B. X. IC EXPRESSIONS FOR THE FORMATION AND

STABILITY OF HYDROCARBONS

SUMMARY

The temperature range for which the formation from $CO + H_2$ various hydrocarbons (saturated and unsaturated) is possible is determined from consideration of the free energies of formation of the reactants and products. Calculations are carried over a range of pressures between 1 and 100 atmospheres. The conditions of thermodynamic stability are applied to consideration of condensation and decomposition reactions.

THEORETICAL CONSIDERATIONS

The expressions are derived from the free energies of formation as represented in graphs 1 to 7 (these free energy values are taken from Parks and Huffman, Free Energies of Some Organic Compounds, New York, 1932). The difference in energies of formation indicates whether a reaction is possible. When the difference is equal to zero, the reaction is at equilibrium (equilibrium constant = 1).

In order to represent conditions at higher pressures, the standard method of referring free energy to atmospheric pressure has been extended to include the "free energy at 100 atmospheres" in addition to the usual expression, "free energy at 1 atmosphere". When the "free energy at 100 atmospheres" equals zero, the corresponding equilibrium constant, 100 E_p, equals 1. This means that 100 atmospheres are to be taken as unit pressure.

For example

| Methane,	at 25 atmospheres	$P_{CH_4} = 0.25$
H_2O vapor,	at 25 atmospheres	$P_{H_2O} = 0.25$
Carbon monoxide,	at 50 atmospheres	$P_{CO} = 0.50$
Hydrogen,	at 50 atmospheres	$P_{H_2} = 0.50$

$$100\ E_p = \frac{(0.25)(0.25)}{(0.5)(0.5)^3} = 1 \text{ (free energy at 100 atmospheres = 0)}$$

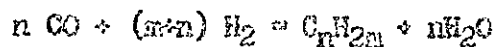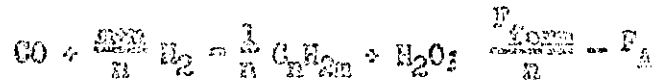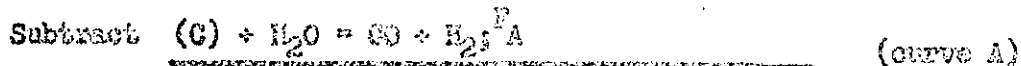ro value of "free energy at 100 atmospheres",
version for pressures of less than 100

Figure 1 gives the energy for formation $\left(\dfrac{F_{form}}{n}\right)$ at 1 atmosphere
of normal paraffin hydrocarbons and of ethylene (based on one C-atom).

$$n\,(c) + m\,H_2 = C_nH_{2m}; \quad F_{form}.$$
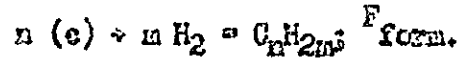
Curves A and B are used in calculating the formation of these hydrocarbons from the CO-H_2 mixture.

$$A. \quad (C) + H_2O = CO + H_2; \quad F_A$$
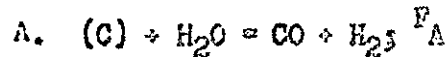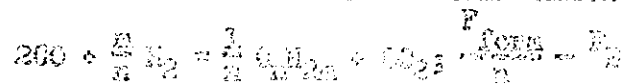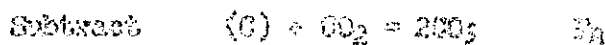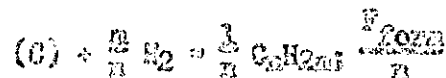
The free energy of synthesis of a hydrocarbon formed from
CO + H_2 is equal to the difference between curve A and the hydrocarbon
curve. Formation of the hydrocarbon is possible as long as its curve
remains below the A curve.

$$(C) + \frac{1}{n} H_2 = \frac{1}{n} C_nH_{2m}; \quad \frac{F_{form}}{n} \qquad \text{(hydrocarbon curve)}$$

