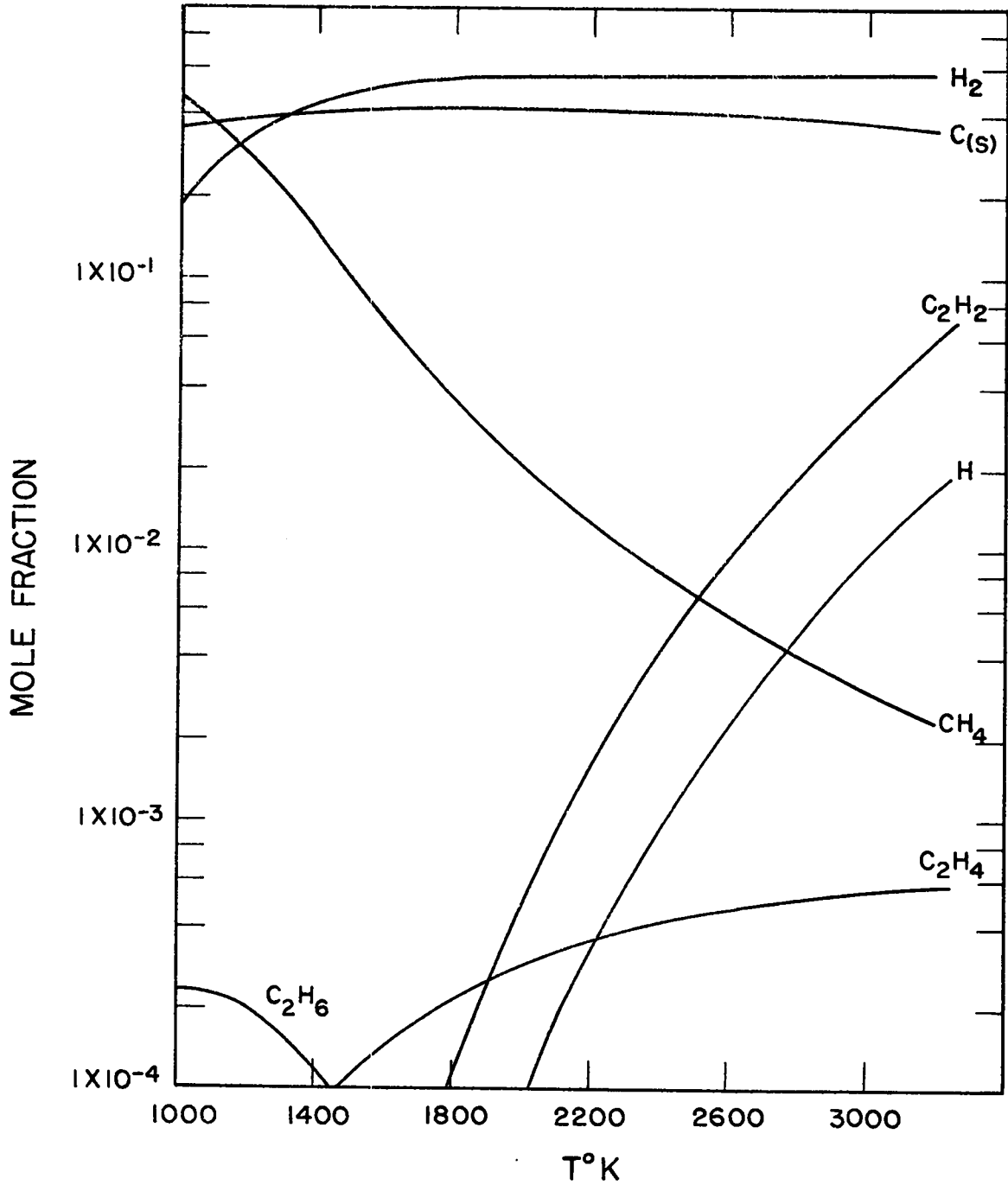
Fig. 3 Principal decomposition products of propane
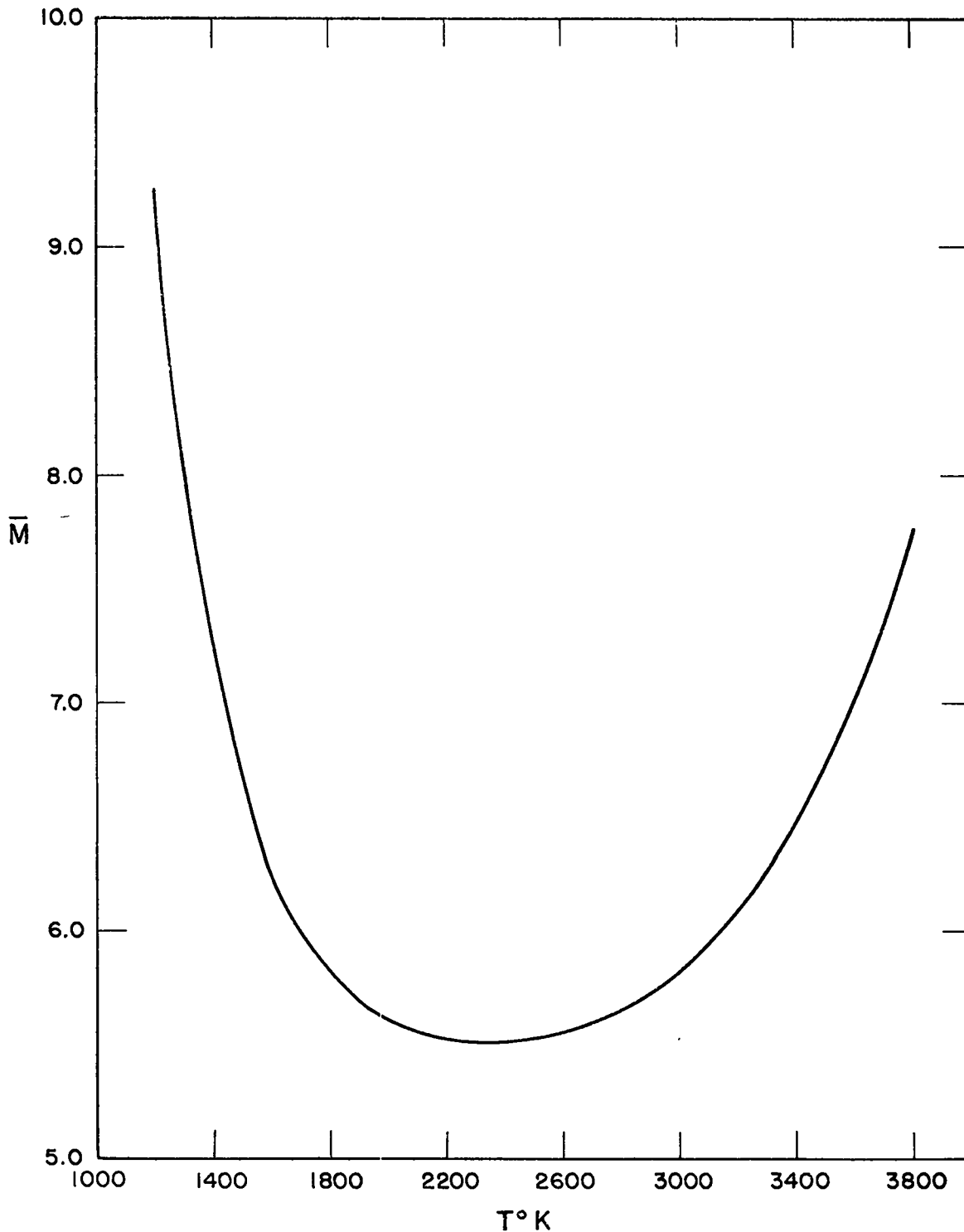