

centage of sugar increased. This is probably due to a decrease of solubility of the salt as the amount of sugar increases in the solution. This indicates the reason for the known fact, in practice, that the ratio of sugar to salts decreases very rapidly, as the density drops, during the process of sweetening off char filters.

Conclusion

It appears from these experiments that in refining sugars the solutions should be kept as dense as possible where the maximum of ash is to be removed from the solutions by the use of bone char.

The Free Energies of Some Hydrocarbons¹

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Equations have been derived for the free energies of formation of methane, ethane, octane, ethylene, acetylene, benzene, toluene, naphthalene, and cyclohexane as functions of temperature. These equations have been plotted with the ordinates reduced to free energy of formation per carbon atom to show the true stability relations between various hydrocarbons.

The equations have been simplified to linear equations for cracking temperatures, 427–727° C. By suitable interpolations similar equations for the other paraffin, olefin, acetylene, and naphthene hydrocarbons have been estimated. The equations have been tested and found consistent with several known reactions. Some predic-

tions as to the possibility of other desirable reactions have been made.

The direct production of higher paraffin hydrocarbons from lower ones is shown to be impossible except with simultaneous production of still lower ones in at least equivalent amounts. The catalytic formation of acetylene in more than traces is likewise impossible. The direct removal of hydrogen from a paraffin to form an olefin with the same number of carbon atoms is possible only at high temperatures and to a very limited extent. The synthesis of gasoline from water gas can take place only below about 450° C. The isomerization of olefins to naphthenes requires temperatures below about 430° C., while the production of aromatics requires 550–900° C.

THE recent interest in synthetic gasoline makes it desirable to have reliable free-energy values for the pure hydrocarbons involved.² Such data would throw light also upon the chemistry of cracking and other reactions involving hydrocarbons. From the free-energy change of a proposed reaction predictions may be made as to its possibility and the conditions of temperature and pressure required.

Some of the data assumed in the present calculations are only approximate, but in many cases this fact does not introduce the error which it seems to do. An error in the specific-heat equation of a substance, for example, makes a tremendous difference in the chemical constant, I , but because of compensating errors, the resulting free energy is almost unchanged. The values of free energy calculated will be tested by several known reactions. Consistency with them will increase the reliability of the results. The figures are offered only as estimates, which can be revised when more data become available, but they are believed to be sufficiently accurate for any prediction that is made from them. The symbols used throughout conform to the system of Lewis and Randall.³

Methane

Methane is the only hydrocarbon with sufficient stability for accurate data on equilibrium with its elements, and even with this compound the numerous calculations which have been made are not very consistent because some of them are based upon equilibria with "amorphous carbon," which is not a definite chemical individual, and which is converted

gradually to graphite during the experiments. For this reason graphite is taken as the standard form of carbon in this paper.

The heat of formation of methane from graphite and hydrogen is given by Lewis and Randall⁴ as $\Delta H_{291} = -18,300$.

The specific-heat data employed by them were admittedly by a rough estimate, and should be replaced by those of Dixon, Campbell, and Parker⁵ as calculated by Partington and Shilling.⁶

$$C_p = 2.57 + 0.0231T - 0.0042T^2 \quad (1)$$

Similarly for hydrogen⁶

$$C_p = 6.65 + 0.0007T \quad (2)$$

and for graphite⁷

$$C_p = 1.1 + 0.0048T - 0.0012T^2 \quad (3)$$

(except in the case of methane, (3) will be simplified to

$$C_p = 1.1 + 0.004T) \quad (4)$$

Combining (1), (2), and (3)

$$\Delta C_p = -11.83 + 0.0169T - 0.0033T^2 \quad (5)$$

Then

$$\Delta H_{291} = H_0 - 11.83T + 0.00845T^2 - 0.001T^3 = -18,300 \quad (6)$$

from which

$$\Delta H_0 = -15,500 \quad (7)$$

Employing the same equilibrium data as given by Lewis and Randall,⁸ the value of I is found to be -52.07 ± 0.17 , with slightly better agreement than that found by them.

Then, for $C + 2H_2 \rightarrow CH_4$

$$\Delta F = -15,500 + 11.83T \ln T - 0.00845T^2 + 0.005T^3 - 52.07T \quad (8)$$

$$\Delta F_{298} = -11,670 \quad (9)$$

This is intermediate between the value of Lewis and Randall,

⁴ L. and R., pp. 80, 571.

⁵ *Proc. Roy. Soc. (London)*, **A100**, 1 (1921).

⁶ "Specific Heats of Gases," p. 206, Ernest Benn, Ltd., London, 1924.

⁷ L. and R., p. 569.

⁸ L. and R., p. 572.

¹ Presented before the Division of Petroleum Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

² Since this paper was written, calculations for a few of these hydrocarbons have been published by Smith, *Ind. Eng. Chem.*, **19**, 801 (1927); but the present paper is much more comprehensive, and different methods have been used in the calculations.

³ "Thermodynamics," McGraw-Hill Book Co., New York, 1923, (hereinafter abbreviated "L. and R.").

-12,800, and that found by Parks and Kelley,⁹ -9800, by an entirely different method.

