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HEATS AND FREE ENERGIES OF FORMATION OF THE PARAFFIN HYDROCARBONS, IN THE GASEOUS STATE, TO 1,500° K[1]

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ABSTRACT

Values are presented for the heats of formation and the free energies of formation, from solid carbon (graphite) and gaseous hydrogen, of all the normal paraffin hydrocarbons and of the isomeric paraffins from the butanes through the octanes, in the gaseous state, to 1,500° K.

CONTENTS

I. INTRODUCTION

This paper presents new values for the heats and free energies of formation, from solid carbon (graphite) and gaseous hydrogen, of each of the 40 paraffin hydrocarbons from methane through the octanes, and of the higher normal paraffins, in the gaseous state, to 1,500° K.

II. UNIT OF ENERGY AND MOLECULAR WEIGHTS

The unit of energy used in this paper is the conventional thermochemical calorie defined as follows [1].[3]

1 calorie=4.1833 international (NBS) joules.

The molecular weights were calculated from the values given in the 1941 table of International Atomic Weights [2].

[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbons."

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[3] Figures in brackets indicate the literature references at the end of this paper.

III. METHOD OF CALCULATION

Values of $\Delta Hf°_0$, the increment in heat content for the reaction of forming the given hydrocarbon in the gaseous state, from the elements carbon (solid, graphite) and hydrogen (gas), with the reactants and the product in their appropriate thermodynamic standard states, at 0° K, were calculated by combining values of $\Delta Hf°_{298.16}$ with values of $H°_{298.16}-H°_0$ for the appropriate compounds, by means of the relation [4]

$$\Delta Hf°_0=\Delta Hf°_{298.16}-\Delta(H°_{298.16}-H°_0), \tag{1}$$

where the last term on the right is the value of $H°_{298.16}-H°_0$ (the heat content at 25° C less that at 0° K) for 1 mole of the gaseous hydrocarbon less that of n moles of solid carbon (graphite) and $(n+1)$ moles of gaseous hydrogen (the molecular formula of the hydrocarbon being C_nH_{2n+2}).

Values of $\Delta Hf°$ for the other temperatures were then systematically calculated by means of the relation

$$\Delta Hf°=\Delta Hf°_0+\Delta(H°-H°_0). \tag{2}$$

Values of $\Delta Ff°$, the increment in free energy for the reaction of forming the given hydrocarbon in the gaseous state, from the elements carbon (solid, graphite) and hydrogen (gas), with the reactants and the product in their appropriate thermodynamic standard states at the given temperature, were calculated by combining values of $\Delta Hf°_0$ with appropriate values of $(F°-H°_0)/T$, the free-energy function, by means of the relation

$$\Delta Ff°=\Delta Hf°_0+T\Delta(F°-H°_0)/T, \tag{3}$$

where the last term on the right is the value of the product of the absolute temperature and $\Delta(F°-H°_0)/T$, the free energy at the given temperature less the heat content at 0° K, divided by the absolute temperature, for 1 mole of the gaseous hydrocarbon less that of n moles of solid carbon (graphite) and $(n+1)$ moles of gaseous hydrogen (the molecular formula of the hydrocarbon being C_nH_{2n+2}).

IV. DATA USED IN THE CALCULATIONS

The data used in the calculations include the following:

Values of the heat of formation, $\Delta Hf°$, for the gaseous hydrocarbons at 25° C are taken from reference [4].

Values of the heat content at a given temperature less that at 0° K, $H°-H°_0$, and of the free-energy function, $(F°-H°_0)/T$, for the gaseous hydrocarbons, are taken from the following sources: For methane, from reference [5]; for ethane, propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane, and the higher normal paraffins, from refer-

[4] The usual convention is followed of letting the subscript denote the absolute temperature. The superscript denotes the thermodynamic standard state. See reference [3].

ence [6]; for isobutane, isopentane, and neopentane, from reference [7]; for the difference between *n*-hexane and its isomers and between *n*-heptane and its isomers, from reference [8]; for the isomeric octanes, from references [7] and [9]. Values of the foregoing properties for several of the intermediate temperatures were calculated by W. J. Taylor of this Bureau in connection with the work of the American Petroleum Institute Research Project 44.