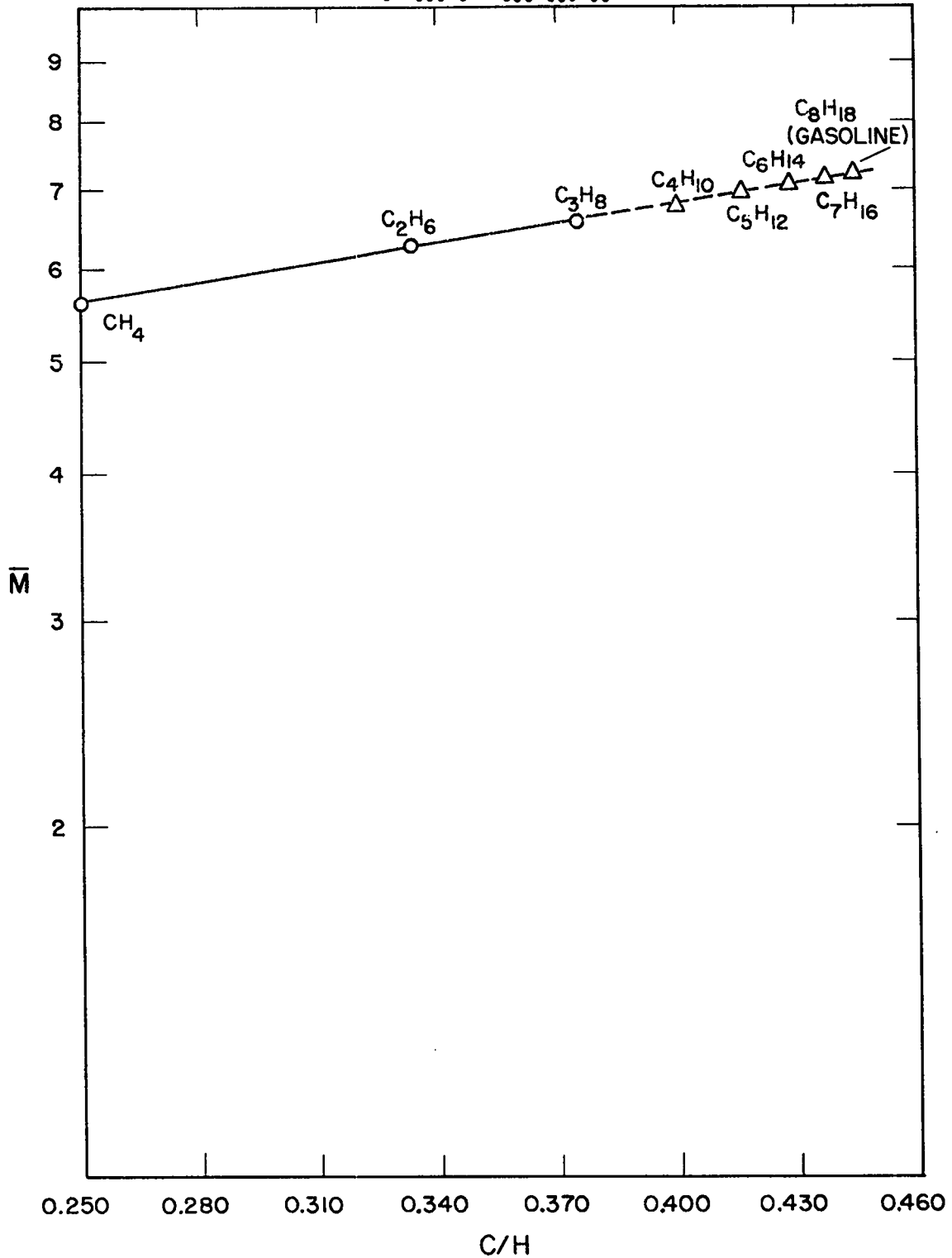
Fig. 4 Mean molecular weight of methane as a function of temperature