Since equations of the type of (8) are awkward to employ, and since they give practically straight lines when plotted (Figure 1), they can be simplified to linear equations. The temperature range 700-1000° K. (427-727° C.) is selected as covering the cracking temperatures, but the equations are only slightly less accurate at other temperatures.

$$\Delta F = -20,000 + 26.2T \quad (10)$$

Octane

To estimate the free energy of a substance for which equilibrium values are not available, it is preferable to employ the third law of thermodynamics. The paraffin hydrocarbon for which heat of combustion data are most accurate is octane, which is fortunately in the middle of the gasoline range. It was considered best to calculate the free energy of this compound and to estimate those of the other paraffin hydrocarbons by interpolation and extrapolation.

The specific heat of liquid octane at 25° C. is 0.5052.¹⁰ The molar heat capacity, C_p , is therefore 57.66. Bushong and Knight¹¹ have shown that the specific heats of paraffin hydrocarbons are proportional to absolute temperature, both as liquid and solid. On this basis, for octane

$$C_p = 0.193T \quad (11)$$

The latent heat of fusion is not known for any pure paraffin hydrocarbon. The heat of solution of paraffin wax in petroleum distillate is given by French, McGill, and Sullivan^{12a} as 40.3 calories per gram. This must be almost identical with the heat of fusion,^{12b} and is probably nearly independent of the molecular weight, since this is true of the specific heats of the members of the paraffin series. Assuming that the above figure is the heat of fusion of octane, by combination with the molecular weight and absolute melting temperature, the entropy of fusion is

$$\frac{40.3 \times 114.14}{216.5} = 21.2$$

The total entropy of liquid octane at 25° C. is

$$S^\circ_{298} = 0.193 \times 298 + 21.2 = 78.7 \quad (12)$$

For $8C + 9H_2$,

$$S^\circ_{298} = 10.4 + 265^{13} = 275.4 \quad (13)$$

$$\Delta S^\circ_{298} = -196.7 \quad (14)$$

The heat of combustion of octane is 1,300,700 calories.¹⁴ Combining with the heat of combustion of its elements,⁴ the heat of formation of octane is

$$\Delta H_{298} = -68,000 \quad (15)$$

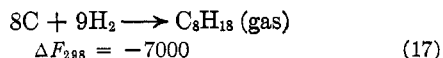
From which

$$\Delta F_{298} = \Delta H - T\Delta S = -9300 \quad (16)$$

The vapor pressure of octane at 25° C. is 15.4 mm.¹⁵ For the evaporation,

$$\Delta F = -RT \ln \frac{P}{760} = +2300$$

and for



However, we are interested primarily in the free energies at higher temperatures, at which most of the reactions of petroleum chemistry take place. For ordinary temperatures the heat capacity of liquid octane is represented by

$$C_p = 10 + 0.161T \quad (18)$$

better than by (11). From (2), (4), and (18) for liquid octane

$$\Delta C_p = -58.6 + 0.122T \quad (19)$$

$$\Delta H_{298} = \Delta H_0 - 58.6T + 0.061T^2 = -68,000 \quad (20)$$

(see equation 15)

from which

$$\Delta H_0 = -56,000 \quad (21)$$

$$\Delta H_{398} = -69,650 \quad (22)$$

From (16), (19), and (21), for $8C + 9H_2 \longrightarrow$

$$C_8H_{18} \text{ (liquid)} \quad (23)$$

$$\Delta F = -56,000 + 58.6T \ln T - 0.061T^2 - 159.2T \quad (24)$$

$$\Delta F_{398} = +19,200 \quad (25)$$

for either liquid or vapor.

The specific heat of octane vapor is not known. It is estimated as follows: The latent heat of vaporization, ΔH_v , is 8060 calories¹⁶ at its boiling point, 125° C.; those of hexane are 6820 at 70° C. and 7680 at 0° C. Assuming that the relative rate of increase of ΔH_v for octane with decreasing temperature is the same as that of hexane (since this is true for a short temperature interval, 2 per cent for 10° C.), the value $\Delta H_v = 9500$ at 25° C. is estimated. The total heat capacity of octane vapor between 25° and 125° C. is that of liquid octane between the same temperatures, plus ΔH_v at 125° C., minus ΔH_v at 25° C., plus a correction due to the Joule-Thomson effect at 25° C., which is assumed equal to that of benzene, below—namely, 70 calories.¹⁷

$$6242 + 8060 - 9500 + 70 = 4832 \text{ calories} \quad (26)$$

$$\text{Mean } C_p = 4832/100 = 48.32 \quad (27)$$

Let us assume

$$C_p = 35 + 0.0383T^{18} \quad (28)$$

From (2), (4); and (28) for octane vapor

$$\Delta C_p = -33.6 \quad (29)$$

$$\Delta H = \Delta H_0 - 33.6T \quad (30)$$

From (22)

$$\Delta H_{398} = \Delta H_0 - 69,650 = -61,600 \quad (31)$$

Combining (30) and (31)

$$\Delta H_0 = -48,200 \quad (32)$$

From (25), (29), and (32), for $8C + 9H_2 \longrightarrow C_8H_{18} \text{ (gas)}$

$$\Delta F = -48,200 + 33.6T \ln T - 53.4T \quad (33)$$

$$\Delta F_{298} = -7000 \quad (34)$$

The agreement with (17) is a check upon some of the assumptions made.