V. RESULTS OF THE CALCULATIONS

The resulting values [5] of the heat of formation, $\Delta Hf°$, are given in table 1. The resulting values [5] of the free energy of formation, $\Delta Ff°$, are given in table 2.

[5] The uncertainty in the values for 2,3-dimethylhexane may be several times that for the other isomeric octanes [4].

TABLE 1.—*Values of the heats of formation of the paraffin hydrocarbons in the gaseous state to 1,500° K*

Compound (gas)	Temperature in °K														
	0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	$\Delta Hf°$ in kcal/mole														
Methane	−15.987	−17.889	−17.903	−18.629	−19.302	−19.893	−20.401	−20.823	−21.166	−21.43	−21.65	−21.79	−21.92	−22.00	−22.06
Ethane	−16.517	−20.236	−20.258	−21.419	−22.437	−23.28	−23.98	−24.53	−24.97	−25.28	−25.50	−25.64	−25.72	−25.75	−25.73
Propane	−19.482	−24.820	−24.848	−26.358	−27.622	−28.66	−29.49	−30.12	−30.58	−30.90	−31.09	−31.16	−31.19	−31.14	−31.06
n-Butane	−23.332	−29.812	−29.847	−31.629	−33.128	−34.33	−35.28	−36.00	−36.54	−36.88	−37.06	−37.11	−37.05	−36.95	−36.79
2-Methylpropane	−24.602	−31.452	−31.489	−33.303	−34.783	−35.97	−36.91	−37.61	−38.10	−38.42	−38.57	−38.58	−38.54	−38.43	−38.28
n-Pentane	−27.27	−35.00	−35.04	−37.12	−38.86	−40.25	−41.34	−42.16	−42.75	−43.10	−43.26	−43.27	−43.18	−42.99	−42.74
2-Methylbutane	−28.66	−36.92	−36.96	−39.07	−40.78	−42.12	−43.17	−43.94	−44.47	−44.80	−44.92	−44.88	−44.78	−44.58	−44.36
2, 2-Dimethylpropane	−31.30	−39.67	−39.71	−41.77	−43.42	−44.67	−45.63	−46.29	−46.73	−46.96	−47.01	−46.90	−46.70	−46.42	−46.12
n-Hexane	−30.98	−39.96	−40.01	−42.38	−44.36	−45.93	−47.15	−48.06	−48.71	−49.07	−49.23	−49.19	−49.04	−48.78	−48.47
2-Methylpentane	−32.03	−41.66	−41.71	−44.04	−45.92	−47.35	−48.43	−49.23	−49.84	−50.27					
3-Methylpentane	−31.36	−41.02	−41.07	−43.40	−45.27	−46.68	−47.73	−48.49	−49.05	−49.40					
2,2-Dimethylbutane	−34.52	−44.35	−44.40	−46.76	−48.64	−50.03	−51.05	−51.75	−52.22	−52.46					