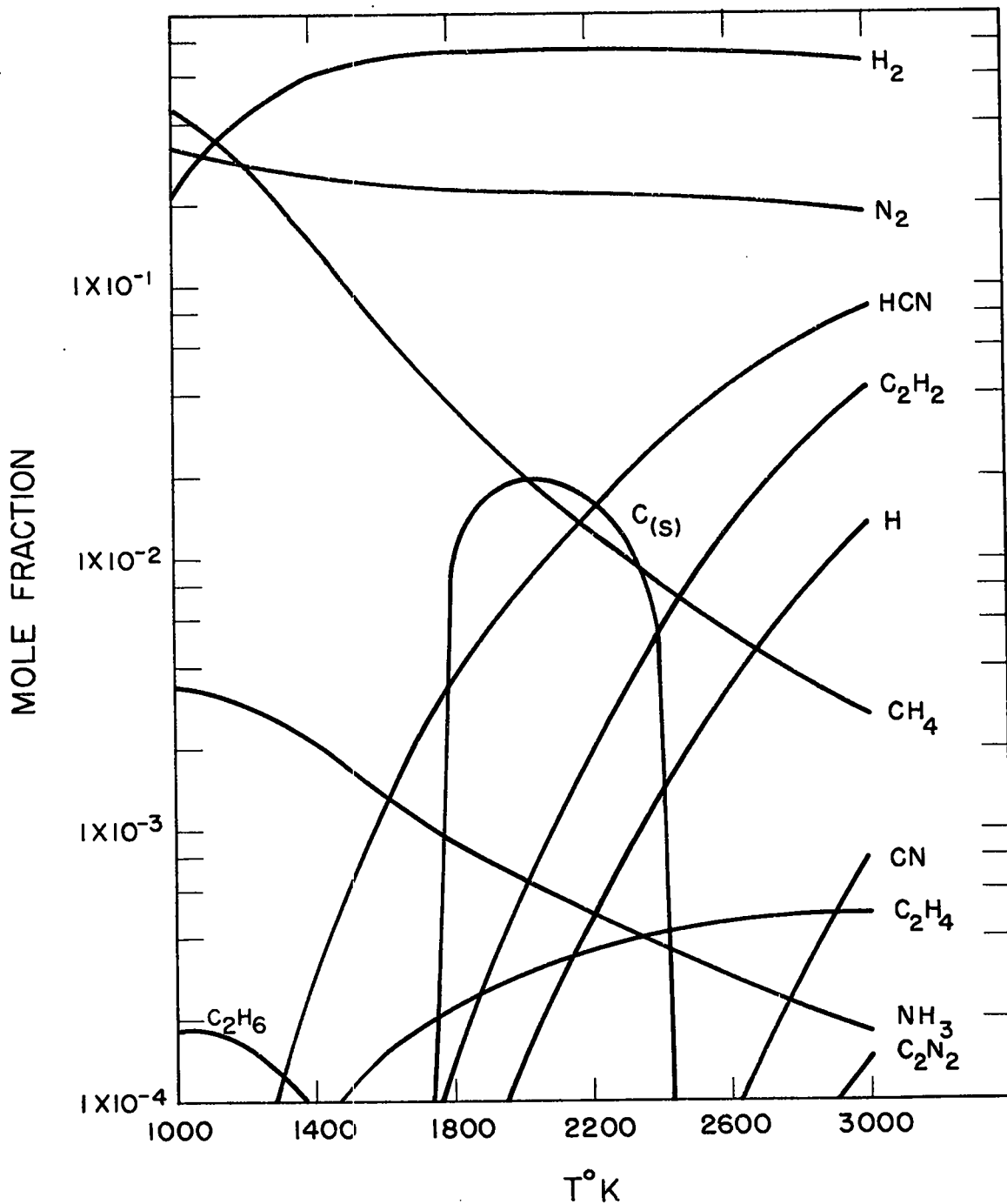
Fig. 5 Mean molecular weights of various hydrocarbons at $2773^{\circ}K$

