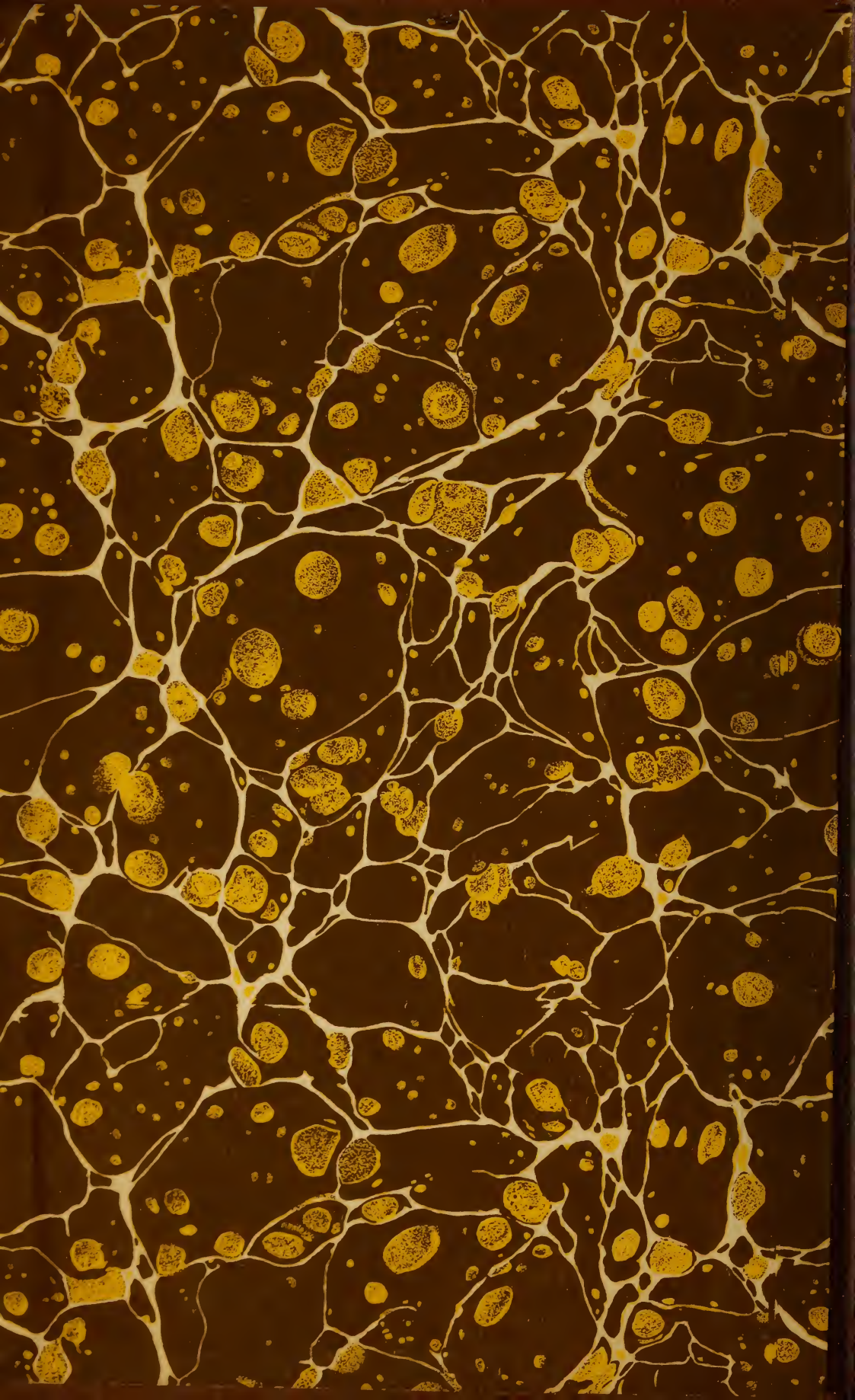
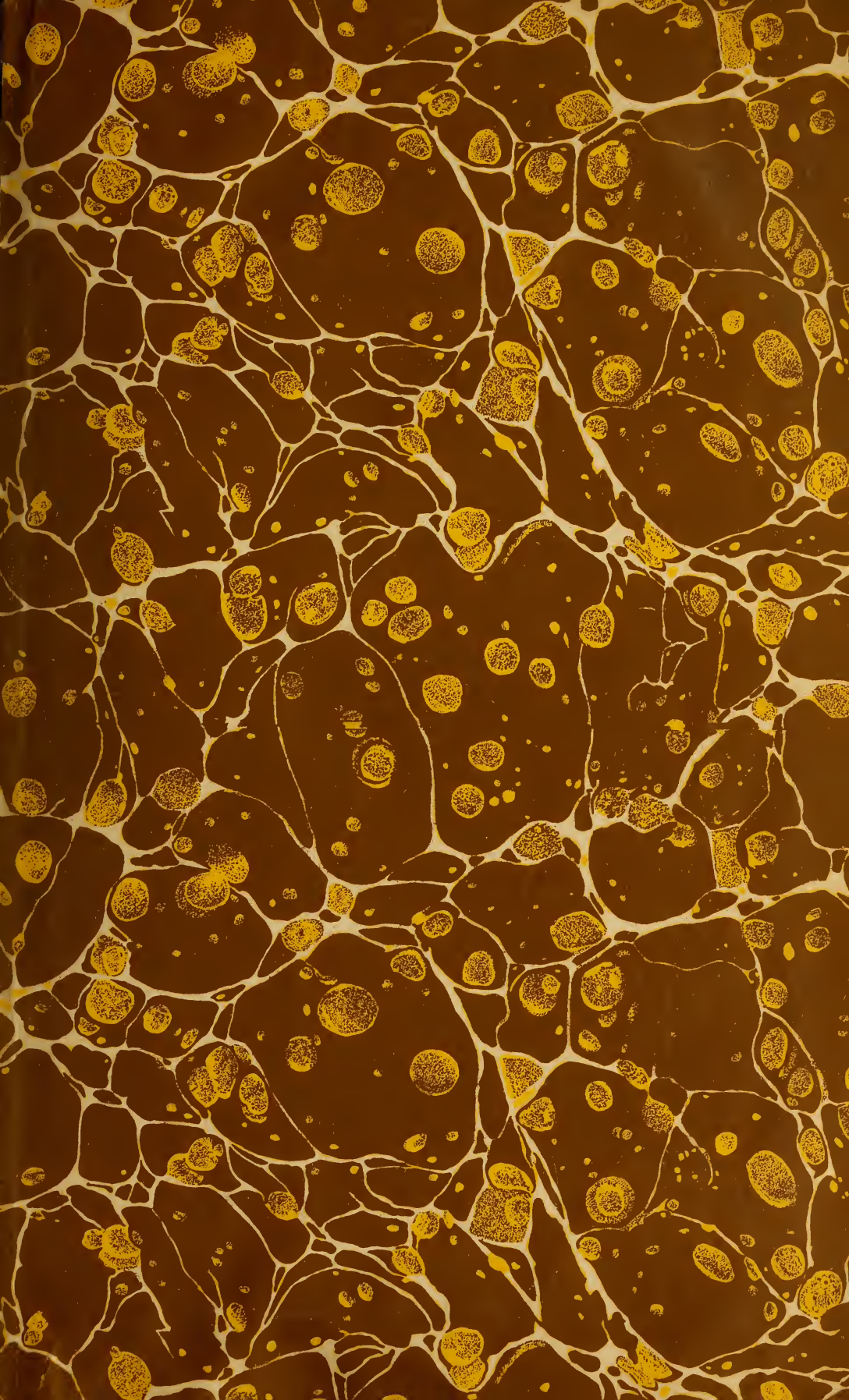