2,3-Dimethylbutane	−32.82	−42.49	−42.54	−44.81	−46.59	−47.93	−48.92	−49.65	−50.23	−50.65					
n-Heptane	−34.65	−44.89	−44.94	−47.60	−49.83	−51.58	−52.93	−53.94	−54.63	−55.01	−55.15	−55.08	−54.88	−54.55	−54.16
2-Methylhexane	−35.77	−46.60	−46.66	−49.30	−51.45	−53.09	−54.33	−55.25	−55.91	−56.33					
3-Methylhexane	−34.96	−45.96	−46.02	−48.71	−50.90	−52.58	−53.84	−54.77	−55.42	−55.82					
3-Ethylpentane	−34.10	−45.34	−45.40	−48.15	−50.40	−52.12	−53.43	−54.41	−55.11	−55.56					
2,2-Dimethylpentane	−38.00	−49.29	−49.35	−52.02	−54.14	−55.72	−56.87	−57.69	−58.25	−58.56					
2,3-Dimethylpentane	−36.29	−47.62	−47.68	−50.39	−52.56	−54.21	−55.43	−56.35	−57.01	−57.45					
2,4-Dimethylpentane	−36.98	−48.30	−48.36	−51.02	−53.13	−54.70	−55.85	−56.69	−57.27	−57.64					
3,3-Dimethylpentane	−36.92	−48.17	−48.23	−50.88	−52.98	−54.54	−55.67	−56.46	−56.98	−57.28					
2,2,3-Trimethylbutane	−37.57	−48.96	−49.02	−51.64	−53.69	−55.19	−56.25	−57.01	−57.52	−57.83					
n-Octane	−38.33	−49.82	−49.88	−52.83	−55.30	−57.23	−58.71	−59.81	−60.57	−60.96	−61.08	−60.97	−60.71	−60.31	−59.86
2-Methylheptane	−39.42	−51.50	−51.56	−54.49	−56.87	−58.67	−60.04	−61.13	−61.91	−62.19					
3-Methylheptane	−38.64	−50.82	−50.88	−53.84	−56.23	−58.03	−59.40	−60.49	−61.27	−61.57					
4-Methylheptane	−38.43	−50.69	−50.75	−53.73	−56.13	−57.97	−59.39	−60.47	−61.23	−61.55					
3-Ethylhexane	−37.71	−50.40	−50.46	−53.59	−56.10	−58.04	−59.53	−60.64	−61.42	−61.81					
2,2-Dimethylhexane	−41.23	−53.71	−53.77	−56.72	−59.06	−60.85	−62.16	−63.02	−63.66	−63.96					
2,3-Dimethylhexane	−38.76	−51.13	−51.19	−54.08	−56.26	−57.88	−59.11	−60.10	−60.83	−61.16					
2,4-Dimethylhexane	−39.74	−52.44	−52.51	−55.50	−57.92	−59.72	−61.06	−62.10	−62.86	−63.23					
2,5-Dimethylhexane	−40.61	−53.21	−53.27	−56.24	−58.58	−60.33	−61.66	−62.70	−63.45	−63.77					
3,3-Dimethylhexane	−39.90	−52.61	−52.68	−55.65	−58.03	−59.78	−61.04	−61.93	−62.54	−62.84					