Simplifying (33)

$$\Delta F = -76,100 + 206.6T \quad (35)$$

Ethane

An interpolation between (10) and (35) might be made to estimate the free-energy equations of ethane and other paraffin hydrocarbons. Thus for ethane

$$\Delta F = -28,000 + 52T \quad (36)$$

However, since methane lacks a carbon-carbon bond, it may be slightly inconsistent with the other paraffins, and since specific heat values are available for ethane, we will evaluate its equation independently. At room temperature we will accept Smith's value²

$$\Delta F_{298} = -10,700 \quad (37)$$

The heat capacity of ethane is estimated¹⁹ as

$$C_p = 6.26 + 0.0181T \quad (38)$$

from which

$$\Delta C_p = -15.88 + 0.008T \quad (39)$$

$$\Delta H = \Delta H_0 - 15.88T + 0.004T^2 \quad (40)$$

⁹ J. Am. Chem. Soc., **47**, 2096 (1925).

¹⁰ Mabery and Goldstein, Proc. Am. Acad. Arts Sci., **37**, 539 (1902).

¹¹ Ind. Eng. Chem., **12**, 1197 (1920).

¹² (a) Ind. Eng. Chem., **19**, 1041 (1927); (b) Gehlhoff, Z. physik. Chem., **98**, 252-9 (1921); C. A., **15**, 3419 (1921).

¹³ L. and R., p. 464.

¹⁴ J. Am. Chem. Soc., **49**, 2478 (1927).

¹⁵ Landolt-Börnstein-Roth-Scheele, "Tabellen," p. 1356 (1923); (hereinafter abbreviated "L-B").

¹⁶ L-B, p. 1481.

¹⁷ It is about 50 calories for H₂O and about 200 calories for CH₃OH.

¹⁸ The slope of equation (28) is taken as about double those for methane and ethane, but so that $\Delta G_f = 0$ for convenience. However, any other equation which satisfied (27) would give practically the same values for free energy as those obtained.

¹⁹ Shilling, op. cit., p. 194, 195, 201.

From the heat of formation at 18° C. from diamonds,²⁰ we estimate

$$\Delta H_{298} = -23,075 \quad (41)$$

$$\Delta H_0 = -18,595 \quad (42)$$

From (37), (39), and (42) for $2C + 3H_2 \rightarrow C_2H_6$

$$\Delta F = -18,595 + 15.88T \ln T - 0.004T^2 - 62.8T \quad (43)$$

Simplified for the cracking range

$$\Delta F = -29,000 + 53.3T \quad (44)$$

which compares favorably with (36).

Interpolating now between (35) and (44), for any normal paraffin vapor, C_nH_{2n+2} , approximately

$$F = -13,300 - 7850n + 2.2T + 25.55nT \quad (45)$$

Branched-chain paraffin hydrocarbons probably have slightly greater stability (more negative values for ΔF). This is based upon the work of Richards and Jesse²¹ on the heats of combustion of the isomeric octanes, which are lower than that of normal octane in three cases out of four. The differences in heats, and probably also in free energies, are of the order of 1000 to 2000 calories.

Ethylene

From the heat of formation of ethylene from diamonds 14,600 calories²⁰

$$\Delta H_{298} = 14,865 \quad (46)$$

The heat capacity is estimated¹⁹ as

$$C_p = 4.4 + 0.0204T \quad (47)$$

from which

$$\Delta C_p = -11.1 + 0.011T \quad (48)$$

$$\Delta H = \Delta H_0 - 11.1T + 0.0055T^2 \quad (49)$$

Combining (46) and (49)

$$\Delta H_0 = 17,680 \quad (50)$$

Employing the results of Pring and Fairlie²²

T	$K = \frac{(C_2H_4)}{(H_2)^2}$	$-RT \ln K$	I
1548	0.032	46,150	-54.72
1673	0.035	33,000	-64.09
2048	0.041	46,800	-59.41
2223	0.032	36,800	-64.85
2323	0.036	34,700	-66.00

The agreement in the value of I is poor. It seems probable that this is due to partial hydrogenation during cooling, $C_2H_4 + 2H_2 \rightarrow 2CH_4$, as suggested by the authors. If this is true, the ethylene found would be too low, and the free energy, $-RT \ln K$, too large. It seems preferable to reject the first and third values and take the mean of the other three, which agree more closely. We will take $I = -65$. Hence for $2C + 2H_2 \rightarrow C_2H_4$

$$\Delta F = 17,680 + 11.1T \ln T - 0.0055T^2 - 65T \quad (51)$$

Or, approximately

$$\Delta F = 12,260 + 11.6T \quad (52)$$

Acetylene

The heat of formation of acetylene is given²⁰

$$\Delta H_{298} = 53,880 \quad (53)$$

The heat capacity is estimated²³ as

$$C_p = 6.1 + 0.015T \quad (54)$$

from which

$$\Delta C_p = -2.75 + 0.0066T \quad (55)$$

$$\Delta H = \Delta H_0 - 2.75T + 0.0033T^2 \quad (56)$$

$$\Delta H_0 = 54,400 \quad (57)$$

²⁰ L-B, p. 1492.

²¹ J. Am. Chem. Soc., **32**, 292 (1910).