Subtract $\quad (C) + H_2O = CO + H_2; \quad F_A \qquad \text{(curve A)}$

$$CO + \frac{m+n}{n} H_2 = \frac{1}{n} C_nH_{2m} + H_2O; \quad \frac{F_{form}}{n} - F_A$$

$$n\,CO + (m+n)\,H_2 = C_nH_{2m} + nH_2O$$

The synthesis formula in this case is based on one atom of
carbon. The formula based on 1 molecule reads as follows:

$$n\,CO + (m+n)\,H_2 = C_nH_{2m} + nH_2O.$$
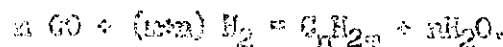
The oxygen fraction of CO is present here as water. It could
also be present as CO_2. The free energy of the latter reaction is given
by the difference from the B curve, corresponding to reaction B:

$$B. \quad (C) + CO_2 = 2CO; \quad F_B$$

$$(C) + \frac{m}{n} H_2 = \frac{1}{n} C_nH_{2m}; \quad \frac{F_{form}}{n}$$

Subtract $\quad (C) + CO_2 = 2CO; \quad F_B$

$$2CO + \frac{m}{n} H_2 = \frac{1}{n} C_nH_{2m} + CO_2; \quad \frac{F_{form}}{n} - F_B$$

$$2n\,CO + m\,H_2 = C_nH_{2m} + n\,CO_2.$$
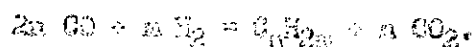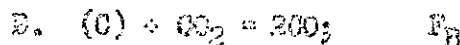
APPLICATIONS

figure 1 shows that all hydrocarbons may
below certain temperatures. The limiting
hydrocarbons, for which the free energy
zero, are shown in Table 1.

Table 1

Limiting Temperatures for Hydrocarbon Synthesis from $CO + H_2$
(Free Energy at 1 Atmosphere Equals Zero)

Hydrocarbon	Temperature for Reaction to $HC* + H_2O$		Temperature for Reaction to $HC* + CO_2$	
	°K	°C	°K	°C
methane	675	400	725	450
ethane	900	625	920	645
ethylene	655	380	220	445

$*HC$ = hydrocarbon.

The intersection of the ethylene curve with the ethane curve
shows that the zero point for the dehydrogenation of ethane according
to the equation,

$$C_2H_6 = C_2H_4 + H_2$$
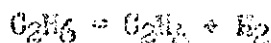
is at 1080°K. = 805°C. for 1 atmosphere.

Figure 2 gives the free energy of reaction for the same
hydrocarbons at 100 atmospheres. Compared with figure 1, the displace-
ment of the curves is calculated to given by the equation

$$F_{100\ atm.} - F_{1\ atm.} = \Delta N\ RT \ln 100 = (\Delta N)(T)(4.573)(2)$$

where ΔN is the change in number of molecules in the gas.