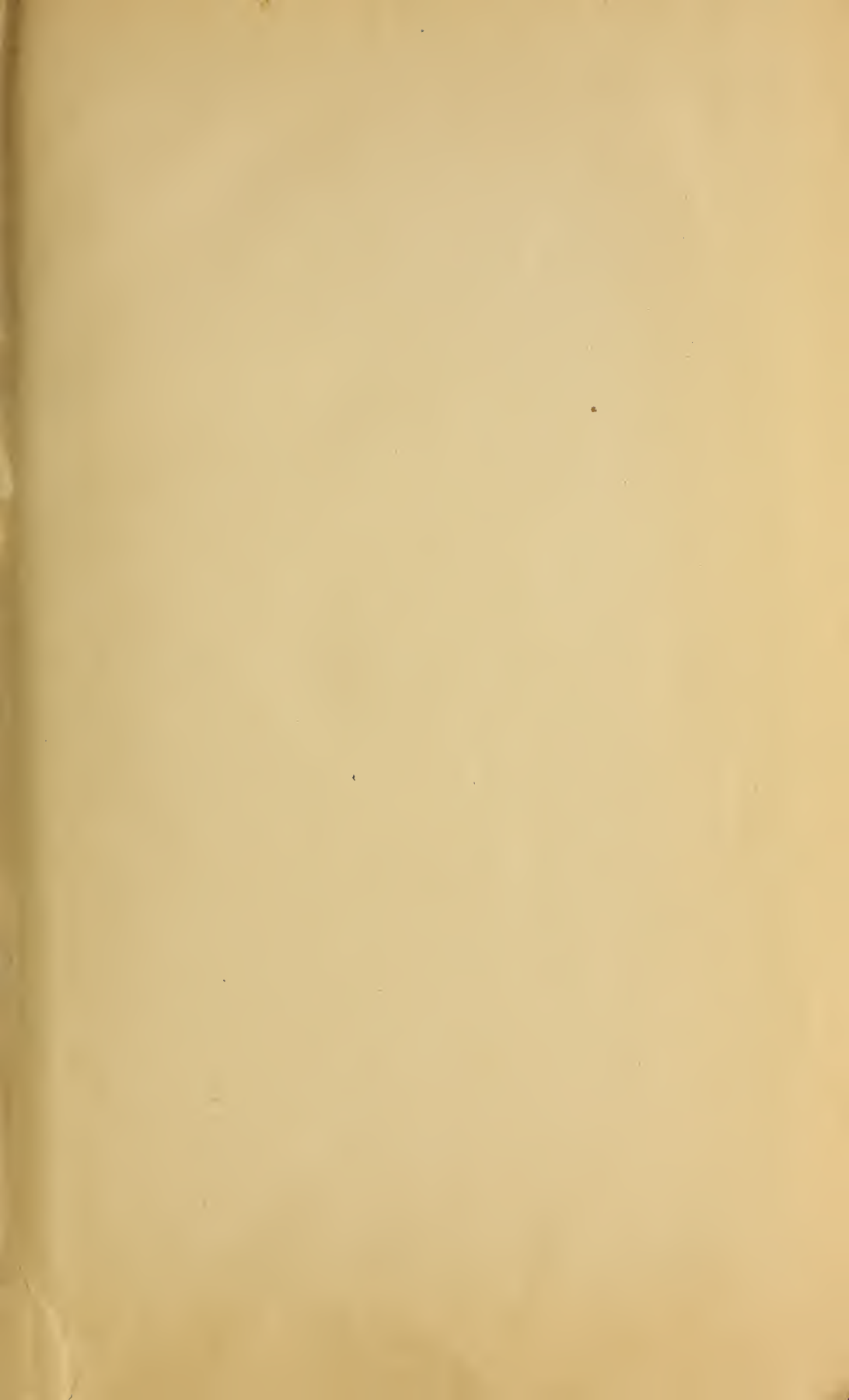
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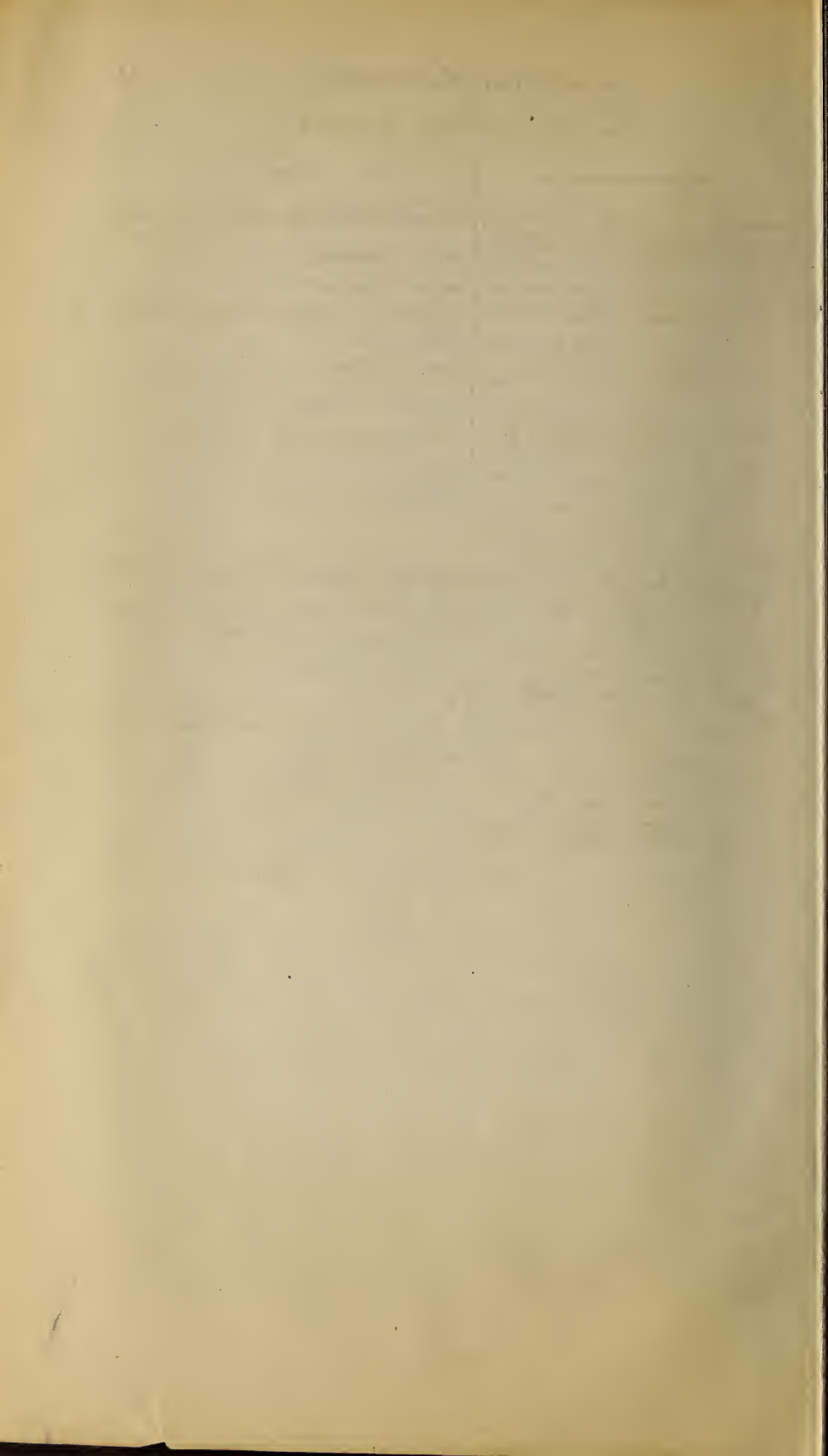
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UNITED STATES DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS

**THERMAL PROPERTIES OF
PETROLEUM PRODUCTS**

MISCELLANEOUS PUBLICATION OF THE BUREAU OF STANDARDS, No. 97



UNITED STATES DEPARTMENT OF COMMERCE

R. P. LAMONT, Secretary

BUREAU OF STANDARDS

GEORGE K. BURGESS, Director

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THERMAL PROPERTIES OF PETROLEUM PRODUCTS

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THERMAL PROPERTIES OF PETROLEUM PRODUCTS

By C. S. Cragoe

ABSTRACT

Various thermal properties of petroleum products are given in numerous tables which embody the results of a critical study of the data in the literature, together with unpublished data obtained at the Bureau of Standards. The tables contain what appear to be the most reliable values at present available. The experimental basis for each table, and the agreement of the tabulated values with experimental results, are given. Accompanying each table is a statement regarding the estimated accuracy of the data and a practical example of the use of the data. The tables have been prepared in forms convenient for use in engineering.

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I. INTRODUCTION

The Bureau of Standards receives many requests for information on the thermal properties of petroleum products from other departments of the Government, from the petroleum industry, and from users of these products which have found so wide a variety of applications. Information of this sort is rarely to be found in systematic form such that appropriate values for a desired property may readily be assigned to the particular product in question. Engineering handbooks and physical and chemical tables, the more accessible sources of such information, are surprisingly

deficient in this respect and the values given in these publications differ widely in many instances.

The Bureau of Standards has made no extensive experimental study of the subject as a whole, but has had occasion during the past few years to make numerous determinations of some of the thermal properties of petroleum products in combination with other investigations carried out in the laboratories of the Government. In 1927 an investigation was undertaken on the thermodynamic properties of petroleum hydrocarbons, listed as project No. 38 of American Petroleum Institute Research. In order to lay out an experimental program intelligently, it was necessary to make a critical study of the data available on the subject in the literature. The results obtained from this critical study when combined with unpublished results obtained at the bureau, including some preliminary results obtained under project No. 38, appeared of sufficient technical importance to warrant the preparation of preliminary tables covering several of the properties which have been investigated experimentally. Because of the lack of published information in a form readily usable by the industry, tables have been prepared in engineering units.

Most petroleum products consist essentially of a large number of different hydrocarbons which are so nearly alike physically that a mixture of them exhibits a thermodynamic behavior somewhat analogous to that shown by a mixture of isotopes. Experimental evidence indicates that many of the thermodynamic properties of mixtures of hydrocarbons are not seriously affected by considerable changes in composition. In fact, it has been found that many of these properties are very closely related to the density of the liquid which is usually known or can be readily determined with a hydrometer. This relationship afforded a very useful means of correlating existing data on commercial products. By the same means a valuable check was obtained from data on pure hydrocarbons known to exist as constituent parts of these products. Although some consistent differences were found between data on paraffin and naphthene base products of the same density, these differences were small and, consequently, of little significance in practical applications of the data. It must be realized, however, that values for the properties of petroleum products, which are subject to considerable variation in composition, can not be assigned with the same degree of accuracy as can be done in the case of materials which have a definite composition.

II. FUNDAMENTAL UNITS AND CONSTANTS

Temperature scale.—The Fahrenheit scale as used in this paper is derived from the International centigrade scale by means of the relation

$$\text{Fahrenheit temperature} = (1.8 \times \text{centigrade temperature}) + 32$$

The International centigrade scale adopted by the International Conference of Weights and Measures at Paris in 1927 is realized in the temperature interval 0° to 660° C., by means of the resistance thermometer of pure platinum, standardized at the temperatures of melting ice (0° C.), condensing steam (100° C.), and condensing sulphur vapor (444.6° C.), all at standard atmospheric pressure.

In accordance with common practice in the United States, 60° F. is used here as the reference temperature for specifying the density and volume of petroleum products.

Mass.—The fundamental unit of mass, the kilogram, is used indirectly here. All units of weight used in this paper are weights in vacuo (mass) and not apparent weights in air. The difference is small in all cases involved here, amounting to 0.1 or 0.2 per cent. Since most of the experimental data considered were given in terms of unit mass, these units were retained and used consistently throughout. The units used are related as follows:

$$1 \text{ pound} = 0.453592 \text{ kilograms}$$

Volume.—The fundamental unit of liquid volume, the liter, is defined as the volume occupied by 1 kilogram of pure water at its maximum density (4° C.). The unit of liquid volume actually used throughout this circular, however, is the gallon (231 cubic inches) because of the general use of this unit in engineering and industrial practice in the United States. This unit is defined in terms of the fundamental unit by the relation

$$1 \text{ gallon} = 3.78533 \text{ liters}$$

It is often convenient to determine the volume of liquid containers by weighing them both empty and filled with water. Since the mass of a gallon of pure water at 60° F. is known, the unit of liquid volume used here may be realized directly from the fundamental unit of mass, by the relation.

$$1 \text{ gallon} = 3.78170 \text{ kilograms or } 8.33722 \text{ pounds of water at } 60^\circ \text{ F.}$$

Density.—Mass per unit volume is the universal definition of density. In this circular, densities are expressed in pounds per gallon which are related to the fundamental units by

$$1 \text{ pound per gallon} = 0.119829 \text{ kilograms per liter}$$

Densities are also expressed in terms of specific gravity, defined by

$$\text{Specific gravity at } 60^\circ \text{ F.} = \frac{\text{density of oil at } 60^\circ \text{ F.}}{\text{density of water at } 60^\circ \text{ F.}}$$

which is equivalent to the following numerical relation

$$\text{Density of oil at } 60^\circ \text{ F. in lbs. per gal.} = 8.33722 \times \text{specific gravity of oil at } 60^\circ/60^\circ \text{ F.}$$

Densities are commonly determined by means of a hydrometer, an instrument familiar to large numbers of persons who take an interest in their storage batteries. Some hydrometers are graduated to indicate density or specific gravity directly, although there are almost an infinite variety of arbitrary hydrometer scales in existence. Each industry in which hydrometers are used appears to have its own selection of arbitrary scales. The petroleum industry has had, in the past, two such arbitrary scales, both of which were known as Baumé scales for liquids lighter than water. In order to avoid confusion, the American Petroleum Institute, the Bureau of Mines, and the Bureau of Standards agreed, in 1921, to recommend that in the future only one arbitrary scale be used in the petroleum industry, and that it be known as the A. P. I. scale. This scale is defined by the relation

$$\text{Degrees A. P. I.} = \frac{141.5}{\text{Sp. gr. at } 60^\circ/60^\circ \text{ F.}} - 131.5$$

The A. P. I. scale is used extensively in the classification and description of petroleum products. In order to make the data contained in this circular of convenience to those unfamiliar with this scale, it appeared desirable to use both, degrees A. P. I.

and its equivalent, specific gravity at 60°/60° F. Degrees A. P. I. are used as one of the independent variables in the tabulation of the data partly because they are equivalent to a uniform scale of specific volume.

Heat unit.—The fundamental heat unit used here is the international joule, or watt second, since electric heating was employed in most of the calorimetric measurements considered. The relation between this unit and the corresponding cgs unit, as given in Bureau of Standards Circular No. 60, 2d ed. (1920) is

$$1 \text{ international joule} = 1.00034 \text{ absolute joules}$$

The difference between these units is of little importance here.