²² Ind. Eng. Chem., **4**, 812 (1912). Although amorphous carbon was used in some of this work, the text makes it evident that in the second experiment above (at 1673° K.) the carbon had been graphitized completely. The same can be assumed for those at higher temperatures.

²³ L-B, p. 1275.

Employing the data of Pring and Fairlie,²² Pring,²⁴ and von Wartenberg²⁵

T	$K = \frac{C_2H_2}{H_2}$	$-RT \ln K$	I
2097	0.0013	27,800	-26.35
2223	0.0031	25,600	-26.34
2273	0.0088	21,500	-27.80
2323	0.008	22,400	-26.92
2373	0.0027	27,850	-24.34
2773	0.38	18,050	-25.23
2973	0.029	21,000	-22.77

The falling off in the value of I at high temperatures may be due partly to the formation of atomic hydrogen,²⁶ since that would decrease the concentration of molecular hydrogen (H_2); but probably it is due mainly to decomposition of acetylene during cooling, as suggested by the authors.²² We will take $I = -26.4$. Hence for $2C + H_2 \rightarrow C_2H_2$

$$\Delta F = 54,400 + 2.75T \ln T - 0.0033T^2 - 26.4T \quad (58)$$

or approximately,

$$\Delta F = 54,400 - 10.8T \quad (59)$$

Higher Unsaturated Hydrocarbons

The specific heat data on higher olefins and acetylenes are too meager for calculations of their free energies. A rough approximation might be obtained by applying the increments of (45) to (52) and (59) giving for olefins

$$\Delta F = 27,960 - 7850n - 39.5T + 25.55nT \quad (60)$$

and for acetylenes

$$\Delta F = 70,100 - 7850n - 61.9T + 25.55nT \quad (61)$$

but this would imply that the free energy of hydrogenation of the double or triple bond is independent of the molecular weight. Since the heats of hydrogenation are not identical, it seems preferable to assume the corresponding variations in the free energies. From the heats of combustion of the several hydrocarbons, the following heats of hydrogenation were calculated:

	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	C_8H_{16}
Olefin Heat	-38,260	-35,580	-31,780	-33,280	-30,080	-19,080
Olefin Heat			$C_{10}H_{20}$			
			-34,780			
Acetylene Heat			C_2H_2	C_3H_4		
			-76,900	-80,800		

The values for olefins are somewhat erratic because they are small differences between large values, which are not extremely accurate. Smoothing out the values, the heats of hydrogenation are

$$\text{For olefins } \Delta H = -41,400 + 1550n \quad (62)$$

$$\text{For acetylenes } \Delta H = -75,300 - 800n \quad (63)$$

Correcting (60) and (61) for the formation of olefins, $nC + nH_2 \rightarrow C_nH_{2n}$ (gas)

$$\Delta F = 31,060 - 9400n - 39.5T + 25.55nT \quad (64)$$

and for acetylenes $nC + (n-1)H_2 \rightarrow C_nH_{2n-2}$ (gas)

$$\Delta F = 68,400 - 7000n - 61.9T + 25.55nT \quad (65)$$

Benzene

For liquid benzene, Lewis and Randall²⁷ give

$$\Delta H_{298} = 11,700 \quad (66)$$

$$\Delta F_{298} = 27,100 \quad (67)$$

The heat capacity is estimated²⁸

$$C_p = 7.1 + 0.084T \quad (68)$$

$$\Delta C_p = -19.45 + 0.058T \quad (69)$$

from which

$$\Delta H_0 = 14,920 \quad (70)$$

$$\Delta H_{353} = 11,670 \quad (71)$$

for $6C + 3H_2 \rightarrow C_6H_6$ (liquid)

²⁴ J. Chem. Soc. (London), **89**, 1591 (1907); C. A., **1**, 550 (1907).

²⁵ Z. anorg. Chem., **52**, 299 (1907); C. A., **1**, 1122 (1907).

²⁶ Langmuir, Ind. Eng. Chem., **19**, 668 (1927).

²⁷ L. and R., p. 573.

²⁸ Williams and Daniels, J. Am. Chem. Soc., **46**, 912 (1924).

$$\Delta F = 14,920 + 19.45T \ln T - 0.029T^2 - 61.3T \quad (72)$$

From the heat of vaporization,²⁹ $\Delta H_{v298} = 8040$, and the vapor pressure,³⁰ 94.5 mm., both at 25° C., combined with (66) and (67), for benzene vapor

$$\Delta H_{298} = 19,740 \quad (73)$$

$$\Delta F_{298} = 28,340 \quad (74)$$

We estimate²⁴

$$C_p = 6.55 + 0.052T \quad (75)$$

$$\Delta C_p = -20 + 0.026T \quad (76)$$

from which

$$\Delta H_0 = 24,545 \quad (77)$$

$$\Delta H_{353} = 19,100 \quad (78)$$

for $6C + 3H_2 \rightarrow C_6H_6$ (gas)

$$\Delta F = 24,545 + 20T \ln T - 0.013T^2 - 97.4T \quad (79)$$

Adding ΔH_{v353} , which is 7360,²⁹ to (71), for benzene vapor

$$\Delta H_{353} = 19,030 \quad (80)$$

which checks (78) satisfactorily, the slight difference being due probably to the Joule-Thomson effect. From (72) for liquid benzene