For paraffin hydrocarbons ΔN equals 1, since

$$(C) + \frac{n+1}{2} H_2 = \frac{1}{n} C_nH_{2n+2}; \quad \Delta N = 1$$

For ethylene ΔN equals 1/2,

For olefins and naphthenes in general $\Delta N = \frac{n-1}{n}$

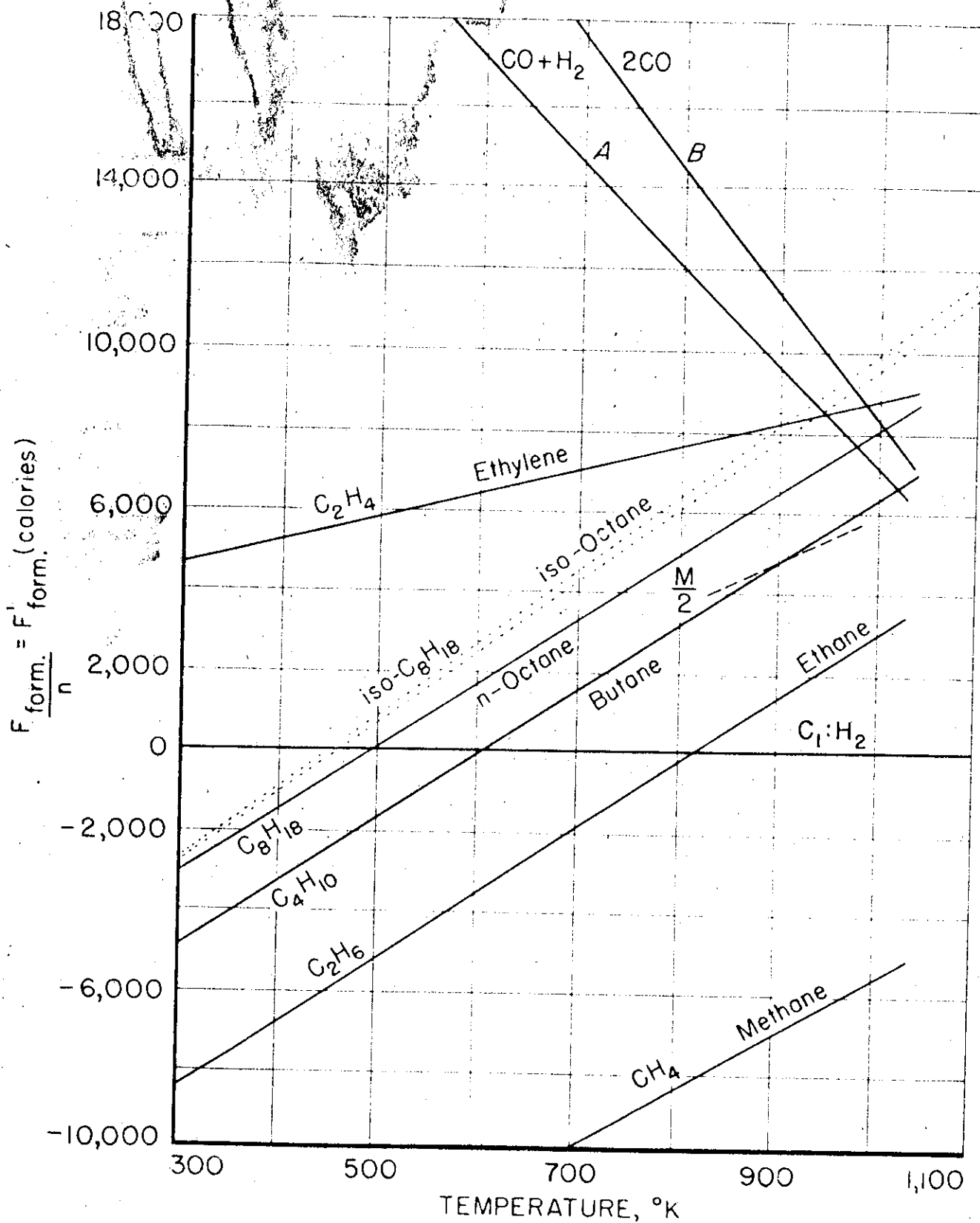For benzene $\Delta N = 1/2$.

For curves A and B $\Delta N = -1$.

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Figure 2.– Free energy of formation of several paraffin hydrocarbons at 100 atmospheres.
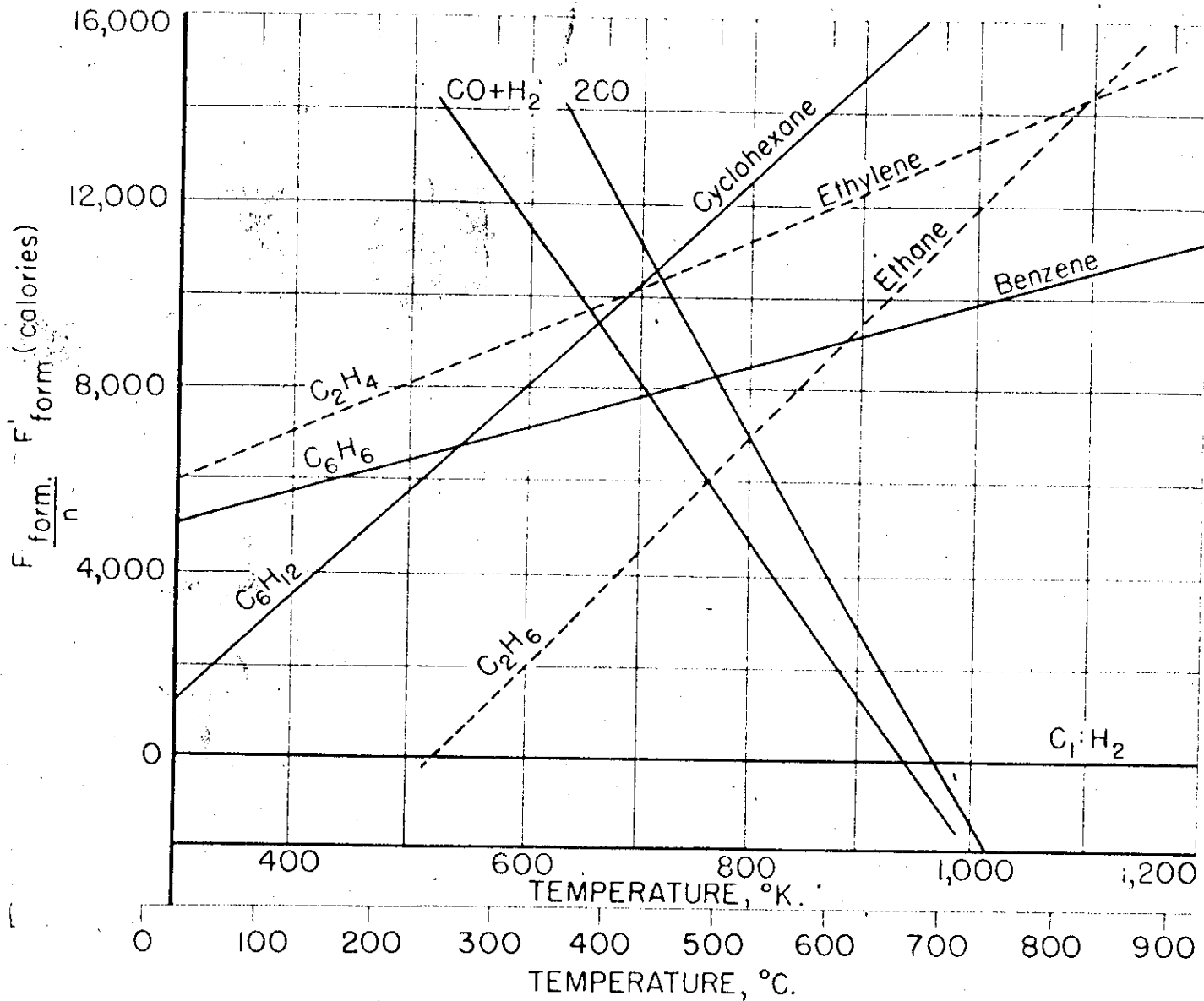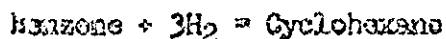
Table 2