As secondary heat units the calorie and the British thermal unit (Btu.) have been used. The calorie is defined for the purposes of this circular as 4.183 absolute joules. According to present evidence, this corresponds approximately to the 15° calorie. The Btu. as here used is derived from the calorie by means of the relation between the centigrade and Fahrenheit degrees and the relation between the kilogram and the pound. Thus

$$1 \text{ Btu.} = \frac{5}{9} \times 453.592 = 252.00 \text{ calories} = 1054.1 \text{ absolute joules}$$

This method of defining the Btu. retains the convenient relation

$$1 \text{ calorie per gram} = 1.8 \text{ Btu. per pound}$$

III. THERMAL EXPANSION

The results of measurements of thermal expansion made in 1912–1915 on 87 petroleum oils, ranging in density from 0.62 to 0.96 (16° to 97° A. P. I.) are recorded in Bureau of Standards Technologic Paper No. 77, Density and Thermal Expansion of American Petroleum Oils, by H. W. Bearce and E. L. Peffer. These measurements form the basis for the extensive tables given in Bureau of Standards Circular No. 154, National Standard Petroleum Oil Tables, also the abridged tables given in the supplement to Circular No. 154, Abridged Volume Correction Table for Petroleum Oils, which are sold only by the Superintendent of Documents, Government Printing Office, Washington, D. C., at 30 cents and 5 cents, respectively.

The investigation on thermal expansion, made in 1912–1915, did not include the following groups of commercial products:

- (a) Petroleum asphalts and fluxes,
- (b) volatile petroleum liquids (specific gravity 0.50 to 0.62),
- (c) mixtures of gasoline and benzol, and
- (d) gasolines obtained from various cracking processes.

Consequently, the data in Circular No. 154 do not extend to products (a) and (b). The data given in Circular No. 154 for gasolines are based upon expansion measurements made on "straight-run" gasolines and, therefore, are not applicable with the same accuracy to products (c) and (d). In order to supply approximate expansion data on products (a) and (b) and also to indicate the order of magnitude of departures of expansion data on products (c) and (d) from the data given in Circular No. 154, Tables 1 to 5, inclusive, have been compiled.

1. THERMAL EXPANSION OF PETROLEUM ASPHALTS AND FLUXES

Values of V_{60}/V_t given in Table 1 represent volumes at 60° F. occupied by a unit volume at indicated temperatures, t° F. For example, 1 gallon of petroleum asphalt measured at 350° F. will have a volume of 0.9031 gallon at 60° F. Table 1 is similar in form to the corresponding table given in National Standard Petroleum Oil Tables, B. S. Circular No. 154, and to the abridged volume correction table given in the supplement to Circular No. 154. In fact, Table 1 might well be considered as an addition to that supplement; that is, as group O for the gravity range 0° to 15° A. P. I.

The data given in Table 1 were calculated from the equation,

$$V_t = V_{60} [1 + A (t - 60) + B (t - 60)^2]$$

using $A = 0.000341$ and $B = 0.0000001$, which is equivalent to the following:

Temperature range in °F.	Mean coefficient of expansion
60 to 150.....	0.00035
60 to 250.....	.00036
60 to 350.....	.00037
60 to 450.....	.00038

These are average values based on unpublished measurements made at the Bureau of Standards on 25 samples within the temperature range 32° to 176° F., and two samples within the range 60° to 400° F. These coefficients and the expansions, $(V_{60}/V_t) - 1$, obtained from Table 1 apply to petroleum asphalts and fluxes in general with an estimated accuracy of 5 per cent, which is equivalent to the following percentage accuracy in the relative volumes, V_{60}/V_t , for various temperature ranges: 0.1 per cent, 0° to 100°; 0.2 per cent, 100° to 200°; 0.4 per cent, 200° to 300°; 0.6 per cent, 300° to 400°; and 0.8 per cent, 400° to 500° F.

Products containing wax, gas bubbles, or nonbituminous materials have expansions which differ from those given by Table 1 in proportion to the amount present.

The experimental data obtained by:

Observer	Material	Reference
Zeitfuchs.....	California asphalt.....	Ind. Eng. Chem., 17 , p. 1280; 1925.
Roszbacher.....	Petroleum residuums.....	Ind. Eng. Chem., 7 , p. 577; 1915.

agree with the expansions $(V_{60}/V_t) - 1$ given by Table 1 to about 5 per cent. These constitute the only data found in the literature on this class of petroleum products.

Example.—If the volume of a given quantity of petroleum asphalt is 10,000 gallons at 350° F., what is its volume at 60° F.? Calculate from the value given in Table 1 as follows:

$$V_{60} = 10,000 \times 0.9031 = 9031 \text{ gallons at } 60^\circ \text{ F.}$$

TABLE 1.—*Thermal expansion of petroleum asphalts and fluxes*

Temp. t°F.	V ₆₀ V _t	Temp. t°F.	V ₆₀ V _t	Temp. t°F.	V ₆₀ V _t	Temp. t°F.	V ₆₀ V _t	Temp. t°F.	V ₆₀ V _t
0	1. 0205	100	0. 9864	200	0. 9527	300	0. 9195	400	0. 8869
2	1. 0198	102	. 9857	202	. 9520	302	. 9188	402	. 8863
4	1. 0191	104	. 9850	204	. 9513	304	. 9181	404	. 8856
6	1. 0185	106	. 9844	206	. 9506	306	. 9175	406	. 8850
8	1. 0178	108	. 9837	208	. 9500	308	. 9168	408	. 8843
10	1. 0171	110	. 9830	210	. 9493	310	. 9162	410	. 8837
12	1. 0164	112	. 9823	212	. 9486	312	. 9155	412	. 8831
14	1. 0157	114	. 9816	214	. 9480	314	. 9149	414	. 8824
16	1. 0150	116	. 9810	216	. 9473	316	. 9142	416	. 8818
18	1. 0143	118	. 9803	218	. 9466	318	. 9135	418	. 8811
20	1. 0137	120	. 9796	220	. 9460	320	. 9129	420	. 8805
22	1. 0130	122	. 9789	222	. 9453	322	. 9122	422	. 8799
24	1. 0123	124	. 9783	224	. 9446	324	. 9116	424	. 8792
26	1. 0116	126	. 9776	226	. 9440	326	. 9109	426	. 8786
28	1. 0109	128	. 9769	228	. 9433	328	. 9103	428	. 8779
30	1. 0102	130	. 9762	230	. 9426	330	. 9096	430	. 8773
32	1. 0095	132	. 9755	232	. 9420	332	. 9090	432	. 8767
34	1. 0089	134	. 9749	234	. 9413	334	. 9083	434	. 8760
36	1. 0082	136	. 9742	236	. 9406	336	. 9077	436	. 8754
38	1. 0075	138	. 9735	238	. 9400	338	. 9070	438	. 8747
40	1. 0068	140	. 9728	240	. 9393	340	. 9064	440	. 8741
42	1. 0061	142	. 9722	242	. 9386	342	. 9057	442	. 8735
44	1. 0054	144	. 9715	244	. 9380	344	. 9051	444	. 8728
46	1. 0048	146	. 9708	246	. 9373	346	. 9044	446	. 8722
48	1. 0041	148	. 9701	248	. 9367	348	. 9038	448	. 8716
50	1. 0034	150	. 9695	250	. 9360	350	. 9031	450	. 8709
52	1. 0027	152	. 9688	252	. 9353	352	. 9025	452	. 8703
54	1. 0020	154	. 9681	254	. 9347	354	. 9018	454	. 8697
56	1. 0014	156	. 9674	256	. 9340	356	. 9012	456	. 8690
58	1. 0007	158	. 9668	258	. 9333	358	. 9005	458	. 8684
60	1. 0000	160	. 9661	260	. 9327	360	. 8999	460	. 8678
62	. 9993	162	. 9654	262	. 9320	362	. 8992	462	. 8671
64	. 9986	164	. 9647	264	. 9313	364	. 8986	464	. 8665
66	. 9980	166	. 9641	266	. 9307	366	. 8979	466	. 8659
68	. 9973	168	. 9634	268	. 9300	368	. 8973	468	. 8652
70	. 9966	170	. 9627	270	. 9294	370	. 8966	470	. 8646
72	. 9959	172	. 9620	272	. 9287	372	. 8960	472	. 8640
74	. 9952	174	. 9614	274	. 9280	374	. 8953	474	. 8633
76	. 9945	176	. 9607	276	. 9274	376	. 8947	476	. 8627
78	. 9939	178	. 9600	278	. 9267	378	. 8940	478	. 8621
80	. 9932	180	. 9594	280	. 9260	380	. 8934	480	. 8614
82	. 9925	182	. 9587	282	. 9254	382	. 8927	482	. 8608
84	. 9918	184	. 9580	284	. 9247	384	. 8921	484	. 8602
86	. 9912	186	. 9573	286	. 9241	386	. 8914	486	. 8595
88	. 9905	188	. 9567	288	. 9234	388	. 8908	488	. 8589
90	. 9898	190	. 9560	290	. 9228	390	. 8901	490	. 8583
92	. 9891	192	. 9553	292	. 9221	392	. 8895	492	. 8577
94	. 9884	194	. 9547	294	. 9214	394	. 8888	494	. 8570
96	. 9878	196	. 9540	296	. 9208	396	. 8882	496	. 8564
98	. 9871	198	. 9533	298	. 9201	398	. 8876	498	. 8558
100	. 9864	200	. 9527	300	. 9195	400	. 8869	500	. 8552

2. THERMAL EXPANSION OF VOLATILE PETROLEUM LIQUIDS

The thermal expansion of a particular product; for example, liquefied petroleum gas, may be estimated from Table 2 if any one of the following characteristics of the product is known: Normal bubble point,¹ vapor pressure,¹ or density. The expansion coefficients, A and B , given in Table 2, are defined by the equation

$$V_t = V_{60} [1 + A(t - 60) + B(t - 60)^2]$$

The estimated accuracy of expansions $(V_t - V_{60})/V_{60}$, calculated from the tabulated values of A and B , is 10 per cent for the temperature range 0° to 130° F.

The values given in the last two columns of Table 2 represent the maximum charge for each 1-pound water capacity of container at 60° F., which will not completely fill the container with liquid at 100° F. or 130° F. (See Interstate Commerce Commission Regulations, Pt. I, par. 562; Pt. II, par. 148.) The estimated accuracy of these values is 5 per cent.

The data in Table 2 were compiled from experimental data on propane, *n*-butane, *iso*-butane, *n*-pentane, and *iso*-pentane published by Dana, Jenkins, Burdick and Timm, *Refrigerating Eng.*, **12**, p. 387; 1926; and by Sidney Young, *Sci. Proc. Royal Dublin Soc.*, **12**, p. 374; 1910, using mixture rules. Expansion data given in International Critical Tables, Volume III, indicate that the above hydrocarbons of the paraffin series expand less rapidly than hydrocarbons of other series with corresponding densities and conversely that these paraffin series hydrocarbons expand more rapidly than those of other series with corresponding vapor pressures at a given temperature. Therefore, in cases involving safety, it is desirable that values in the last two columns of Table 2 be chosen from determinations of vapor pressure rather than density, since some commercial products are known to contain variable amounts of hydrocarbons other than the paraffin series.

Example 1.—What is the maximum weight of material having a vapor pressure of 100 lbs./in.² gauge at 70° F., which can be charged into a cylinder of 90 pounds water capacity at 60° F. which will not completely fill the cylinder with liquid at 130° F.? Answer: $0.454 \times 90 = 40.86$ pounds.