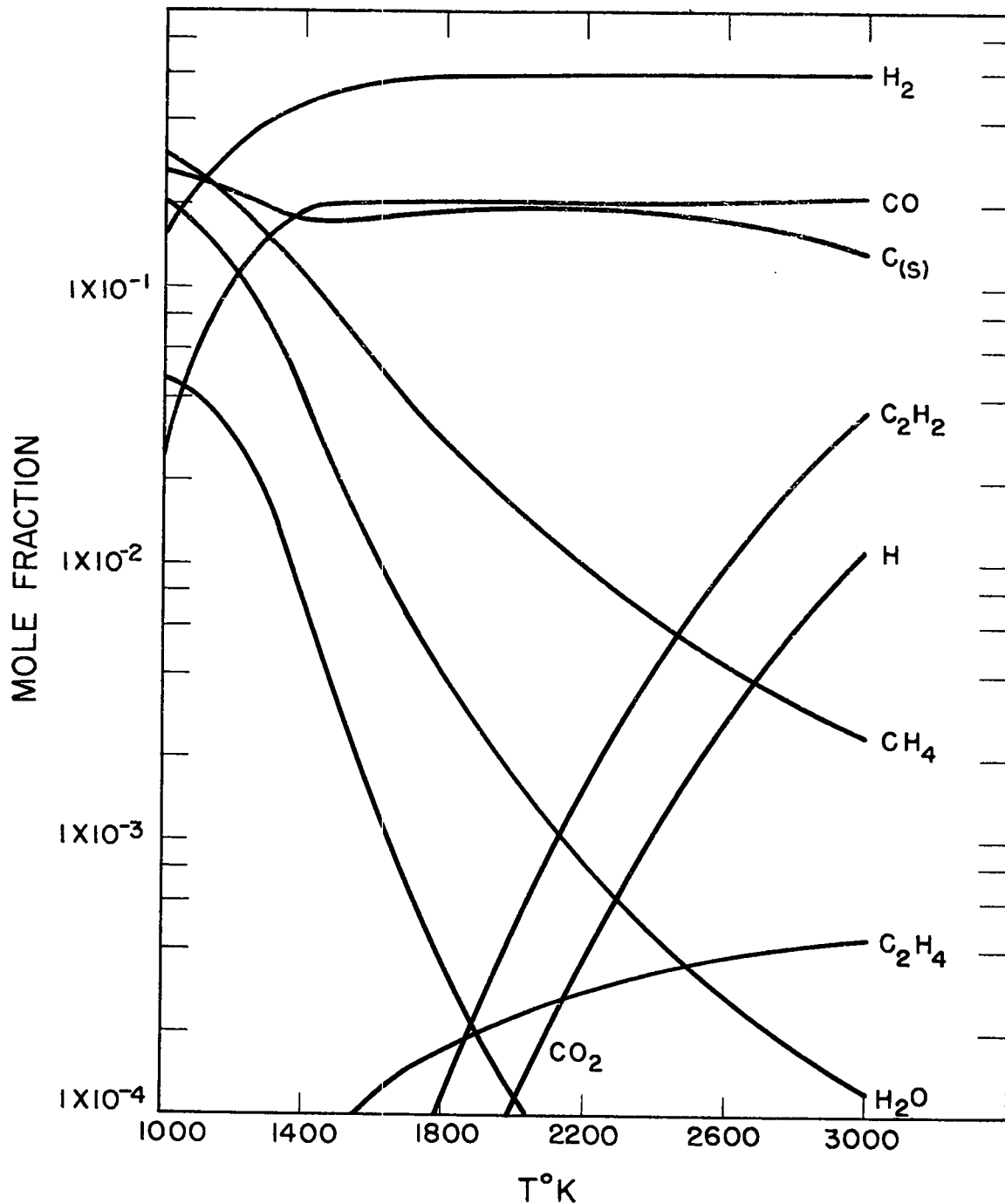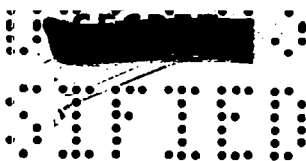