$$\Delta F_{353} = 29,965 \quad (81)$$

and from (79) for benzene vapor

$$\Delta F_{353} = 29,970 \quad (82)$$

The agreement at the boiling point increases the reliability of the results. Simplifying (79), approximately

$$\Delta F = 17,000 + 35.3T \quad (83)$$

Toluene

From the heat of combustion of toluene, 935,230 calories³¹

$$\Delta H_{298} = 2250 \quad (84)$$

Let us assume that the mean atomic entropy is the same as that of benzene—namely, 3.³² This assumption is supported by the fact that the entropy of ethane, 47, exceeds that of methane, 38, by 9, and that that of the latter exceeds that of hydrogen, 29.44,¹³ by nearly the same figure. The entropy of fusion of toluene, 6.5, is calculated from its heat of fusion, 1150 calories.³³ The total entropy of toluene is therefore $15 \times 3 + 6.5 = 51.5$. The entropy of $7C + 4H_2$ is 126.9.¹³ Combining, $\Delta S_{298}^\circ = -75.4$. Then

$$\Delta F_{298} = \Delta H - T\Delta S = 24,700 \quad (85)$$

The vapor pressure at 25° C. is 28 mm.,³⁰ from which, as in (17), for toluene vapor

$$\Delta F_{298} = 26,650 \quad (86)$$

The heat capacity of liquid toluene is estimated³⁴ as $13 + 0.078T$, from which

$$\Delta C_p = -21.3 + 0.0472T \quad (87)$$

From (84) and (87)

$$\Delta H_0 = 7950 \quad (88)$$

and from (85), (87), and (88) for $7C + 4H_2 \rightarrow C_7H_8$ (liquid)

$$\Delta F = 7950 + 21.3T \ln T - 0.0236T^2 - 58.17T \quad (89)$$

$$\Delta F_{353} = 30,750 \quad (90)$$

Since equation (90) holds also for toluene vapor, we have, with (86) the value of ΔF at two different temperatures, so that a very rough approximation of the heat capacity will suffice to extrapolate the free energy to higher temperatures. Let us assume

$$C_p = 10.3 + 0.052T \quad (91)$$

$$\Delta C_p = -24 + 0.02T \quad (92)$$

Then adjusting ΔH_0 and I to satisfy (86) and (90), for $7C + 4H_2 \rightarrow C_7H_8$ (gas)

²⁹ L-B, p. 1483.

³⁰ L-B, p. 1370.

³¹ Richards and Davis, *J. Am. Chem. Soc.*, **42**, 1614 (1920).

³² Lewis and Gibson, *Ibid.*, **39**, 2575 (1917).

³³ Nakatsuchi, *C. A.*, **20**, 1020 (1926).

³⁴ L-B, p. 1272.

$$\Delta F = 19,270 + 24T \ln T - 0.017T^2 - 109T \quad (93)$$

or, approximately,

$$\Delta F = 6860 + 59.2T \quad (94)$$

It is interesting to note that if (83) is subtracted from (94), the last coefficient, 23.9, is nearly the same as those in (45), (64), and (65), which are thus considered typical of homologs.

Naphthalene

Proceeding as with toluene, for solid naphthalene the heat of combustion is 1,231,600³¹

$$\Delta H_{298} = 15,840 \quad (95)$$

$$S_{298}^\circ = 54, \Delta S_{298}^\circ = -76.8$$

$$\Delta F_{298} = 38,730 \quad (96)$$

$$C_p = 0.137T^{35} \quad (97)$$

$$\Delta C_p = -37.6 + 0.094T \quad (98)$$

$$\Delta H_0 = 22,880 \quad (99)$$

for $10C + 4H_2 \rightarrow C_{10}H_8$ (solid)

$$\Delta F = 22,880 + 37.6T \ln T - 0.047T^2 - 147.1T \quad (100)$$

$$\Delta F_{353} = 42,960 \quad (101)$$

for either solid or liquid naphthalene. Adding the latent heat of fusion, 4560,³⁶ to (99), and combining with (101), for $10C + 4H_2 \rightarrow C_{10}H_8$ (liquid)

$$\Delta F = 27,440 + 37.6T \ln T - 0.047T^2 - 160T \quad (102)$$

$$\Delta F_{491} = 51,940 \quad (103)$$

The vapor pressures³⁷ are: at 25° C., 0.092 mm.; at 80° C., 7.4 mm.; and at 218° C., 760 mm. From these and (96), (101), and (103) we find for naphthalene vapor, $\Delta F = 44,100$, 46,200, and 51,940, respectively. Combining these and a rough estimate of the heat capacity of the vapor, for $10C + 4H_2 \rightarrow C_{10}H_8$ (gas)

$$\Delta F = 38,540 + 21T \ln T - 0.01T^2 - 98T \quad (104)$$

or for the cracking range,

$$\Delta F = 28,100 + 47.5T \quad (105)$$

Cyclohexane

The equilibria between benzene, hydrogen, and cyclohexane have been studied by Burrows and Lucarini.³⁸ They find at 266.5° C., $K_p = 5.47$ and at 280° C., $K_p = 1.62$. From these