Example 2.—What is the maximum weight of material, having a normal bubble point of 20° F., which can be charged into an insulated tank car of 8,000 pounds water capacity at 60° F. in order to be free from hydrostatic pressure at 100° F.? Answer: $0.547 \times 8,000 = 4,376$ pounds.

¹ The vapor pressure of a many-component liquid, as used here, is defined as the equilibrium pressure on a two-phase system composed of a relatively large volume of liquid and such a small volume of vapor that any decrease in the vapor volume would not alter the pressure appreciably. The temperature at which the vapor pressure, as defined above, is equal to one standard atmosphere is designated the normal bubble point.

THERMAL PROPERTIES OF PETROLEUM PRODUCTS

TABLE 2.—*Thermal expansion of volatile petroleum liquids*

Normal bubble point, ° F.	Vapor pressure, lbs./in. ² gauge at—				Approximate gravity, at 60° F.		Expansion coefficients		Pounds of fluid per pound water capacity, hydrostatic pressure, at—	
	70° F.	90° F.	100° F.	130° F.	Specific	° A. P. I.	A×10 ⁵	B×10 ⁷	100° F.	130° F.
—50	126	171	197	291	0.501	151.5	170	98	0.461	0.428
—48	121	165	190	281	.504	149.5	167	93	.465	.433
—46	116	159	183	272	.507	147.5	164	88	.469	.438
—44	111	153	176	263	.510	146.0	161	83	.473	.442
—42	107	147	170	254	.513	144.5	158	78	.477	.447
—40	103	141	164	246	.516	142.5	155	74	.481	.451
—38	99	136	158	238	.519	141.0	152	70	.485	.455
—36	95	131	152	230	.522	139.5	150	67	.488	.459
—34	91	126	147	222	.525	138.0	147	63	.492	.463
—32	87	121	141	214	.528	136.5	145	60	.495	.467
—30	83	117	136	207	.531	135.0	142	57	.498	.471
—28	80	112	131	200	.533	134.0	140	55	.501	.474
—26	76	108	126	193	.536	132.5	138	53	.504	.478
—24	73	104	121	187	.538	131.5	137	51	.506	.481
—22	70	100	117	180	.540	130.5	135	49	.509	.484
—20	67	96	112	174	.542	129.5	134	47	.511	.487
—18	64	92	108	168	.544	128.5	132	46	.513	.489
—16	61	88	104	162	.546	127.5	131	44	.516	.492
—14	58	84	100	157	.548	126.5	129	43	.518	.494
—12	56	81	96	151	.550	125.5	128	42	.520	.496
—10	53	78	92	146	.552	125.0	127	41	.522	.498
—8	51	75	89	141	.553	124.0	126	40	.523	.500
—6	48	71	85	136	.555	123.5	125	39	.525	.502
—4	46	68	82	131	.556	123.0	124	38	.526	.503
—2	44	66	78	126	.557	122.5	124	37	.528	.505
0	42	63	75	122	.558	122.0	123	37	.529	.506
2	40	60	72	117	.560	121.0	122	36	.531	.508
4	38	57	69	113	.561	120.5	121	35	.532	.509
6	36	55	66	109	.562	120.0	120	34	.533	.511
8	34	52	64	105	.564	119.5	119	33	.535	.512
10	32	50	61	101	.565	119.0	119	33	.536	.514
12	30	48	58	97	.567	118.0	118	32	.538	.516
14	29	46	56	94	.568	117.5	117	31	.540	.518
16	27	43	53	90	.570	117.0	116	31	.542	.520
18	26	41	51	87	.572	116.0	115	30	.544	.522
20	24	39	49	84	.574	115.0	113	29	.547	.525
22	23	37	46	80	.576	114.0	112	28	.549	.527
24	21	36	44	77	.578	113.0	111	27	.551	.530
26	20	34	42	74	.580	112.5	110	26	.553	.532
28	19	32	40	72	.582	111.5	109	26	.555	.535
30	17	30	38	69	.584	111.0	108	25	.558	.537
32	16	29	37	66	.586	110.0	107	24	.560	.540
34	15	27	35	63	.588	109.0	106	24	.562	.542
36	14	26	33	61	.590	108.0	105	23	.564	.544
38	13	24	31	58	.592	107.0	104	22	.567	.547
40	12	23	30	56	.595	106.0	102	21	.570	.550
45	9	20	26	50	.600	104.5	100	20	.575	.556
50	7	17	22	45	.605	102.5	98	19	.580	.561
55	5	14	19	40	.610	100.5	96	17	.585	.567
60	3	11	16	35	.615	98.5	94	16	.590	.573
70	0	7	11	28	.620	96.5	92	15	.596	.579

3. THERMAL EXPANSION OF GASOLINE-BENZOL MIXTURES²

The values given in the columns marked 0 per cent in Tables 3, 4, and 5 are equivalent to those given in Bureau of Standards Circular No. 154. These values are based on expansion measurements made in 1912-1915 on "straight run" gasolines. They are included here to facilitate comparisons and interpolations.

The values given in the columns marked 25 per cent and 50 per cent in Tables 3, 4, and 5 were calculated by means of mixture rules using average values for the coefficients of expansion of motor benzol and the coefficients of expansion of "straight run" gasolines used as a basis for Circular 154. Unpublished measurements made recently at this bureau under research project No. 38 of the American Petroleum Institute, have confirmed the mixture rules used for this purpose.

The values given in the column marked "motor benzol 100 per cent" are based on the following average values for the coefficients of expansion of motor benzol: $A=0.00065$ and $B=0.0000005$.

The estimated accuracy of the values given in Tables 4 and 5 and of expansions, $(V_t - V_{60})/V_t$, obtained from Table 3, is 5 per cent for mixtures of benzol and "straight run" gasolines. Thus the relative volumes, V_{60}/V_t , given in Table 3, are probably accurate to better than 0.1 per cent in the temperature range 30° to 90° F. and to better than 0.2 per cent outside this temperature range.

Example 1.—A tank car contains, at 20 °F., 10,000 gallons of a mixture of gasoline and 40 per cent benzol whose gravity is 47.5° A. P. I. at 60° F. What is the volume of the mixture at 60° F.? The result may be obtained from Table 3 by "double interpolation" as follows:

$$V_{60}=10,000 \left[1.0258 - \frac{10}{25} (0.0029) + \frac{1}{2} (0.0017) \right] = 10,255 \text{ gallons}$$

Example 2.—At 90° F. the indication of a hydrometer in a mixture of gasoline and 50 per cent benzol is (a) 54.5° A. P. I. or (b) 0.7609. What is the gravity of the mixture at 60° F.? (a) Applying the correction given in Table 4 gives 54.5-3.9=50.6° A. P. I. at 60° F.; or (b) applying the correction given in Table 5 gives 0.7609+0.0161=0.7770 at 60°/60° F.

4. THERMAL EXPANSION OF "CRACKED" GASOLINES²

The limited information available indicates that "nonblended" gasolines obtained from liquid phase cracking processes have expansions approximately equivalent to mixtures of "straight run" gasoline and 10 per cent benzol, and those obtained from vapor phase cracking processes have expansions approximately equivalent to mixtures of "straight run" gasolines and 20 per cent benzol, for corresponding gravities in each case.

² The data given in Tables 3, 4, and 5, and the statement on cracked gasolines are based, in part, upon experimental results to be presented in detail in a separate publication under project No. 38 of American Petroleum Institute Research,

TABLE 3.—*Thermal expansion of gasoline-benzol mixtures*

[Ratio of volume at 60° F. to volume at t° F., V_{60}/V_t , for mixtures containing 0, 25, 50, and 100 per cent motor benzol, by volume]

Temp. t° F.	45° A. P. I. at 60° F. Sp. gr. 0.8017 at 60°/60° F.			50° A. P. I. at 60° F. Sp. gr. 0.7796 at 60°/60° F.			55° A. P. I. at 60° F. Sp. gr. 0.7587 at 60°/60° F.			Motor benzol, 100 per cent
	Percentage motor-benzol									
	0	25	50	0	25	50	0	25	50	
0	1.0301	1.0342	1.0386	1.0324	1.0367	1.0410	1.0347	1.0391	1.0440	1.0387
5	1.0276	1.0314	1.0354	1.0297	1.0337	1.0376	1.0318	1.0359	1.0404	1.0355
10	1.0251	1.0286	1.0322	1.0270	1.0307	1.0343	1.0290	1.0326	1.0368	1.0323
15	1.0226	1.0257	1.0290	1.0243	1.0276	1.0309	1.0261	1.0294	1.0332	1.0291
20	1.0201	1.0229	1.0258	1.0216	1.0246	1.0275	1.0232	1.0261	1.0295	1.0259
22	1.0191	1.0217	1.0245	1.0205	1.0233	1.0261	1.0220	1.0248	1.0280	1.0246
24	1.0181	1.0206	1.0232	1.0194	1.0221	1.0248	1.0209	1.0235	1.0266	1.0233
26	1.0171	1.0194	1.0219	1.0184	1.0209	1.0234	1.0197	1.0222	1.0251	1.0220
28	1.0161	1.0183	1.0207	1.0173	1.0197	1.0220	1.0186	1.0209	1.0237	1.0207
30	1.0151	1.0171	1.0194	1.0162	1.0184	1.0206	1.0174	1.0196	1.0222	1.0194
32	1.0141	1.0160	1.0181	1.0151	1.0172	1.0193	1.0162	1.0183	1.0207	1.0181
34	1.0131	1.0149	1.0168	1.0140	1.0160	1.0179	1.0151	1.0170	1.0192	1.0168
36	1.0121	1.0138	1.0155	1.0130	1.0148	1.0165	1.0139	1.0157	1.0178	1.0156
38	1.0110	1.0126	1.0142	1.0119	1.0135	1.0151	1.0128	1.0144	1.0163	1.0143
40	1.0100	1.0115	1.0129	1.0108	1.0123	1.0138	1.0116	1.0131	1.0148	1.0130
42	1.0090	1.0103	1.0116	1.0097	1.0111	1.0124	1.0104	1.0118	1.0133	1.0117
44	1.0080	1.0092	1.0103	1.0086	1.0099	1.0110	1.0093	1.0105	1.0119	1.0104
46	1.0070	1.0080	1.0090	1.0076	1.0086	1.0096	1.0081	1.0092	1.0104	1.0091
48	1.0060	1.0069	1.0078	1.0065	1.0074	1.0083	1.0070	1.0079	1.0089	1.0078
50	1.0050	1.0057	1.0065	1.0054	1.0061	1.0069	1.0058	1.0066	1.0074	1.0065
52	1.0040	1.0046	1.0052	1.0043	1.0049	1.0055	1.0046	1.0053	1.0059	1.0052
54	1.0030	1.0034	1.0039	1.0032	1.0037	1.0041	1.0035	1.0039	1.0044	1.0039
56	1.0020	1.0023	1.0026	1.0022	1.0025	1.0028	1.0023	1.0026	1.0030	1.0026
58	1.0010	1.0011	1.0013	1.0011	1.0012	1.0014	1.0012	1.0013	1.0015	1.0013
60	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
62	.9990	.9988	.9987	.9989	.9987	.9986	.9988	.9987	.9985	.9987
64	.9980	.9977	.9974	.9978	.9975	.9972	.9977	.9974	.9970	.9974
66	.9970	.9965	.9961	.9968	.9963	.9958	.9965	.9960	.9955	.9961
68	.9960	.9954	.9948	.9957	.9951	.9944	.9954	.9947	.9940	.9948
70	.9950	.9942	.9935	.9946	.9938	.9930	.9942	.9934	.9925	.9935
72	.9940	.9931	.9922	.9935	.9926	.9917	.9930	.9921	.9911	.9922
74	.9929	.9919	.9909	.9924	.9913	.9903	.9919	.9908	.9896	.9909
76	.9919	.9908	.9896	.9913	.9901	.9889	.9907	.9895	.9881	.9896
78	.9909	.9896	.9883	.9902	.9888	.9875	.9896	.9881	.9866	.9883
80	.9899	.9885	.9870	.9891	.9876	.9861	.9884	.9868	.9851	.9870
82	.9889	.9873	.9857	.9880	.9864	.9847	.9871	.9855	.9836	.9857
84	.9879	.9862	.9844	.9869	.9852	.9833	.9860	.9842	.9821	.9844
86	.9869	.9850	.9831	.9859	.9839	.9819	.9848	.9828	.9806	.9830
88	.9859	.9839	.9818	.9848	.9827	.9806	.9837	.9815	.9791	.9817
90	.9849	.9827	.9805	.9837	.9814	.9792	.9825	.9802	.9776	.9804
92	.9839	.9816	.9792	.9826	.9802	.9778	.9813	.9789	.9761	.9791
94	.9829	.9804	.9779	.9815	.9789	.9764	.9802	.9776	.9746	.9778
96	.9819	.9793	.9766	.9805	.9777	.9750	.9790	.9763	.9731	.9765
98	.9809	.9781	.9753	.9794	.9764	.9736	.9779	.9749	.9716	.9752
100	.9799	.9770	.9740	.9783	.9752	.9722	.9767	.9736	.9701	.9739
105	.9773	.9741	.9707	.9756	.9727	.9687	.9737	.9703	.9663	.9706
110	.9748	.9712	.9675	.9729	.9690	.9652	.9708	.9670	.9626	.9673
115	.9723	.9684	.9642	.9702	.9659	.9617	.9679	.9637	.9588	.9640
120	.9698	.9655	.9609	.9674	.9628	.9582	.9650	.9604	.9550	.9607
125	.9673	.9626	.9577	.9647	.9597	.9547	.9620	.9571	.9513	.9574