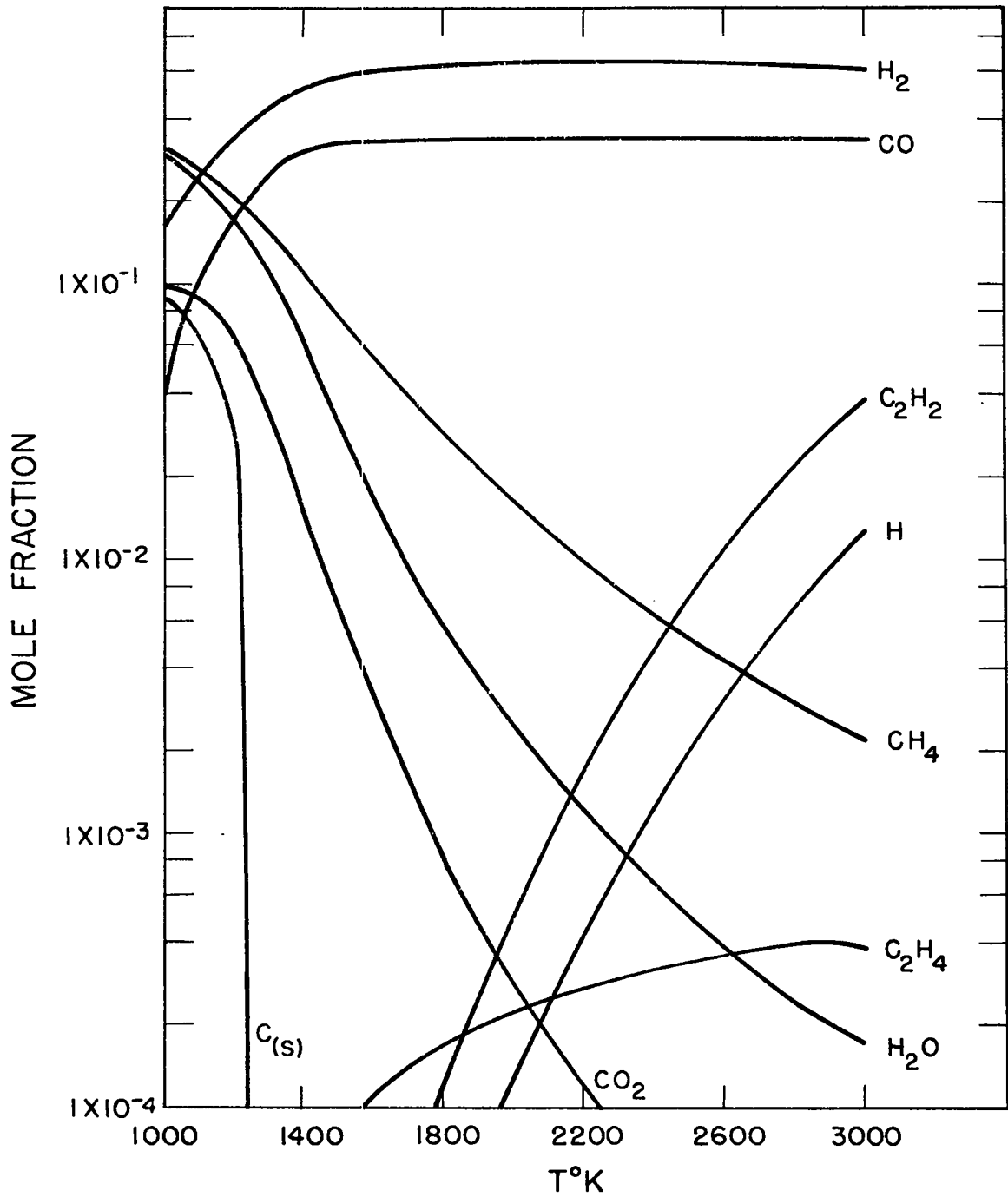Fig. 6 Principal decomposition products of 90 mole % ammonia - 10 mole % methane