Limiting Temperatures for Hydrocarbon Synthesis from CO + H₂
(Free Energy at 100 Atmospheres Equals Zero)

Hydrocarbon	Temperature for Reaction to HC* + H₂O		Temperature for Reaction to HC* + CO₂	
	°K	°C	°K	°C
Propane	975	700	1000	725
Methane	about 1300	about 1000	about 1300	about 1000
ethylene	945	670	937	730

*HC = hydrocarbon.

Figures 3 and 4 give the free energy of formation for benzene
and for cyclohexane at 1 and 100 atmospheres, respectively. Tables 3 and
4 summarize the data.

Table 3

Limiting Temperatures for Hydrocarbon Synthesis from CO + H₂
(Free Energy at 1 Atmosphere Equals Zero)

Hydrocarbon	Temperatures for Reaction to HC* + H₂O		Reaction to HC* + CO₂		Reaction to Polyhydrocarbon	
	°K	°C	°K	°C	°K	°C
benzene	710	435	770	495	545	270
cyclohexane	665	365	735	460		

*HC = hydrocarbon.

Table 4

Limiting Temperatures for Hydrocarbon Synthesis from CO + H₂
(Free Energy at 100 Atmospheres Equals Zero)

Hydrocarbon	Temperatures for Reaction to HC* + H₂O		Reaction to HC* + CO₂		Reaction to Polyhydrocarbon	
	°K	°C	°K	°C	°K	°C
benzene	1000	730	1080			
cyclohexane					760	485

*HC = hydrocarbon.

Figure 3.— Free energy of formation of benzene and cyclohexane at 1 atmosphere.

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..., the formation of benzene and of cyclohexane
... thermodynamically speaking, up to 400°C. at 1
... at 100 atmospheres.

... of the benzene and cyclohexane curves show
... points of ... gy for the hydrogenation - dehydrogenation
... brium.

Examples of the benzene-cyclohexane equilibrium,

$$benzene + 3H_2 = Cyclohexane$$

... shown in Table 5.

Table 5

Examples of Benzene-Cyclohexane Equilibrium

Temperature at which free energy equals zero, °C.	1 atmosphere		100 atmospheres	
	270		435	
examples	1	2	3	4
partial) benzene	1	0.6	100	80
pressure) cyclohexane	1	0.4	100	40
atmospheres) hydrogen	1	0.6	100	80
total pressure, atmospheres	3	2	300	200

Free energies of formation for a few olefins are given in
figures 5 and 6. The olefin curves intersect (in closely grouped
points) at 415°C. (for 1 atmosphere). In other words, below this
temperature we may expect polymerization, and above it, dissociation.
At higher pressures, the points of intersection (free energy of
polymerization equals zero) are displaced towards higher temperatures,
as for example, 760 to 780°C. at 100 atmospheres.