TABLE 4.—*Corrections to readings of hydrometers in gasoline-benzol mixtures to reduce to ° A. P. I. at 60° F*

[Mixtures containing 0, 25, and 50 per cent motor benzol, by volume]

Obs. Temp. °F.	45° A. P. I. observed			50° A. P. I. observed			55° A. P. I. observed			Obs. Temp. °F.
	Percentage motor benzol									
	0	25	50	0	25	50	0	25	50	
Add to observed ° A. P. I.										
0	5.7	6.5	7.5	6.3	7.2	8.4	6.9	7.9	9.3	0
5	5.1	5.9	6.8	5.7	6.5	7.6	6.3	7.2	8.4	5
10	4.6	5.3	6.1	5.2	5.9	6.8	5.7	6.5	7.5	10
15	4.1	4.8	5.4	4.6	5.3	6.1	5.1	5.8	6.7	15
20	3.7	4.2	4.8	4.1	4.6	5.3	4.5	5.1	5.9	20
25	3.2	3.7	4.2	3.5	4.0	4.6	3.9	4.4	5.1	25
30	2.7	3.1	3.5	3.0	3.4	3.9	3.3	3.8	4.4	30
32	2.5	2.9	3.3	2.8	3.2	3.7	3.1	3.5	4.1	32
34	2.3	2.7	3.0	2.6	3.0	3.4	2.8	3.2	3.8	34
36	2.2	2.5	2.8	2.4	2.7	3.1	2.6	3.0	3.5	36
38	2.0	2.3	2.6	2.2	2.5	2.9	2.4	2.7	3.2	38
40	1.8	2.0	2.3	2.0	2.3	2.6	2.2	2.5	2.9	40
42	1.6	1.8	2.1	1.8	2.0	2.3	1.9	2.2	2.6	42
44	1.4	1.6	1.8	1.6	1.8	2.1	1.7	2.0	2.3	44
46	1.2	1.4	1.6	1.4	1.6	1.8	1.5	1.7	2.0	46
48	1.1	1.2	1.4	1.2	1.3	1.5	1.3	1.5	1.7	48
50	.9	1.0	1.1	1.0	1.1	1.3	1.1	1.2	1.4	50
52	.7	.8	.9	.8	.9	1.0	.9	1.0	1.1	52
54	.5	.6	.7	.6	.7	.8	.6	.7	.8	54
56	.4	.4	.5	.4	.4	.5	.4	.5	.6	56
58	.2	.2	.2	.2	.2	.3	.2	.2	.3	58
Subtract from observed ° A. P. I.										
60	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60
62	.2	.2	.2	.2	.2	.2	.2	.2	.3	62
64	.4	.4	.4	.4	.4	.5	.4	.5	.5	64
66	.5	.6	.7	.6	.7	.7	.6	.7	.8	66
68	.7	.8	.9	.8	.9	1.0	.8	.9	1.1	68
70	.9	1.0	1.1	1.0	1.1	1.2	1.0	1.2	1.3	70
72	1.0	1.2	1.3	1.1	1.3	1.4	1.2	1.4	1.6	72
74	1.2	1.4	1.5	1.3	1.5	1.7	1.4	1.6	1.9	74
76	1.4	1.6	1.7	1.5	1.7	1.9	1.6	1.9	2.1	76
78	1.5	1.7	2.0	1.7	1.9	2.2	1.8	2.1	2.4	78
80	1.7	1.9	2.2	1.9	2.1	2.4	2.0	2.3	2.6	80
82	1.9	2.1	2.4	2.0	2.3	2.7	2.2	2.5	2.9	82
84	2.0	2.3	2.6	2.2	2.5	2.9	2.4	2.8	3.1	84
86	2.2	2.5	2.8	2.4	2.7	3.1	2.6	3.0	3.4	86
88	2.4	2.7	3.0	2.6	2.9	3.3	2.8	3.2	3.6	88
90	2.5	2.9	3.2	2.8	3.1	3.6	3.0	3.4	3.9	90
92	2.7	3.0	3.4	2.9	3.3	3.8	3.2	3.7	4.1	92
94	2.8	3.2	3.6	3.1	3.5	4.0	3.4	3.9	4.4	94
96	3.0	3.4	3.8	3.3	3.7	4.2	3.6	4.1	4.6	96
98	3.1	3.6	4.0	3.4	3.9	4.4	3.8	4.3	4.9	98
100	3.3	3.8	4.2	3.6	4.1	4.7	4.0	4.5	5.1	100
105	3.7	4.2	4.7	4.0	4.6	5.2	4.5	5.0	5.7	105
110	4.1	4.6	5.2	4.5	5.1	5.7	4.9	5.6	6.3	110
115	4.5	5.1	5.7	4.9	5.6	6.3	5.4	6.1	6.9	115
120	4.8	5.5	6.2	5.3	6.0	6.8	5.8	6.6	7.4	120

TABLE 5.—Corrections to readings of hydrometers in gasoline-benzol mixtures to reduce to specific gravity at 60°/60° F.

[Mixtures containing 0, 25, and 50 per cent motor benzol, by volume]

Obs. Temp. ° F.	Obs. Sp. gr.=0.760			Obs. Sp. gr.=0.780			Obs. Sp. gr.=0.800			Obs. Temp. ° F.
	Percentage motor benzol									
	0	25	50	0	25	50	0	25	50	
Subtract from observed specific gravity										
0	0.0272	0.0307	0.0360	0.0263	0.0296	0.0342	0.0251	0.0285	0.0325	0
5	.0248	.0280	.0328	.0239	.0270	.0311	.0228	.0260	.0296	5
10	.0224	.0253	.0296	.0215	.0245	.0281	.0207	.0235	.0268	10
15	.0201	.0227	.0265	.0193	.0219	.0251	.0184	.0210	.0240	15
20	.0177	.0201	.0234	.0171	.0194	.0222	.0164	.0186	.0212	20
25	.0155	.0175	.0204	.0149	.0169	.0193	.0142	.0162	.0185	25
30	.0132	.0150	.0174	.0127	.0144	.0165	.0121	.0139	.0158	30
32	.0123	.0140	.0162	.0118	.0134	.0154	.0113	.0129	.0147	32
34	.0114	.0129	.0150	.0110	.0124	.0142	.0105	.0120	.0136	34
36	.0105	.0119	.0138	.0101	.0114	.0131	.0097	.0111	.0126	36
38	.0096	.0109	.0126	.0093	.0105	.0120	.0089	.0101	.0115	38
40	.0087	.0099	.0114	.0084	.0095	.0109	.0081	.0092	.0104	40
42	.0078	.0089	.0103	.0076	.0085	.0098	.0072	.0083	.0093	42
44	.0069	.0079	.0091	.0067	.0076	.0087	.0064	.0073	.0083	44
46	.0061	.0069	.0079	.0059	.0066	.0076	.0056	.0064	.0073	46
48	.0051	.0059	.0068	.0050	.0057	.0065	.0048	.0055	.0062	48
50	.0043	.0049	.0056	.0041	.0047	.0054	.0040	.0046	.0052	50
52	.0035	.0039	.0045	.0033	.0038	.0043	.0032	.0036	.0041	52
54	.0025	.0029	.0033	.0025	.0028	.0032	.0024	.0027	.0031	54
56	.0017	.0019	.0022	.0017	.0019	.0022	.0016	.0018	.0020	56
58	.0008	.0010	.0011	.0008	.0009	.0011	.0008	.0009	.0010	58
Add to observed specific gravity										
60	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	60
62	.0009	.0010	.0011	.0008	.0009	.0011	.0008	.0009	.0010	62
64	.0017	.0019	.0022	.0017	.0019	.0021	.0016	.0018	.0021	64
66	.0026	.0029	.0033	.0025	.0028	.0032	.0024	.0027	.0031	66
68	.0034	.0039	.0044	.0033	.0037	.0042	.0031	.0036	.0041	68
70	.0042	.0048	.0055	.0041	.0046	.0053	.0039	.0045	.0051	70
72	.0051	.0058	.0066	.0049	.0056	.0063	.0047	.0054	.0061	72
74	.0059	.0067	.0076	.0057	.0065	.0074	.0055	.0063	.0071	74
76	.0068	.0077	.0087	.0065	.0074	.0084	.0063	.0072	.0081	76
78	.0076	.0087	.0098	.0073	.0083	.0094	.0070	.0081	.0091	78
80	.0084	.0096	.0108	.0081	.0092	.0104	.0078	.0089	.0101	80
82	.0092	.0105	.0119	.0089	.0101	.0115	.0086	.0098	.0111	82
84	.0101	.0115	.0129	.0097	.0110	.0125	.0094	.0107	.0121	84
86	.0109	.0124	.0140	.0105	.0119	.0135	.0101	.0115	.0130	86
88	.0117	.0133	.0150	.0113	.0128	.0145	.0109	.0124	.0140	88
90	.0125	.0142	.0161	.0120	.0137	.0155	.0116	.0133	.0150	90
92	.0133	.0152	.0171	.0128	.0146	.0165	.0123	.0141	.0160	92
94	.0141	.0161	.0182	.0135	.0155	.0175	.0131	.0150	.0169	94
96	.0150	.0170	.0192	.0143	.0164	.0185	.0137	.0159	.0179	96
98	.0158	.0179	.0203	.0150	.0173	.0195	.0145	.0167	.0188	98
100	.0166	.0188	.0213	.0158	.0181	.0205	.0153	.0176	.0198	100
105	.0186	.0211	.0239	.0178	.0203	.0230	.0172	.0197	.0222	105
110	.0206	.0234	.0264	.0198	.0225	.0254	.0191	.0218	.0246	110
115	.0224	.0257	.0289	.0215	.0247	.0279	.0209	.0239	.0270	115
120	.0244	.0279	.0314	.0234	.0269	.0303	.0227	.0260	.0293	120

IV. HEATS OF COMBUSTION

Determinations of the heat of combustion of petroleum oils are usually made by means of a bomb calorimeter. The results so obtained yield values of the total heat of combustion at constant volume, which may be defined as the quantity of heat liberated by the combination of unit quantity of oil with oxygen in a constant volume inclosure, the products of combustion, carbon dioxide, sulphur dioxide, and water being cooled to the initial temperature with the water condensed to the liquid state. This quantity is sometimes called total, gross, or high heating value (calorific power).