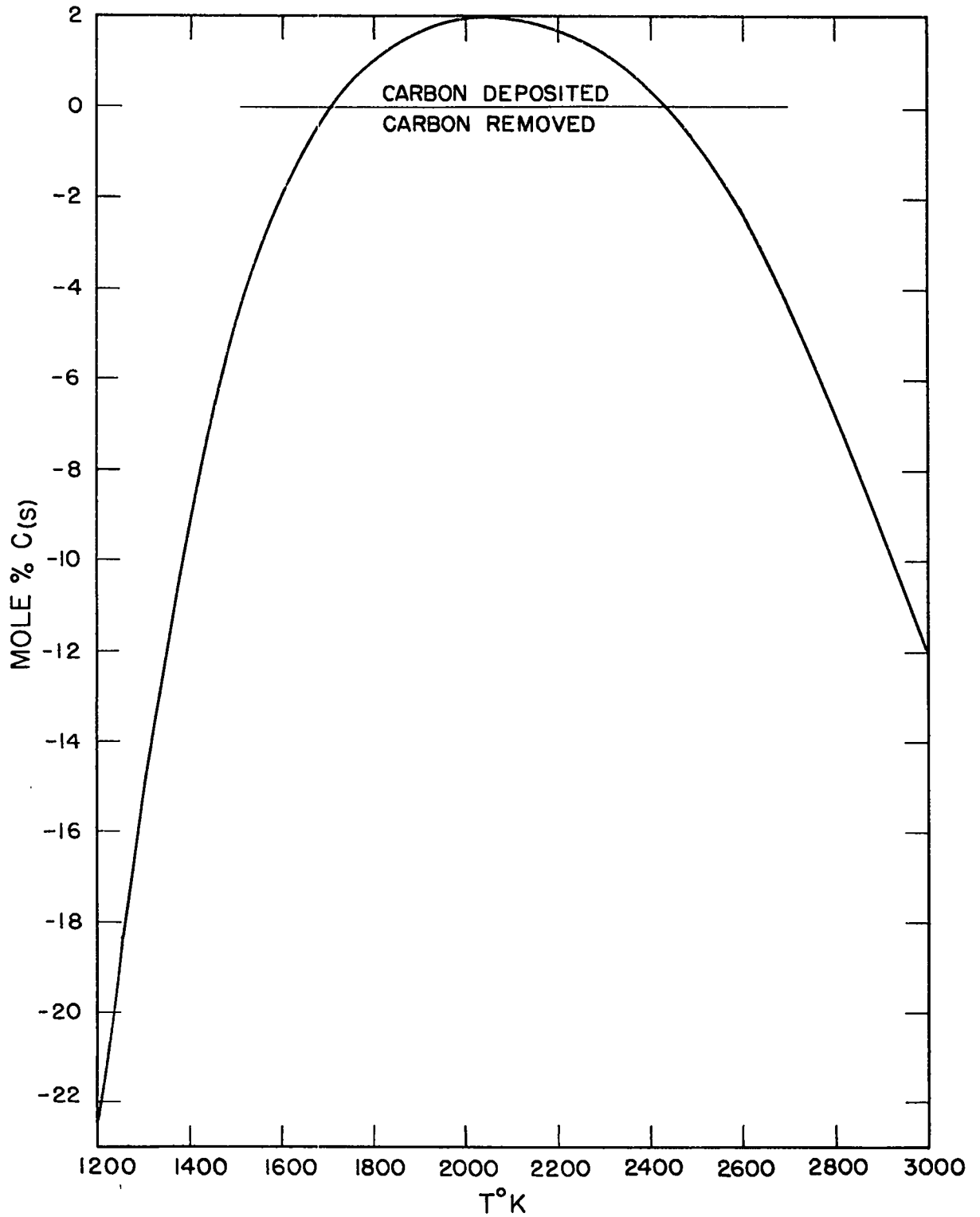
Fig. 7 Mole per cent of solid carbon from the 90-10 NH_3 - CH_4 system