Comparison with saturated hydrocarbons having the same
number of carbon atoms shows the olefin curves to be flatter and
situated higher in the usual temperature range, so that, for higher
temperatures, the free energy of dehydrogenation equals zero. In
other words, above this temperature dehydrogenation of paraffins to
olefins becomes possible.

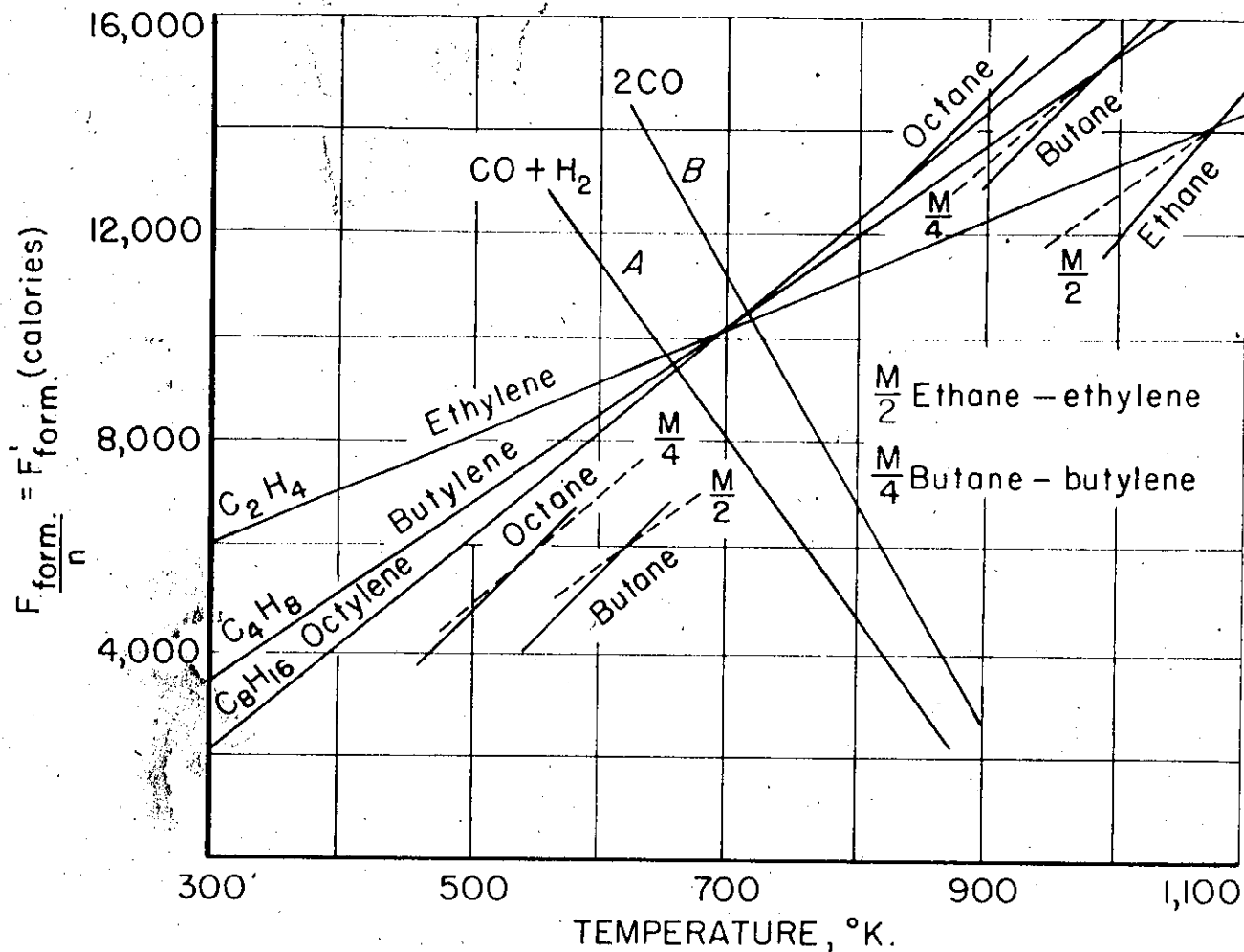| Examples	Limiting temperatures at which free energy at 1 atmosphere equals zero, °C.
ethane to ethylene	805
butane to butylene	725
octane to octylene	550

Figure 5.— Free energy of formation of several olefins at 1 atmosphere.