Determinations made by means of calorimeters of the flow type, with the water formed in combustion remaining in the gaseous state, yield values of the net heat of combustion at constant pressure. This quantity is sometimes called net or low heating value (calorific power).

In what follows, it will be convenient to use symbols defined as follows:

\bar{Q}_v = total heat of combustion at constant volume per unit quantity of commercial product; final products: Ash, gaseous CO_2 , SO_2 , and liquid H_2O .

\bar{Q}_p = net heat of combustion at constant pressure per unit quantity of commercial product; final products: Ash, gaseous CO_2 , SO_2 , and H_2O .

Q_v = total heat of combustion at constant volume per unit quantity of oil free from water, ash, and sulphur, final products: Gaseous CO_2 and liquid H_2O .

Q_p = net heat of combustion at constant pressure per unit quantity of oil free from water, ash, and sulphur; final products: Gaseous CO_2 and H_2O .

d = Specific gravity at $60^\circ/60^\circ$ F.

% H_2O = water content of commercial product in per cent by weight.

%S = sulphur content of commercial product in per cent by weight.

% ash = noncombustible content of commercial product in per cent by weight.

The relation between total heat of combustion at constant volume and specific gravity selected as best representing the available results on pure hydrocarbons found in petroleum and on water, ash, and sulphur free petroleum oils is as follows:

$$Q_v = 12,400 - 2,100 d^2 \quad (1)$$

in which Q_v is expressed in calories per gram. Values of Q_v given in Tables 6 and 7 were calculated from this equation. Values in calories per gram multiplied by 1.8 yield values in Btu. per pound, and the latter multiplied by pounds per gallon yield values in Btu. per gallon.

In most practical applications of the combustion of petroleum products, the process is carried out at constant pressure (atmospheric) and the water vapor formed in combustion is not condensed. For such processes, therefore, the net heat of combustion at constant pressure is the more significant quantity in making comparisons of fuels and in calculating the efficiencies of heating appliances.

Since nearly all of the determinations of heat of combustion have been made at constant volume, which are somewhat more precise, the values of net heat of combustion at constant pressure in calories per gram, given in Tables 6 and 7, were calculated by means of the relation

$$Q_p = Q_v - \%H [(9 \times 585) - 220] 0.01$$

in which 9 represents the number of grams of water formed from 1 gram of hydrogen, 585 represents the latent heat of vaporization of water at 20° C. (68° F.), and 220 is a small correction to take into account the change in volume from initial to final

products. Average values for percentages of hydrogen in oils of various specific gravities were obtained from the relation

$$\%H = 26 - 15d \quad (2)$$

This relation agrees, within 1 per cent hydrogen, with values obtained from combustion analyses of a wide variety of petroleum oils recorded in International Critical Tables, Vol. II, and also with known values for hydrocarbons of the paraffin series. High accuracy in the values of %H are not needed since the difference between total and net heats of combustion is relatively small, less than 10 per cent.

Suppose two oils, A and B, of the same specific gravity contained considerably different amounts of hydrogen and, in consequence thereof, their total heats of combustion differed by 1 per cent, then their net heats of combustion would differ only about half this amount as shown by the following:

Oil	%H	Calories per gram	
		Q^o	Q^p
A	13	10,710	10,052
B	12	10,610	10,002

It appears, therefore, that the net heats of combustion of paraffin base and naphthene base oils of the same specific gravity are more nearly alike than are their total heats of combustion.

1. HEATS OF COMBUSTION OF CRUDE OILS, FUEL OILS, AND KEROSENES

The data on heats of combustion (heating values) given in Table 6 apply to petroleum oils free from water, ash, and sulphur with an estimated accuracy of 1 per cent. These data are based on experimental results obtained, on a total of 630 petroleum oils from 8 States and 10 foreign countries, by 5 groups of observers, as follows:

Number of samples	Authority	Reference
50.....	(1) Bureau of Standards.....	(Unpublished.)
109.....	(2) Constam and Schlapfer.....	Z. Ver. Deutsch. Ing., 57, p. 1576; 1913.
252.....	(3) Bureau of Mines.....	Tech. Paper No. 74; 1914.
158.....	(4) Bureau of Mines.....	Bulletin 19; 1911.
61.....	(5) Sherman and Kropff.....	J. Am. Chem. Soc., 30, p. 1626; 1908.

due allowance being made for the water, ash, and sulphur contents of these oils where such information was available. With complete data available on water, ash, and sulphur, the results obtained by (1) and (2) agree with Table 6 within 1 per cent. With incomplete data available on water, ash, and sulphur, 80 per cent of the results obtained by (3), (4), and (5) agree with Table 6 within 1 per cent. Differences greater than 1 per cent were probably due, in most cases to the presence of undetermined amounts of water, ash, and sulphur.

Many petroleum oils contain only negligible amounts of these foreign materials, and their heats of combustion may be estimated with fair accuracy from their specific gravities by means of Table 6. The heats of combustion of petroleum oils containing appreciable amounts of foreign matter may be estimated by means of the following relations:

$$\bar{Q}_v = Q_v - 0.01 Q_v (\% \text{ H}_2\text{O} + \% \text{ ash} + \% \text{ S}) + X(\% \text{ S})$$

$$\bar{Q}_p = Q_p - 0.01 Q_p (\% \text{ H}_2\text{O} + \% \text{ ash} + \% \text{ S}) + X(\% \text{ S}) - Y(\% \text{ H}_2\text{O})$$

taking values of Q_v and Q_p from Table 6 in the particular units desired, corresponding to the gravity of the oil and values of X and Y in the desired units from the following:

Units	X	Y
Cal/g.....	22.5	5.85
Btu./lb.....	40.5	10.53
Btu./gal.....	338 d	87.8 d

Since the heats of combustion of the hydrocarbon contents of fuel oils differ but little, the usefulness of a fuel oil depends largely upon its content of water, ash, and sulphur and its viscosity. Minimum water and ash represent freedom from combustion difficulties, minimum sulphur represents freedom from corrosion, and minimum viscosity represents freedom of flow.

Example 1.—What are the heats of combustion (heating values) of a gallon of fuel oil which has a gravity of 25° A. P. I. at 60° F. and contains 0.5 per cent water, 0.1 per cent ash, and 1.0 per cent sulphur? These may be calculated from the above relations as follows:

Total heat of combustion at constant volume (total heating value), $\bar{Q}_v = 145,000 - 1,450(0.5 + 0.1 + 1.0) + 338(0.9042) = 142,936$ Btu. per gallon.

Net heat of combustion at constant pressure (net heating value), $\bar{Q}_p = 136,400 - 1,364(0.5 + 0.1 + 1.0) + 338(0.9042) - 87.8(0.9042)(0.5) = 134,178$ Btu. per gallon.

TABLE 6.—Heats of combustion of crude oils, fuel oils, and kerosenes

Gravity		Density	Total heat of combustion at constant volume, Q_v			Net heat of combustion at constant pressure, Q_p			Degrees A. P. I. at 60° F.
Degrees A. P. I. at 60° F.	Specific at 60°/60° F.	Pounds per gallon	Cal./g	Btu./lb.	Btu./gal.	Cal./g	Btu./lb.	Btu./gal.	
10	1.0000	8.337	10,300	18,540	154,600	9,740	17,540	146,200	10
11	.9930	8.279	10,330	18,590	153,900	9,770	17,580	145,600	11
12	.9861	8.221	10,360	18,640	153,300	9,790	17,620	144,900	12
13	.9792	8.164	10,390	18,690	152,600	9,810	17,670	144,200	13
14	.9725	8.108	10,410	18,740	152,000	9,840	17,710	143,600	14
15	.9659	8.053	10,440	18,790	151,300	9,860	17,750	142,900	15
16	.9593	7.998	10,470	18,840	150,700	9,880	17,790	142,300	16
17	.9529	7.944	10,490	18,890	150,000	9,900	17,820	141,600	17
18	.9465	7.891	10,520	18,930	149,400	9,920	17,860	140,900	18
19	.9402	7.839	10,540	18,980	148,800	9,940	17,900	140,300	19
20	.9340	7.787	10,570	19,020	148,100	9,960	17,930	139,600	20
21	.9279	7.736	10,590	19,060	147,500	9,980	17,960	139,000	21
22	.9218	7.686	10,620	19,110	146,800	10,000	18,000	138,300	22
23	.9159	7.636	10,640	19,150	146,200	10,020	18,030	137,700	23
24	.9100	7.587	10,660	19,190	145,600	10,040	18,070	137,100	24
25	.9042	7.538	10,680	19,230	145,000	10,050	18,100	136,400	25
26	.8984	7.490	10,710	19,270	144,300	10,070	18,130	135,800	26
27	.8927	7.443	10,730	19,310	143,700	10,090	18,160	135,200	27
28	.8871	7.396	10,750	19,350	143,100	10,110	18,190	134,600	28
29	.8816	7.350	10,770	19,380	142,500	10,120	18,220	133,900	29
30	.8762	7.305	10,790	19,420	141,800	10,140	18,250	133,300	30
31	.8708	7.260	10,810	19,450	141,200	10,150	18,280	132,700	31
32	.8654	7.215	10,830	19,490	140,600	10,170	18,310	132,100	32
33	.8602	7.171	10,850	19,520	140,000	10,180	18,330	131,500	33
34	.8550	7.128	10,860	19,560	139,400	10,200	18,360	130,900	34
35	.8498	7.085	10,880	19,590	138,800	10,210	18,390	130,300	35
36	.8448	7.043	10,900	19,620	138,200	10,230	18,410	129,700	36
37	.8398	7.001	10,920	19,650	137,600	10,240	18,430	129,100	37
38	.8348	6.960	10,940	19,680	137,000	10,260	18,460	128,500	38
39	.8299	6.920	10,950	19,720	136,400	10,270	18,480	127,900	39
40	.8251	6.879	10,970	19,750	135,800	10,280	18,510	127,300	40
41	.8203	6.839	10,990	19,780	135,200	10,300	18,530	126,700	41
42	.8155	6.799	11,000	19,810	134,700	10,310	18,560	126,200	42
43	.8109	6.760	11,020	19,830	134,100	10,320	18,580	125,600	43
44	.8063	6.722	11,030	19,860	133,500	10,330	18,600	125,000	44
45	.8017	6.684	11,050	19,890	132,900	10,340	18,620	124,400	45
46	.7972	6.646	11,070	19,920	132,400	10,360	18,640	123,900	46
47	.7927	6.609	11,080	19,940	131,900	10,370	18,660	123,300	47
48	.7883	6.572	11,100	19,970	131,200	10,380	18,680	122,800	48
49	.7839	6.536	11,110	20,000	130,700	10,390	18,700	122,200	49

Example 2.—How do the heats of combustion (heating values) of a 15° A. P. I. oil compare with those of a 30° A. P. I. oil, assuming negligible amounts of water, ash, and sulphur present in each oil? The following values are obtained from Table 6:

Quantity	15° A. P. I. oil	30° A. P. I. oil	Difference
Total heat, Q_v	151,300	141,800	9,500
Net heat, Q_p	142,900	133,300	9,600

Thus, the 15° A. P. I. oil has the greater heat of combustion (heating value) by about 7 per cent.