3,4-Dimethylhexane	−38.52	−50.91	−50.97	−53.81	−56.05	−57.71	−58.98	−60.05	−60.82	−61.01					
2-Methyl-3-ethylpentane	−37.96	−50.48	−50.54	−53.46	−55.77	−57.52	−58.87	−59.95	−60.70	−60.93					
3-Methyl-3-ethylpentane	−38.68	−51.38	−51.45	−54.32	−56.65	−58.42	−59.74	−60.65	−61.18	−61.29					
2,2,3-Trimethylpentane	−39.77	−52.61	−52.68	−55.62	−57.92	−59.63	−60.89	−61.82	−62.43	−62.63					
2,2,4-Trimethylpentane	−40.73	−53.57	−53.64	−56.58	−58.88	−60.59	−61.85	−62.78	−63.39	−63.59					
2,3,3-Trimethylpentane	−39.01	−51.73	−51.80	−54.72	−56.98	−58.66	−59.93	−60.92	−61.56	−61.62					
2,3,4-Trimethylpentane	−39.12	−51.97	−52.04	−54.97	−57.18	−58.83	−60.11	−61.17	−61.91	−62.03					
2,2,3,3-Tetramethylbutane	−41.09	−53.99	−54.06	−56.96	−59.14	−60.65	−61.70	−62.51	−63.02	−63.03					
n-Nonane	−42.00	−54.74	−54.81	−58.05	−60.76	−62.88	−64.49	−65.68	−66.50	−66.90	−67.01	−66.85	−66.54	−66.07	−65.55
n-Decane	−45.67	−59.67	−59.74	−63.28	−66.23	−68.53	−70.27	−71.55	−72.42	−72.84	−72.94	−72.74	−72.37	−71.82	−71.24
n-Undecane	−49.34	−65.60	−64.67	−68.50	−71.69	−74.17	−76.04	−77.42	−78.35	−78.78	−78.87	−78.63	−78.20	−77.58	−76.93
n-Dodecane	−53.02	−69.52	−69.60	−73.72	−77.16	−79.82	−81.82	−83.29	−84.28	−84.72	−84.79	−84.51	−84.03	−83.34	−82.63
n-Tridecane	−56.69	−74.45	−74.53	−78.94	−82.62	−85.47	−87.60	−89.17	−90.20	−90.66	−90.72	−90.40	−89.86	−89.10	−88.32
n-Tetradecane	−60.36	−79.38	−79.46	−84.17	−88.09	−91.12	−93.38	−95.04	−96.13	−96.60	−96.65	−96.28	−95.69	−94.86	−94.01
n-Pentadecane	−64.04	−84.31	−84.39	−89.39	−93.55	−96.77	−99.16	−100.91	−102.06	−102.54	−102.57	−102.17	−101.52	−100.61	−99.70
n-Hexadecane	−67.71	−89.23	−89.33	−94.61	−99.02	−102.41	−104.93	−106.78	−107.99	−108.48	−108.50	−108.06	−107.35	−106.37	−105.39
n-Heptadecane	−71.38	−94.15	−94.26	−99.84	−104.48	−108.06	−110.71	−112.65	−113.91	−114.42	−114.43	−113.94	−113.19	−112.13	−111.08
n-Octadecane	−75.06	−99.08	−99.19	−105.06	−109.95	−113.71	−116.49	−118.52	−119.84	−120.37	−120.35	−119.83	−119.02	−117.89	−116.78
n-Nonadecane	−78.73	−104.00	−104.12	−110.28	−115.41	−119.36	−122.27	−124.39	−125.77	−126.31	−126.28	−125.71	−124.85	−123.64	−122.47
n-Eicosane	−82.40	−108.93	−109.05	−115.50	−120.88	−125.01	−128.04	−130.26	−131.69	−132.25	−132.21	−131.60	−130.68	−129.40	−128.16
Δ per CH_2	−3.673	−4.926	−4.931	−5.223	−5.465	−5.648	−5.778	−5.871	−5.927	−5.941	−5.927	−5.886	−5.830	−5.758	−5.692