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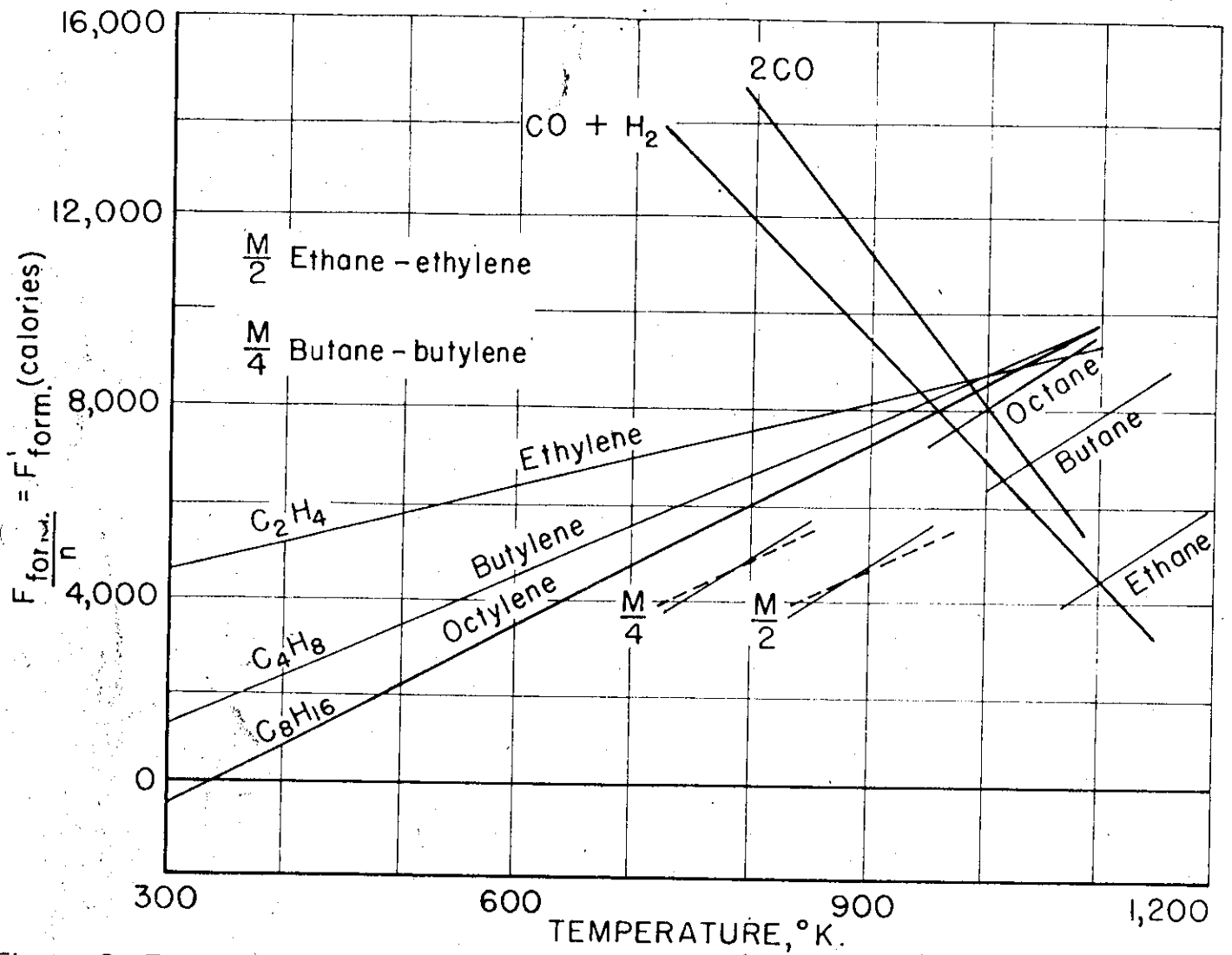
Figure 6.- Free energy of formation of several olefins at 100 atmospheres.

It will be seen from the examples of octane, that from C_6
on the dehydrogenation temperature for paraffins lies within the
region of cracking temperatures. The presence of hydrogen under
pressure* (figure 6) increases the dehydrogenation temperature
considerably. For octane it rises to 800°C. and it is still higher
for the lower paraffins. Consequently, under hydrogen pressure
paraffins are completely stable towards dehydrogenation.