2. HEATS OF COMBUSTION OF VOLATILE PETROLEUM PRODUCTS

The data on heats of combustion (heating values) given in Table 7 apply to volatile petroleum liquids in general with an estimated accuracy of 1 per cent. The values given are probably too high by 1 or 2 per cent for products containing unusually large amounts of aromatic hydrocarbons; for example, "vapor phase cracked" gasolines. The tabulated values should be increased by about 1 per cent (see Table 15) to yield corresponding values for the heats of combustion of the vapor (vaporized product); that is, for those instances in which the latent heat of vaporization is supplied by the external surroundings and not by the combustion of the product.

The data given in Table 7 are based on experimental results obtained, on a total of 47 volatile petroleum liquids, by five groups of observers, as follows:

Number of samples	Authority	Reference
10.....	(1) Bureau of Standards.....	Nat. Advisory Comm. Aeronautics, Report No. 47; 1920.
10.....	(2) Bureau of Mines.....	Technical Paper No. 163; 1916.
16.....	(3) Bureau of Mines.....	Bulletin No. 43; 1912.
8.....	(4) Ricardo.....	The Internal-Combustion Engine, II; 1923.
3.....	(5) Sherman and Kropff.....	J. Am. Chem. Soc., 30, p. 1626; 1908.

which constitute all of the data found in the literature on this class of petroleum products. The results obtained on all of these samples agree with the data given in Table 7 within 1 per cent, except for the results on four samples, designated here as samples (a), (b), (c), and (d) for convenience. The differences (observed results minus tabulated values) on these samples are as follows: Sample (a) observer (1), -1.3 per cent; sample (b), observer (2), -1.2 per cent; sample (c) observer (4), -1.4 per cent; and sample (d) observer (5), +3.4 per cent. Sample (a) was known to be a "cracked" gasoline, and an analysis of sample (c) indicated a content of 39 per cent aromatics.

Data, taken from International Critical Tables, Volume V, on the total heat of combustion of the following liquid hydrocarbons: Propane, *iso*-butane, *n*-pentane, *iso*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, cyclopentane, cyclohexane, cycloheptane, methylcyclohexane, and 1-1 dimethylcyclohexane, agree with the data in Table 7 within 0.5 per cent.

Example.—What are the heats of combustion (heating values) of liquefied petroleum gas of specific gravity 0.5517 at 60°/60° F. (125° A. P. I.)? Assuming vaporization at 60° F. and adding the latent heat of vaporization given in Table 15 to the heats of combustion of the liquid given in Table 7, yields the following values:

Units	Total heat of combustion at constant volume		Net heat of combustion at constant pressure	
	Liquid	Vapor	Liquid	Vapor
Cal/g.....	11,760	11,870	10,860	10,970
Btu./lb.....	21,170	21,360	19,560	19,750
Btu./gal.....	97,400	98,280	90,000	90,880

TABLE 7.—Heats of combustion of volatile petroleum products

Gravity		Density	Total heat of combustion at constant volume, Q_v			Net heat of combustion at constant pressure, Q_p			Degrees A. P. I. at 60° F.
Degrees A. P. I. at 60° F.	Specific at 60°/60° F.	Pounds per gallon	Cal./g	Btu./lb.	Btu./gal.	Cal./g	Btu./lb.	Btu./gal.	
50	0.7796	6.500	11,120	20,020	130,100	10,400	18,720	121,700	50
51	.7753	6.464	11,140	20,050	129,600	10,410	18,740	121,100	51
52	.7711	6.429	11,150	20,070	129,000	10,420	18,760	120,600	52
53	.7669	6.394	11,160	20,100	128,500	10,430	18,780	120,100	53
54	.7628	6.360	11,180	20,120	128,000	10,440	18,800	119,500	54
55	.7587	6.326	11,190	20,140	127,400	10,450	18,810	119,000	55
56	.7547	6.292	11,200	20,170	126,900	10,460	18,830	118,500	56
57	.7507	6.258	11,220	20,190	126,400	10,470	18,850	118,000	57
58	.7467	6.225	11,230	20,210	125,800	10,480	18,870	117,500	58
59	.7428	6.193	11,240	20,230	125,300	10,490	18,880	116,900	59
60	.7389	6.160	11,250	20,260	124,800	10,500	18,900	116,400	60
61	.7351	6.128	11,270	20,280	124,300	10,510	18,920	115,900	61
62	.7313	6.097	11,280	20,300	123,700	10,520	18,930	115,400	62
63	.7275	6.065	11,290	20,320	123,200	10,530	18,950	114,900	63
64	.7238	6.034	11,300	20,340	122,700	10,540	18,960	114,400	64
65	.7201	6.004	11,310	20,360	122,200	10,540	18,980	113,900	65
66	.7165	5.973	11,320	20,380	121,700	10,550	18,990	113,400	66
67	.7128	5.943	11,330	20,400	121,200	10,560	19,010	112,900	67
68	.7093	5.913	11,340	20,420	120,700	10,570	19,020	112,500	68
69	.7057	5.884	11,350	20,440	120,200	10,580	19,040	112,000	69
70	.7022	5.855	11,360	20,460	119,800	10,580	19,050	111,500	70
72	.6953	5.797	11,380	20,490	118,800	10,600	19,080	110,600	72
74	.6886	5.741	11,400	20,530	117,900	10,610	19,100	109,700	74
76	.6819	5.685	11,420	20,560	116,900	10,630	19,130	108,800	76
78	.6754	5.631	11,440	20,600	116,000	10,640	19,150	107,900	78
80	.6690	5.578	11,460	20,630	115,100	10,650	19,180	107,000	80
82	.6628	5.526	11,480	20,660	114,200	10,670	19,200	106,100	82
84	.6566	5.474	11,490	20,690	113,300	10,680	19,220	105,200	84
86	.6506	5.424	11,510	20,720	112,400	10,690	19,240	104,400	86
88	.6446	5.375	11,530	20,750	111,500	10,700	19,260	103,500	88
90	.6388	5.326	11,540	20,780	110,700	10,710	19,280	102,700	90
92	.6331	5.278	11,560	20,810	109,800	10,720	19,300	101,900	92
94	.6275	5.232	11,570	20,830	109,000	10,740	19,320	101,100	94
96	.6220	5.186	11,590	20,860	108,100	10,750	19,340	100,300	96
98	.6166	5.140	11,600	20,880	107,300	10,760	19,360	99,500	98
100	.6112	5.096	11,620	20,910	106,500	10,770	19,380	98,700	100
105	.5983	4.988	11,650	20,970	104,600	10,790	19,420	96,800	105
110	.5859	4.885	11,680	21,020	102,700	10,810	19,460	95,100	110
115	.5740	4.786	11,710	21,070	100,900	10,830	19,490	93,300	115
120	.5626	4.691	11,740	21,120	99,100	10,850	19,530	91,600	120
125	.5517	4.599	11,760	21,170	97,400	10,860	19,560	90,000	125
130	.5411	4.511	11,790	21,210	95,700	10,880	19,590	88,400	130
135	.5310	4.427	11,810	21,250	94,100	10,900	19,610	86,800	135
140	.5212	4.345	11,830	21,290	92,500	10,910	19,640	85,300	140
145	.5118	4.267	11,850	21,330	91,000	10,920	19,660	83,900	145

3. HEATS OF COMBUSTION OF GASOLINE-BENZOL MIXTURES

The data on heats of combustion given in Table 8 apply to mixtures of gasoline and motor benzol with an estimated accuracy of 1 per cent. The values given in the column marked 0 per cent in Table 8, are the same as those given in Tables 6 and 7 and are based on experimental results described in parts (1) and (2) of this section. The values for gasoline-benzol mixtures were calculated by means of the following mixture rules:

$$100 Q_m = xQ_b + (100-x)Q_g$$

$$100 D_m = xD_b + (100-x)D_g$$

in which the subscripts m , b , and g refer to mixture, benzol, and gasoline, respectively, and

Q = heat of combustion in Btu. per gallon,

D = specific gravity at 60°/60°F.,

x = per cent benzol, by volume.

Values for gasoline given in Table 7 were used in these calculations, together with the following experimental values for benzol: $D = 0.885$; $Q_v = 133,300$ Btu. per gallon; and $Q_p = 128,100$ Btu. per gallon.

Table 8 gives the heat of combustion of the liquid. The net heat of combustion of the vapor should be used in making comparisons of fuels used in internal-combustion engines, since the latent heat of vaporization is supplied largely by the air or by waste heat from the exhaust gases. Values for the heat of combustion of the vapor may be obtained by adding the latent heat of vaporization at 60° F., viz, 880 Btu. per gallon of gasoline (see Table 12) and 1,400 Btu. per gallon of benzol. Thus, for mixtures

$$L(\text{Btu./gal.}) = 14x + 8.8(100-x)$$

Example.—How do the heats of combustion of a gallon of 57° A. P. I. gasoline compare with the heats of combustion of a gallon 50° A. P. I. blend of gasoline and 40 per cent benzol? Adding values of the latent heat of vaporization to the values given by Table 8 gives the following:

Fuel	Total heat of combustion at constant volume		Net heat of combustion at constant pressure	
	Liquid	Vapor	Liquid	Vapor
57° A. P. I. gasoline.....	126,400	127,280	118,000	118,880
50° A. P. I. blend.....	125,800	126,890	118,700	119,790
Difference.....per cent.....	+0.5	+0.3	-0.6	-0.8