$$\Delta F_{298.6} = -1820 \quad (106)$$

$$\Delta F_{553} = -531 \quad (107)$$

We estimate for C_6H_{12} vapor²³

$$C_p = 6.8 + 0.075T \quad (108)$$

whence, for the reaction $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$

$$\Delta C_p = -19.75 + 0.023T \quad (109)$$

For the reaction as liquids³⁸

$$\Delta H_{298} = -51,600 \quad (110)$$

Assuming the latent heats of vaporization to be the same (110) holds for vapors and

$$\Delta H = \Delta H_0 - 19.75 + 0.0115T^2 \quad (111)$$

from which

$$\Delta H_0 = -46,800 \quad (112)$$

Combining (109) and (112) with (106) or (107), $I = -34.5$ and for $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$ (gas)

$$\Delta F = -46,800 + 19.75T \ln T - 0.0115T^2 - 34.5T \quad (113)$$

or, simplifying

$$\Delta F = -55,200 + 98.8T \quad (114)$$

Combining with (83), the free energy of formation of cyclohexane $6C + 6H_2 \rightarrow C_6H_{12}$ (gas), is

³⁵ L-B, p. 1271.

³⁶ L-B, p. 1474. This is permissible if the heat capacity equation (97) holds for both solid and liquid naphthalene, since this would make the heat of fusion independent of temperature.

³⁷ L-B, p. 1371.

³⁸ *J. Am. Chem. Soc.*, **49**, 1160 (1927).

$$\Delta F = -38,100 + 134T \quad (115)$$

This is nearly the mean between those of hexane and hexene by (45) and (64). Accordingly, for naphthenes in general we will use nearly the mean increments of these of paraffins and olefins. For $nC + nH_2 \rightarrow C_nH_{2n}$ (gas)

$$\Delta F = 12,900 - 8500n - 19.3T + 25.55nT \quad (116)$$

Oxygenated Compounds

For convenience the free-energy equations for formation of steam, carbon monoxide, and carbon dioxide are included.

Steam, $^39 H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (gas),

$$\Delta F = -57,410 + 0.94T \ln T + 0.00165T^2 - 0.0637T^3 + 3.92T \quad (117)$$

Carbon monoxide, $^{40} C + \frac{1}{2}O_2 \rightarrow CO$,

$$\Delta F = -26,600 - 2.15T \ln T + 0.00215T^2 - 0.062T^3 - 7.48T \quad (118)$$

Carbon dioxide, $^{40} C + O_2 \rightarrow CO_2$,

$$\Delta F = -94,110 + 0.60T \ln T - 0.00065T^2 + 0.0611T^3 - 2.30T \quad (119)$$

These can be simplified without much error

$$\text{For } H_2O \Delta F = -58,910 + 13.2T \quad (120)$$

$$CO \Delta F = -26,080 - 20.9T \quad (121)$$

$$CO_2 \Delta F = -94,300 + 1.5T \quad (122)$$

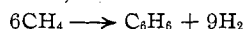
Recapitulation

For comparison the following equations are repeated.

COMPOUND	FREE ENERGY OF FORMATION (GAS)	
CH ₄	-20,000 + 26.2T	(10)
C ₂ H ₆	-29,000 + 53.3T	(44)
C ₃ H ₈	-76,100 + 206.6T	(35)
C ₂ H ₄	12,260 + 11.6T	(52)
C ₃ H ₆	54,400 - 10.8T	(59)
C ₄ H ₆	17,000 + 35.3T	(83)
C ₇ H ₈	6,860 + 59.2T	(94)
C ₁₀ H ₈	28,100 + 47.5T	(105)
C ₆ H ₁₂	-38,100 + 134T	(115)
C _n H _{2n+2} (paraffins)	-13,300 - 7850n + 2.2T + 25.55nT	(45)
C _n H _{2n} (olefins)	31,060 - 9400n - 39.5T + 25.55nT	(64)
C _n H _{2n} (naphthenes)	12,900 - 8500n - 19.3T + 25.55nT	(116)
C _n H _{2n-2} (acetylenes)	68,400 - 7000n - 61.9T + 25.55nT	(65)

The original equations for the individual hydrocarbons have been plotted in the figure. At any given temperature the tendency of a reaction is from a higher to a lower line in the figure. The close approach to straight lines justifies the use of the above linear equations. The line of zero free energy is marked "C + H₂," since it corresponds to the elements.

The ordinates have been reduced to free energy of formation per carbon atom. A comparison of free-energy equations of hydrocarbons on any other basis leads to erroneous conclusions. This is evident, since if it were proposed to make benzene from methane, for example, it would require six molecules of the latter,



The figure shows that for a substantial yield by this reaction a temperature of 850° C. must be exceeded. Moreover, because of the increase in volume the application of pressure would oppose rather than favor the reaction. Smith² concludes incorrectly (p. 803) that the tendency to form higher paraffin and aromatic hydrocarbons (at 300° C.) is greater than that to form lower paraffin hydrocarbons. Although benzene is theoretically capable of formation from water gas at moderate temperatures, the chance of its production in preference to that of the more stable hydrocarbons and alcohols is so small that with our present limited knowledge of catalysts, investigations with that aim are unpromising.

³⁹ L. and R., p. 485.