Olefins may be obtained from the CO-H_2 mixture, at 1
atmosphere, at temperatures below 380°C. (hydrocarbon + H_2O reaction)
and 440°C. (hydrocarbon + CO_2 reaction). At 100 atmospheres the
temperature range lies as high as 700°C.

## EXPRESSIONS FOR CRACKING AND CONDENSATION

Hydrogen Present

The parallel course of the paraffin curves in figures 1 and
2 indicates that the cracking of a paraffin into lower paraffins is
accompanied by a loss in free energy at all temperatures and pressures.
This may be expressed as follows:

$$C_{(m+n)}H_{2(m+n)+2} + H_2 = C_mH_{2m+2} + C_nH_{2n+2}$$
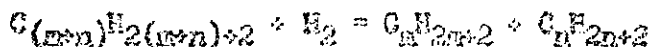
F is always negative.

For ethylene, whose curve lies above that of methane at
ordinary temperatures, the relatively flat course of the curve indicates
that the tendency to cracking at ordinary temperatures, according to the
equation:

$$C_2H_4 + 2H_2 = 2CH_4$$
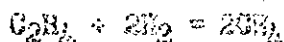
ives way to a tendency on the part of methane to condense to form
ethylene at about 1500°C.

The same is true of the benzene curve, whose course is still
flatter and lies somewhat below that of ethylene. Condensation of
methane to benzene is possible above 1100°C.; condensation of ethane to
benzene may occur above 600°C. (figure 5).

The condensation of ethylene to benzene is possible at all
temperatures at 1 atmosphere, as well as for 100 atmospheres since the
ethylene curve always lies above that of benzene.

_____

*Hydrogen is always present as these considerations are based on
energies of formation from C and H_2.

6

The general case to be considered here is that of the
cracking of paraffin into olefin + paraffin.

$$C_{(m+n)}H_{2(m+n)+2} = C_nH_{2m} + C_nH_{2n+2}$$

Since hydrogen is neither formed nor consumed, its presence
is not a factor and the free energies may be derived from the curves
for the energy of formation. In this connection, it should be observed
that the free energy given in the curves is based on 1 C-atom, $F_{form.}$
are n = 1.

$$F'_{form.} = \frac{F_{form.}}{n} (n = \text{number of C-atoms per molecule})$$

The free energy of cracking, $F_{cracking}$, based on one molecule
of paraffin, may be expressed as follows:

$$F_{cracking} = F_{form.} \; C_m \text{ olefin} + F_{form.} \; C_n \text{ paraffin} - F_{form.} \; C_{(m+n)} \text{ paraffin}$$

Introducing the average value based on 1 atom of carbon.

$$F_{cracking} = \frac{m \; F_{form.} \; C_m \text{ olefin} + n \; F_{form.} \; C_m \text{ paraffin}}{m+n} - F'_{form.} \; C_{(m+n)} \text{ parah}$$

Example 1. - Decomposition and Synthesis of Butane

$$C_4H_{10} = C_2H_4 + C_2H_6$$

The mean curve $\frac{M}{2}$ (figures 1, 2, and 3) gives the behavior
of the decomposition products. Since it intersects the butane curve at
°C., we may expect decomposition above 345°C. and synthesis
(addition) below 345°C. at 1 atmosphere. At a pressure of 100
atmospheres the limiting temperature is 620°C.

Example 2. - Decomposition and Synthesis of Octane

$$C_8H_{18} = C_4H_8 + C_4H_{10}$$
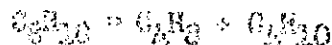
The mean curve for butane + butylene is given by $\frac{M}{2}$ (figures
5 and 6). At 1 atmosphere the curve intersects the octane curve at
250°C. Thus, decomposition occurs above 250°C., and synthesis
(alkylation) below. At 100 atmospheres the point of intersection lies
at 510°C.

... the examples show that at least the lower paraffins are ... towards central cleavage of the molecule. At temperatures ... °C., the synthesis from paraffin + olefin (alkylation) is ... the likely reaction.

... 5. - Decomposition of n-octane to Give Olefin + Paraffin
(figure 7)

The various fractions obtained from n-octane by cleavage at ... different points are shown in figure 7. The greatest decrease in free ... gy occurs for cleavages giving heptylene + methane or hexylene + ... ane. This cleavage is possible even at 160°C. Cleavage of the ... ecule to give a higher order paraffin and an olefin of correspond- ... ingly lower order is accompanied by little increase in free energy. However, the differences are not considerable.*

Hydrogen Eliminated

There are some reactions in which elimination of hydrogen occurs. We may cite, for example, the condensation of ethane with ethylene to give benzene. Another example is the cracking of n-octane to form ethylene, according to the equation,

$$C_8H_{18} = 4 \, C_2H_4 + H_2$$
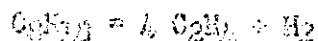
The curves for ethylene and n-octane are shown in figure 1. The cracking reaction is possible at temperatures above 460°C., at 1 atmosphere.