Fig. 8 Principal decomposition products of ethanol
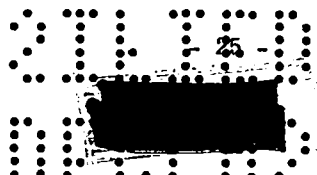
Fig. 9 Principal decomposition products of methanol
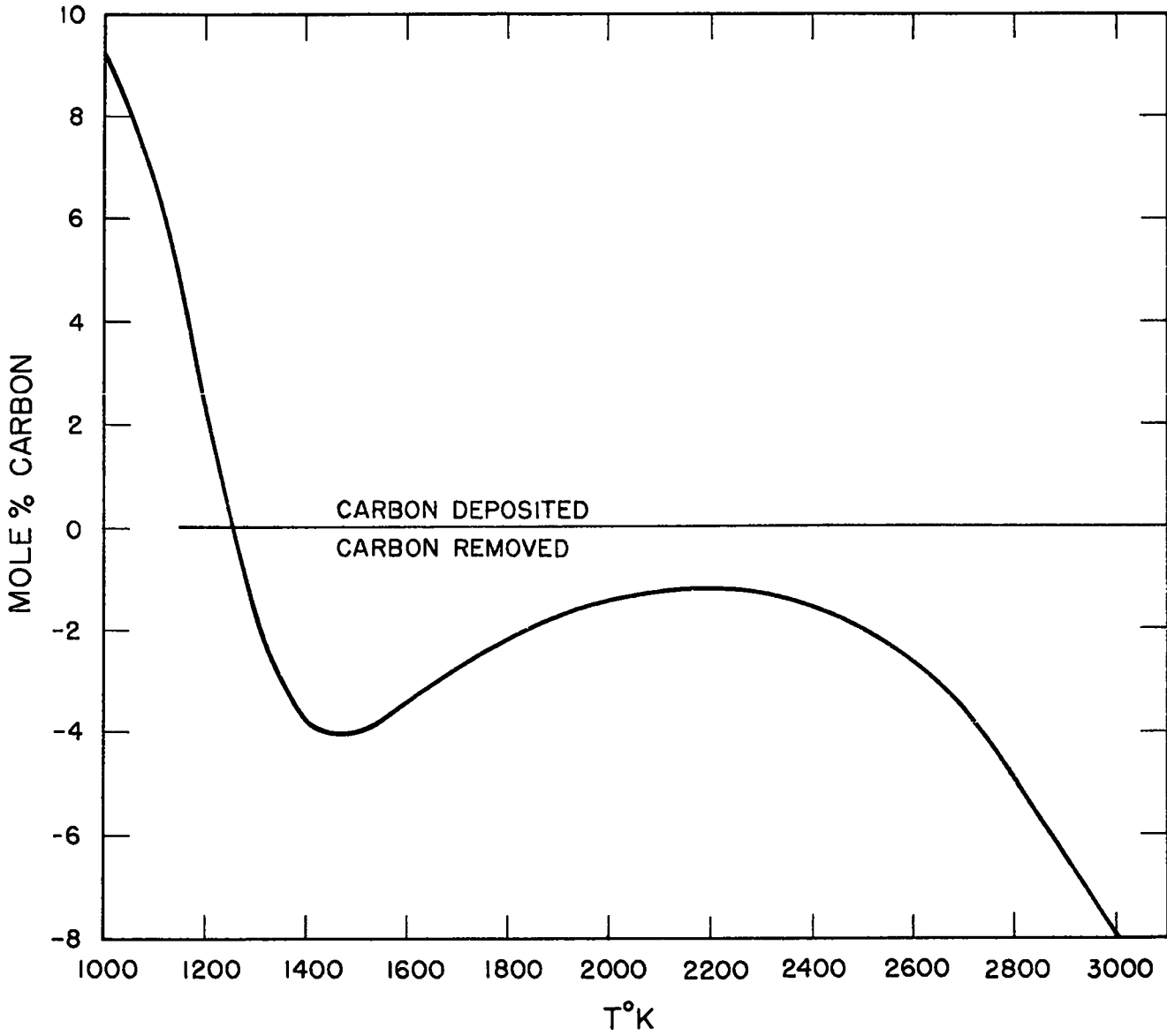
Fig. 10 Mole per cent of solid carbon from methanol