TABLE 2.—*Values of the free energies of formation of the paraffin hydrocarbons in the gaseous state to 1,500 °K*

Compound (gas)	Temperature in °K														
	0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	$\Delta Ff°$ in kcal/mole														
Methane	−15.987	−12.140	−12.105	−10.048	−7.841	−5.49	−3.05	−0.55	2.01	4.61	7.22	9.85	12.50	15.14	17.79
Ethane	−16.517	−7.860	−7.785	−3.447	1.168	5.97	10.90	15.92	21.00	26.13	31.28	36.45	41.62	46.79	51.99
Propane	−19.482	−5.614	−5.541	1.191	8.230	15.50	22.93	30.45	38.05	45.68	53.34	61.01	68.68	76.35	84.08
n-Butane	−23.332	−3.754	−3.595	5.435	14.868	24.59	34.50	44.50	54.59	64.71	74.87	85.05	95.25	105.42	115.61
2-Methylpropane	−24.602	−4.296	−4.127	5.273	15.088	25.18	35.44	45.82	56.29	66.79	77.32	87.86	98.39	108.90	119.44
n-Pentane	−27.27	−1.96	−1.76	9.66	21.57	33.79	46.22	58.77	71.41	84.10	96.81	109.55	122.30	135.01	147.75
2-Methylbutane	−28.66	−3.50	−3.38	8.26	20.29	32.66	45.19	57.84	70.62	83.41	96.23	109.07	121.89	134.68	147.53
2,2-Dimethylpropane	−31.30	−3.64	−3.42	8.99	21.89	35.08	48.46	61.93	75.49	89.08	102.68	116.27	129.88	143.44	157.00
n-Hexane	−30.98	0.05	0.30	14.11	28.46	43.18	58.13	73.21	88.40	103.64	118.90	134.19	149.48	164.75	180.04
2-Methylpentane	−32.03	−0.96	−0.71	13.25	27.79	42.72	57.88	73.15	88.51	103.86	------	------	------	------	------
3-Methylpentane	−31.36	−0.29	−0.04	13.94	28.50	43.45	58.62	73.89	89.23	104.53	------	------	------	------	------
2,2-Dimethylbutane	−34.52	−2.35	−2.09	12.30	27.30	42.69	58.29	73.97	89.71	105.37	------	------	------	------	------
2,3-Dimethylbutane	−32.82	−0.73	−0.47	13.81	28.67	43.92	59.38	74.94	90.57	106.18	------	------	------	------	------
n-Heptane	−34.65	2.09	2.38	18.58	35.39	52.60	70.08	87.70	105.43	123.22	141.02	158.85	176.69	194.50	212.38
2-Methylhexane	−35.77	0.98	1.27	17.61	34.60	52.01	69.67	87.47	105.33	123.18	------	------	------	------	------
3-Methylhexane	−34.96	1.10	1.39	17.57	34.40	51.68	69.21	86.87	104.59	122.29	------	------	------	------	------
3-Ethylpentane	−34.10	2.59	2.88	19.36	36.52	54.15	72.06	90.09	108.19	126.25	------	------	------	------	------
2,2-Dimethylpentane	−38.00	0.09	0.39	17.33	34.95	53.01	71.33	89.73	108.18	126.55	------	------	------	------	------
2,3-Dimethylpentane	−36.29	0.16	0.45	16.83	33.90	51.43	69.24	87.17	105.18	123.16	------	------	------	------	------
2,4-Dimethylpentane	−36.98	0.72	1.02	17.81	35.28	53.19	71.37	89.66	107.99	126.27	------	------	------	------	------
3,3-Dimethylpentane	−36.92	0.63	0.93	17.64	35.02	52.84	70.92	89.10	107.34	125.53	------	------	------	------	------
2,2,3-Trimethylbutane	−37.57	0.76	1.06	18.06	35.75	53.87	72.24	90.72	109.23	127.68	------	------	------	------	------
n-Octane	−38.33	4.14	4.47	23.06	42.32	62.03	82.03	102.17	122.45	142.79	163.14	183.51	203.90	224.26	244.71
2-Methylheptane	−39.42	3.06	3.39	22.14	41.58	61.47	81.63	101.88	122.27	142.83	------	------	------	------	------
3-Methylheptane	−38.64	3.29	3.62	22.21	41.50	61.27	81.31	101.44	121.68	142.07	------	------	------	------	------
4-Methylheptane	−38.43	4.00	4.34	23.12	42.62	62.61	82.88	103.23	123.68	144.26	------	------	------	------	------
3-Ethylhexane	−37.71	3.95	4.28	22.94	42.39	62.37	82.64	102.98	123.42	143.98	------	------	------	------	------
2,2-Dimethylhexane	−41.23	2.56	2.91	22.18	42.20	62.71	83.48	104.30	125.21	146.27	------	------	------	------	------