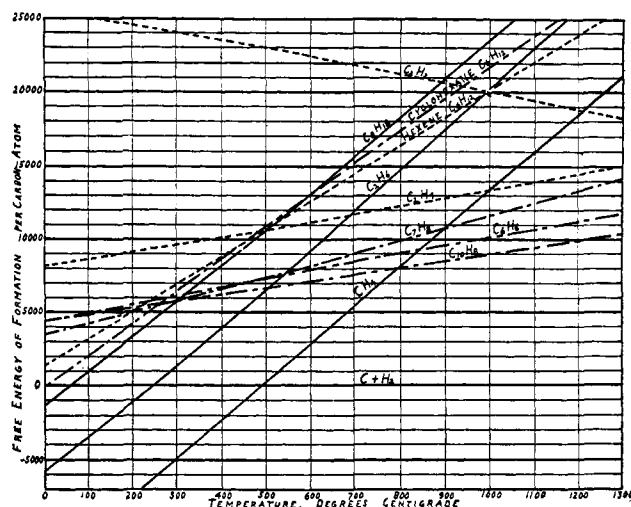
⁴⁰ L. and R., p. 576, as modified by Eastman and Evans, *J. Am. Chem. Soc.*, **46**, 902 (1924).

Discussion

The paraffin hydrocarbons—methane, ethane, octane—have nearly parallel lines. The aromatics—benzene, toluene, naphthalene—have lines which slope much less (the most aromatic with the least slope), indicating less decomposing effect of temperature. Ethylene has a line nearly parallel with those of the aromatics, but the higher olefins—for example, hexene—partake more of the nature of paraffins. Naphthenes, such as cyclohexane, are intermediate between paraffins and olefins. Acetylene is the only hydrocarbon whose stability is increased by temperature, but it never becomes stable with respect to its elements. Even at 5000° C., where it would be stable according to equation (59), this is not the case, because far below that temperature hydrogen is dissociated to atomic hydrogen, and the acetylene equilibrium would be $C_2H_2 \rightleftharpoons 2C + 2H$, which is displaced to the right by increasing temperatures.

Although for convenience the equations for the formation of gas (or vapor) will be used in all cases, this is not intended to imply that all cracking operations are in the vapor phase. The difference in result for liquid-phase reactions will be considered qualitatively in each case where applicable. For any individual case, calculations for liquids can be made readily from the vapor pressures, but no general equation can be set up.

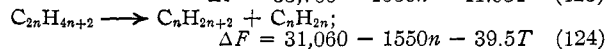
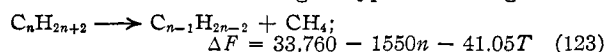
It is understood also that certain reactions which normally would be accompanied by a slight increase in free energy can be forced to proceed under pressure, if there is a decrease



in volume; but practical pressures will not usually overcome an unfavorable free-energy change of more than 5000 calories. Moreover, a reaction found thermodynamically impossible cannot be induced to proceed by means of a catalyst.

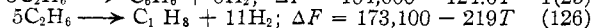
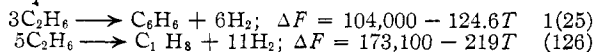
It will be observed that according to the above equations and the figure, only the paraffins and the higher olefins have any thermodynamic stability whatever, and above 260° C. methane is the only stable hydrocarbon. This seems inconsistent with the ordinary cracking reactions, in which large quantities of olefins and some aromatics are produced from paraffin hydrocarbons.

Let us assume the following as typical cracking reactions:

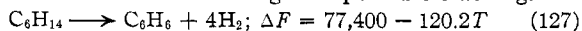


which become negative at cracking temperatures even in the case of the lowest members. Thermodynamics does not show which mechanism is preferred. Liquid-phase reactions

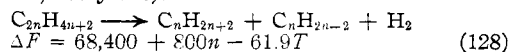
would be very slightly less favored, but could be calculated readily from (123) and (124) if the pressures employed and the vapor pressures of the reactants were known. The simultaneous production of coke and hydrogen is even more consistent with the equations. Similarly in the case of benzene and naphthalene from ethane,⁴¹ as shown also by the figure,



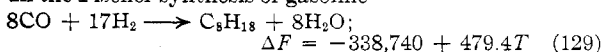
which are evidently possible at the temperatures employed (above 550° C.). Similar conclusions would apply to the production of aromatics in high-temperature cracking.



The explanation is, of course, that in all cracking operations true chemical equilibrium is never attained, but only a condition nearer to equilibrium—that is, lower free energy. It is significant that members of the acetylene series are not found in the products of cracking operations, since these would require a much higher temperature (above 850° C. in the most favorable case, acetylene).

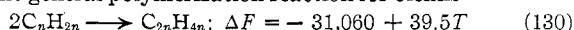


In the Fischer synthesis of gasoline

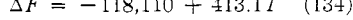
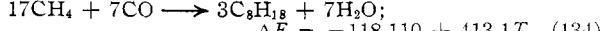
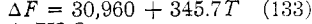
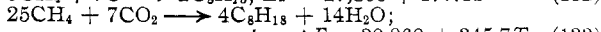
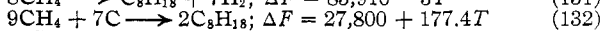
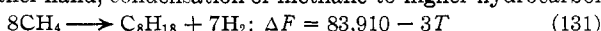


which is negative up to 700° K. or 427° C. His operating temperature for gasoline is 275–300° C. Higher temperatures give lower hydrocarbons, especially methane, as should be expected.