Translator's note: Interpretation of the last two sentences in this paragraph is not clear.
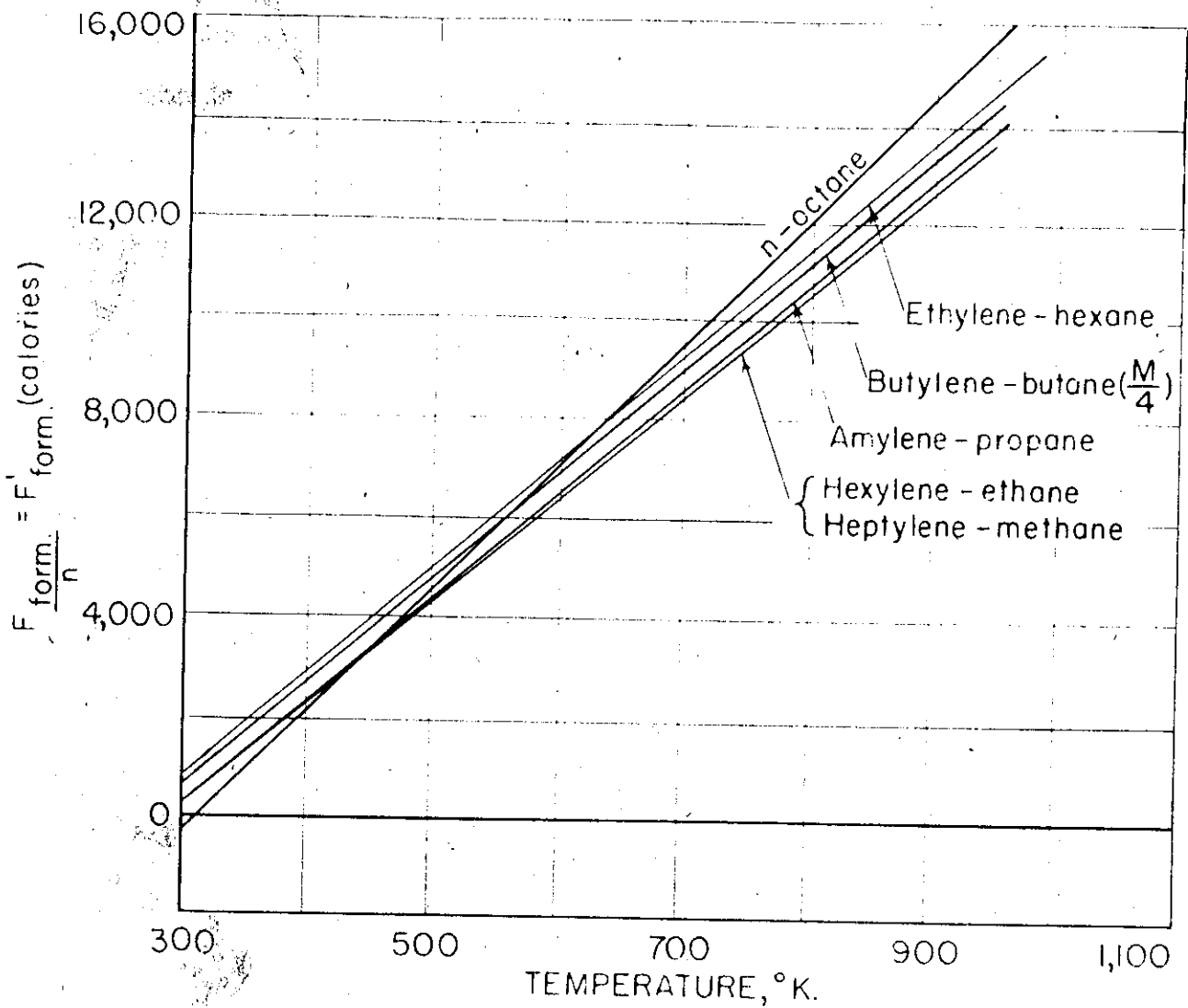
Figure 7 — Free energy of formation of n-octane and cleavage at 1 atmosphere.