2,3-Dimethylhexane	−38.76	4.23	4.57	23.51	43.16	63.27	83.64	104.09	124.63	145.30					
2,4-Dimethylhexane	−39.74	2.80	3.14	22.05	41.72	61.89	82.32	102.84	123.43	144.07					
2,5-Dimethylhexane	−40.61	2.50	2.84	21.92	41.75	62.08	82.69	103.41	124.20	144.99					
3,3-Dimethylhexane	−39.90	3.17	3.51	22.63	42.50	62.85	83.47	104.16	124.93	145.76					
3,4-Dimethylhexane	−38.52	4.97	5.31	24.42	44.27	64.57	85.12	105.75	126.49	147.35					
2-Methyl-3-ethylpentane	−37.96	5.08	5.43	24.47	44.24	64.47	84.96	105.52	126.21	147.09					
3-Methyl-3-ethylpentane	−38.68	4.76	5.11	24.32	44.30	64.77	85.48	106.22	127.05	148.01					
2,2,3-Trimethylpentane	−39.77	4.09	4.44	23.82	43.98	64.63	85.54	106.52	127.57	148.68					
2,2,4-Trimethylpentane	−40.73	3.13	3.48	22.86	43.02	63.67	84.58	105.56	126.61	147.72					
2,3,3-Trimethylpentane	−39.01	4.52	4.86	24.09	44.08	64.55	85.30	106.10	126.98	147.90					
2,3,4-Trimethylpentane	−39.12	4.32	4.67	23.89	43.89	64.37	85.11	105.94	126.84	147.80					
2,2,3,3-Tetramethylbutane	−41.09	4.88	5.24	25.34	46.19	67.47	88.97	110.52	132.19	154.05					
n-Nonane	−42.00	6.18	6.56	27.54	49.25	71.46	93.98	116.66	139.48	162.37	184.20	208.18	231.12	254.03	277.04
n-Decane	−45.67	8.23	8.65	32.01	56.18	80.89	105.93	131.14	156.51	181.95	205.26	232.85	258.33	283.79	309.37
n-Undecane	−49.34	10.28	10.74	36.49	63.11	90.31	117.88	145.63	173.54	201.53	226.32	257.52	285.54	313.55	341.70
n-Dodecane	−53.02	12.33	12.83	40.97	70.04	99.74	129.83	160.11	190.57	221.11	247.38	282.19	312.76	343.32	374.03
n-Tridecane	−56.69	14.37	14.92	45.45	76.97	109.17	141.78	174.59	207.60	240.69	268.45	306.86	339.97	373.08	406.36
n-Tetradecane	−60.36	16.42	17.01	49.93	83.90	118.60	153.73	189.08	224.63	260.26	289.51	331.52	367.19	402.85	438.69
n-Pentadecane	−64.04	18.47	19.10	54.41	90.83	128.03	165.68	203.56	241.66	279.84	310.57	356.19	394.40	432.61	471.02
n-Hexadecane	−67.71	20.52	21.19	58.89	97.76	137.46	177.63	218.04	258.69	299.42	331.63	380.86	421.62	462.38	503.36
n-Heptadecane	−71.38	22.56	23.27	63.36	104.69	146.88	189.58	232.53	275.72	319.00	352.69	405.53	448.83	492.14	535.69
n-Octadecane	−75.06	24.61	25.36	67.84	111.62	156.31	201.53	247.01	292.75	338.58	373.75	430.20	476.05	521.90	568.02
n-Nonadecane	−78.73	26.66	27.45	72.32	118.55	165.74	213.48	261.49	309.78	358.16	394.81	454.86	503.26	551.67	600.35
n-Eicosane	−82.40	28.71	29.54	76.80	125.48	175.17	225.43	275.98	326.81	377.74	415.87	479.53	530.48	581.43	632.68
Δ per CH_2	−3.673	2.048	2.090	4.479	6.931	9.428	11.951	14.484	17.029	19.579	21.061	24.668	27.215	29.764	32.331

Figure 1 is a plot that shows the thermodynamic stability, per carbon atom and with respect to the elements solid carbon (graphite) and gaseous hydrogen, of the normal paraffin hydrocarbons in the gaseous state as a function of the temperature. This plot shows the thermodynamic stability, per carbon atom, with respect to the ele-