The general polymerization reaction for olefins



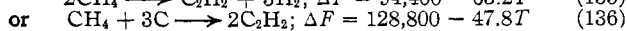
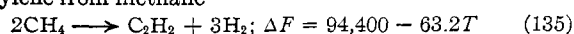
is possible up to about 500° C. It would be favored still more in the liquid phase, or with higher pressures. On the other hand, condensation of methane to higher hydrocarbons,



seems to be impossible (the last should proceed at extremely low temperatures, but methane is much too unreactive).

The actual polymerization of methane, ethane, etc., by means of alpha particles⁴² is not a contradiction to the above conclusion, since the energy is supplied by the alpha particles, which suffer a loss in kinetic energy and possibly in charge. The reaction is not really catalytic. It is significant that the gaseous products were all saturated while the liquids were unsaturated, in agreement with the consequence of the above equations that, for the lower members, the paraffins are more stable than the olefins with the same number of carbon atoms, while for the higher ones the olefins are more stable [cf. equation (138)].

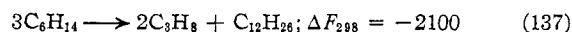
Similarly, as shown also by the figure, the formation of acetylene from methane



could take place only at very high temperatures, at which all but a trace of the acetylene would be decomposed.

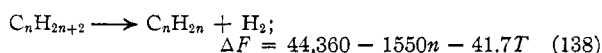
By analogy with (131) no paraffin hydrocarbon should be capable of direct condensation to a higher hydrocarbon; but if lower ones are formed simultaneously with higher ones, there is no change in free energy according to (45) for gaseous reactions. In the case of liquid hexane with aluminum chloride at room temperature,⁴³ the change in free

energy can be calculated from the vapor pressures of hexane and dodecane.



The reverse of this type of reaction is said to be accomplished in a recent patent,⁴⁴ which employs high pressures.

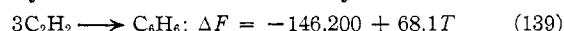
The conversion of a paraffin into an olefin of the same number of carbon atoms would be desirable in some cases.



In order to make ΔF negative, the temperature or the number of carbon atoms, or both, must be fairly high—conditions which favor the more profound disruption of the molecule.

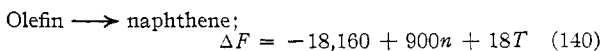
The partial removal of hydrogen by means of atmospheric or other form of oxygen with the purpose of obtaining olefins or higher paraffins is possible thermodynamically because of the high free energy of formation of steam; but actually the chance of success would be very small because the products would be much more reactive with the oxidizing agent than was the starting material.

The synthesis of benzene from acetylene



is possible except at extremely high temperatures, as shown also by the figure.

The isomerization of olefins to naphthenes in presence of aluminum chloride should take place up to about 430° C.



⁴⁴ McAfee, U. S. Patent 1,608,328 (1926).

European Cartels

Thirteen important international cartels enumerated below, most of them formed in the last two years by industrial interests chiefly in Europe, have been listed by the Department of Commerce, and half a dozen more are in process of formation.

These industrial combinations are only a few of those organized since the World War as a result of keener competition for world trade caused by the larger entry of the United States into the export markets. No complete list is available, since a great many of those established have never been acknowledged by the interests involved.

Europe had international cartels before the World War, but they were chiefly of an economic character, whereas the new ones are credited with having a distinctly political flavor which, some think, will lead eventually to closer political connection between the countries interested.

COMMODITY	COUNTRIES INVOLVED	ORGANIZED
Raw steel	France, Germany, Belgium, Czechoslovakia, Luxembourg, Austria, Hungary	September, 1926
Rails	Great Britain, France, Germany, Belgium, Luxembourg	June, 1926
Tubes	Germany, France, Belgium, Luxembourg, Great Britain, Austria, Czechoslovakia, Poland	June, 1926
Aluminum	France, Germany, Great Britain, Switzerland, Norway (in part), Austria (in part)	August, 1926
Enamelware	Germany, Poland, Czechoslovakia, Austria, Hungary	1926
Glue	Most European countries	July, 1926
Artificial silk	Great Britain, Germany, Italy (including a number of plants controlled by Great Britain and Germany in United States)	January, 1927
Copper	United States, Spain, Belgium, Yugoslavia, Great Britain	October, 1926
Electric bulbs	Germany, United States, Canada, Netherlands, France, Italy, Scandinavian countries, Great Britain, Austria, Hungary	1924
Plate glass	France, Belgium	1904
Glass bottles	Germany, France, Austria, the Scandinavian countries, Czechoslovakia, Hungary, Holland	1907
Borax	Great Britain, United States, Germany, France, Austria	1899 ^a
Wire	Germany, Belgium, Czechoslovakia, Netherlands	February, 1927

^a Not certain as to present existence.

⁴¹ Williams-Gardner, *Fuel Science Practice*, 4, 430 (1925).

⁴² Lind and Bardwell, *J. Am. Chem. Soc.*, 48, 2355 (1926).

⁴³ Schneider and Norris, paper read before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.