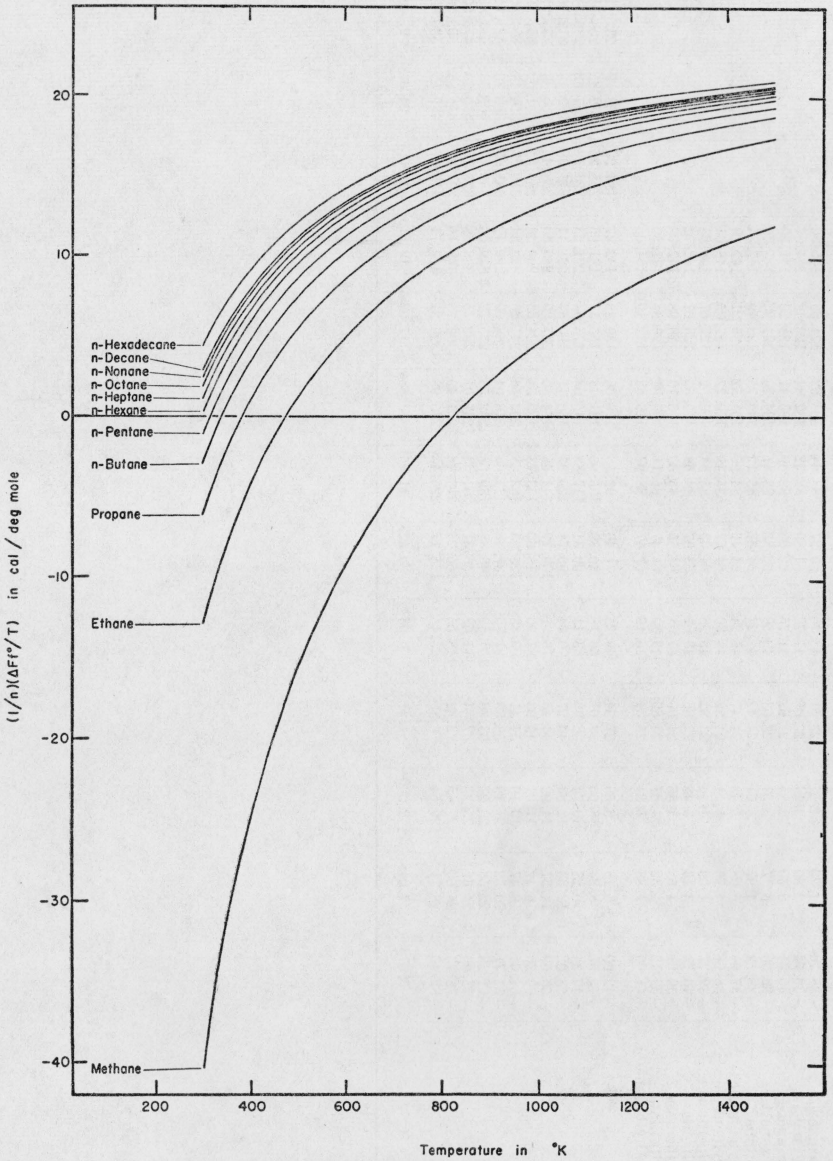

FIGURE 1.—*Thermodynamic stability of the normal paraffin hydrocarbons in the gaseous state as a function of temperature.*

The scale of ordinates gives the value of $(1/n)$ $(\Delta Ff°/T)$ in calories per degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in degrees Kelvin, and $\Delta Ff°$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen, as given in table 2. The scale of abscissas gives the temperature in degrees Kelvin.

ments, of the normal paraffin hydrocarbons in the gaseous state. Points below the zero line indicate that the gaseous hydrocarbon in its standard state has a thermodynamic tendency to be formed from solid carbon (graphite) and gaseous hydrogen in their respective standard states.

Plots showing the relative stability of *n*-butane and isobutane, the 3 pentanes, the 5 hexanes, the 9 heptanes, and the 18 octanes, are given in references [9 and 10].

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