TABLE 8.—Heats of combustion of gasoline-benzol mixtures

Gravity		Total heat of combustion at constant volume in Btu. / gal., Q_v . Mixtures containing 0 to 60 per cent benzol, by volume							Degrees A. P. I. at 60° F.
Degrees A. P. I. at 60° F.	Specific at 60°/60° F.	0	10	20	30	40	50	60	
40	. 8251	135, 800	134, 800	133, 800	132, 800	131, 800	130, 800	129, 700	40
41	. 8203	135, 200	134, 200	133, 200	132, 200	131, 200	130, 100	129, 000	41
42	. 8155	134, 700	133, 700	132, 700	131, 600	130, 600	129, 500	128, 400	42
43	. 8109	134, 100	133, 100	132, 100	131, 000	130, 000	128, 900	127, 700	43
44	. 8063	133, 500	132, 500	131, 500	130, 400	129, 400	128, 300	127, 100	44
45	. 8017	132, 900	131, 900	130, 900	129, 900	128, 800	127, 700	126, 400	45
46	. 7972	132, 400	131, 400	130, 300	129, 300	128, 200	127, 000	125, 800	46
47	. 7927	131, 800	130, 800	129, 700	128, 700	127, 600	126, 400	125, 200	47
48	. 7883	131, 200	130, 200	129, 200	128, 100	127, 000	125, 800	124, 500	48
49	. 7839	130, 700	129, 600	128, 600	127, 500	126, 400	125, 200	123, 800	49
50	. 7796	130, 100	129, 100	128, 000	126, 900	125, 800	124, 500	123, 200	50
51	. 7753	129, 600	128, 500	127, 400	126, 300	125, 200	123, 900	122, 600	51
52	. 7711	129, 000	128, 000	126, 900	125, 700	124, 600	123, 300	122, 000	52
53	. 7669	128, 500	127, 400	126, 300	125, 200	124, 000	122, 700	121, 300	53
54	. 7628	128, 000	126, 900	125, 800	124, 600	123, 400	122, 100	120, 700	54
55	. 7587	127, 400	126, 300	125, 200	124, 000	122, 800	121, 500	120, 000	55
56	. 7547	126, 900	125, 800	124, 700	123, 500	122, 200	120, 900	119, 400	56
57	. 7507	126, 400	125, 200	124, 100	122, 900	121, 700	120, 300	118, 800	57
58	. 7467	125, 800	124, 700	123, 600	122, 300	121, 100	119, 700	118, 100	58
59	. 7428	125, 300	124, 200	123, 000	122, 800	120, 500	119, 100	117, 500	59
60	. 7389	124, 800	123, 600	122, 500	121, 300	120, 000	118, 500	116, 900	60
Gravity		Net heat of combustion at constant pressure in Btu. / gal., Q_p . Mixtures containing 0 to 60 per cent benzol, by volume							Degrees A. P. I. at 60° F.
Degrees A. P. I. at 60° F.	Specific at 60°/60° F.	0	10	20	30	40	50	60	
40	. 8251	127, 300	126, 700	126, 000	125, 300	124, 700	124, 000	123, 200	40
41	. 8203	126, 700	126, 100	125, 400	124, 700	124, 100	123, 400	122, 600	41
42	. 8155	126, 200	125, 500	124, 800	124, 100	123, 500	122, 700	122, 000	42
43	. 8109	125, 600	124, 900	124, 200	123, 600	122, 900	122, 100	121, 300	43
44	. 8063	125, 000	124, 300	123, 700	123, 000	122, 300	121, 500	120, 700	44
45	. 8017	124, 400	123, 800	123, 100	122, 400	121, 700	120, 900	120, 100	45
46	. 7972	123, 900	123, 200	122, 500	121, 800	121, 100	120, 300	119, 400	46
47	. 7927	123, 300	122, 600	121, 900	121, 200	120, 500	119, 700	118, 800	47
48	. 7883	122, 800	122, 100	121, 400	120, 700	119, 900	119, 100	118, 200	48
49	. 7839	122, 200	121, 500	120, 800	120, 100	119, 300	118, 500	117, 600	49
50	. 7796	121, 700	121, 000	120, 300	119, 500	118, 700	117, 900	117, 000	50
51	. 7753	121, 100	120, 400	119, 700	118, 900	118, 100	117, 300	116, 300	51
52	. 7711	120, 600	119, 900	119, 200	118, 400	117, 600	116, 700	115, 700	52
53	. 7669	120, 100	119, 300	118, 600	117, 800	117, 000	116, 100	115, 100	53
54	. 7628	119, 500	118, 800	118, 100	117, 300	116, 400	115, 500	114, 500	54
55	. 7587	119, 000	118, 300	117, 500	116, 700	115, 900	114, 900	113, 900	55
56	. 7547	118, 500	117, 700	117, 000	116, 200	115, 300	114, 400	113, 300	56
57	. 7507	118, 000	117, 200	116, 400	115, 600	114, 800	113, 800	112, 700	57
58	. 7467	117, 500	116, 700	115, 900	115, 100	114, 200	113, 200	112, 100	58
59	. 7428	116, 900	116, 200	115, 400	114, 500	113, 600	112, 600	111, 500	59
60	. 7389	116, 400	115, 600	114, 800	114, 000	113, 100	112, 100	110, 900	60

V. SPECIFIC VOLUME OF VAPOR

The data given in Table 9 on specific volume, V , were calculated by means of the equation, $pVM=RT$, using $p=1$ standard atmosphere, $R=0.7303$, $T=^{\circ}\text{F.}+460$, and values of molecular weight, M , obtained from the equation,

$$\frac{1}{M}=0.0001644 (^{\circ}\text{A. P. I.})-0.000972 \quad (3)$$

which is equivalent to

$$M=1.03 (v-43)=\frac{44.29d}{1.03-d}$$

in which v =molecular volume of liquid at 60°F. and d =specific gravity of liquid at $60^{\circ}/60^{\circ}\text{F.}$

The above relations between molecular weight and liquid density are fair approximations for the lighter hydrocarbons, propane, butane, and pentane, and represent an average of the experimental results on petroleum distillates (20° to 80° A. P. I.) obtained by:

Observer	Reference
Bridgeman.....	J. Soc. Auto. Eng., 23 , p. 478; 1928.
Zeitfuchs.....	Ind. Eng. Chem., 18 , p. 79; 1926.
Stevenson and Stark.....	Ind. Eng. Chem., 17 , p. 679; 1925.
Ormandy and Craven.....	J. Inst. Petr. Techn., 11 , p. 533; 1925.
Wilson and Wylde.....	Ind. Eng. Chem., 15 , p. 801; 1923.
Rittman and Egloff.....	Ind. Eng. Chem., 7 , p. 578; 1915.

The data given in Table 9 apply to petroleum distillates in general with the following estimated accuracies for various ranges of liquid gravity: 20° to 35° A. P. I., 50 per cent; 35° to 50° A. P. I., 25 per cent; 50° to 100° A. P. I., 10 per cent; and 100° to 150° A. P. I., 5 per cent. The tabulated values are probably too high for paraffin-base distillates and too low for naphthene-base distillates and those rich in aromatics.

Saturation temperatures frequently differ considerably for different petroleum products of the same gravity. Saturation temperatures or normal dew points are indicated roughly in Table 9 by means of the staggered lines. Many of the values above the staggered lines are hypothetical values which are useful for rapid estimations of specific volumes at reduced pressures.

The specific volume, V , at any desired temperature and pressure may be obtained conveniently from

$$V=\frac{V_1}{p(\text{atmos.})}=\frac{760V_1}{p(\text{mmHg})}=\frac{14.7V_1}{p(\text{lbs./in.}^2,\text{abs.})}=\frac{30V_1}{p(\text{inches Hg})}$$

selecting V_1 from Table 9, corresponding to the desired temperature and liquid gravity.

Example.—Crude oil having the following fractional distillation characteristics: 5 per cent over at 179°F. , gravity 75.0° A. P. I.; 10 per cent, 229°F. , 68.9° A. P. I.; 15 per cent, 270°F. , 63.1° A. P. I.; 20 per cent, 297°F. , 58.4° A. P. I.; 25 per cent, 327°F. , 55.4° A. P. I.; 30 per cent, 352°F. , 52.7° A. P. I.; 35 per cent, 394°F. , 49.9° A. P. I., is heated in a fire still at such a rate as to yield 500 gallons of distillate per hour. If the vapor outlet from the still is 12 inches in diameter, what is the velocity of the vapors? Table 9 indicates that the specific volume of the vapors of each fraction is approximately 30 cubic feet per gallon of distillate. Thus, $500 \times 30 = 15,000$ cu. ft. per hour flow through an area of $\frac{\pi}{4} = 0.785$ sq. ft. at a velocity of

$$\frac{15,000}{0.785 \times 3,600} = 5.3 \text{ ft. per sec.} = \frac{15,000}{0.785 \times 5,280} = 3.6 \text{ miles per hour}$$

TABLE 9.—Specific volume of petroleum products, completely vaporized at one atmosphere pressure

Gravity		Volume of vapor in cu. ft./lb. at various temperatures in ° F.								
Degrees A. P. I. at 60° F.	Specific at 60°/60° F.	60°	100°	200°	300°	400°	500°	600°	800°	1,000°
20	0.9340							1.8	2.1	2.5
25	.9042						2.2	2.4	2.9	3.4
30	.8762					2.5	2.8	3.1	3.6	4.2
35	.8498				2.7	3.0	3.4	3.7	4.4	5.1
40	.8251			2.7	3.1	3.5	3.9	4.3	5.2	6.0
45	.8017		2.6	3.1	3.6	4.0	4.5	5.0	5.9	6.9
50	.7796	2.8	3.0	3.5	4.0	4.6	5.1	5.6	6.7	7.7
55	.7587	3.1	3.3	3.9	4.5	5.1	5.7	6.3	7.4	8.6
60	.7389	3.4	3.6	4.3	4.9	5.6	6.2	6.9	8.2	9.5
65	.7201	3.7	4.0	4.7	5.4	6.1	6.8	7.5	8.9	10.4
70	.7022	4.0	4.3	5.1	5.9	6.6	7.4	8.2	9.7	11.2
75	.6852	4.3	4.6	5.5	6.3	7.1	8.0	8.8	10.5	12.1
80	.6690	4.6	5.0	5.9	6.8	7.6	8.5	9.4	11.2	13.0
85	.6536	4.9	5.3	6.3	7.2	8.2	9.1	10.1	12.0	13.8
90	.6388	5.3	5.7	6.7	7.7	8.7	9.7	10.7	12.7	14.7
95	.6247	5.6	6.0	7.1	8.1	9.2	10.3	11.3	13.5	15.6
100	.6112	5.9	6.3	7.5	8.6	9.7	10.8	12.0	14.2	16.5
110	.5859	6.5	7.0	8.2	9.5	10.8	12.0	13.2	15.7	18.2
120	.5626	7.1	7.7	9.0	10.4	11.8	13.1	14.5	17.3	20.0
130	.5411	7.7	8.3	9.8	11.3	12.8	14.3	15.8	18.8	21.8
140	.5212	8.4	9.0	10.6	12.2	13.8	15.4	17.1	20.3	23.5
150	.5027	9.0	9.7	11.4	13.1	14.9	16.6	18.3	21.8	25.2

Gravity		Volume of vapor in cu. ft./gal. at various temperatures in ° F.								
Degrees A. P. I. at 60° F.	Specific at 60°/60° F.	60°	100°	200°	300°	400°	500°	600°	800°	1,000°
20	0.9340							14	17	19
25	.9042						17	18	22	25
30	.8762					18	20	22	27	31
35	.8498				19	21	24	26	31	36
40	.8251			19	21	24	27	30	36	41
45	.8017		18	21	24	27	30	33	40	46
50	.7796	18	19	23	26	30	33	36	43	50
55	.7587	19	21	25	28	32	36	39	47	54
60	.7389	21	22	26	30	34	38	42	50	58
65	.7201	22	24	28	32	37	41	45	54	62
70	.7022	23	25	30	34	39	43	48	57	66
75	.6852	25	27	31	36	41	46	50	60	69
80	.6690	26	28	33	38	43	48	53	63	72
85	.6536	27	29	34	39	44	50	55	65	75
90	.6388	28	30	36	41	46	52	57	68	78
95	.6247	29	31	37	42	48	53	59	70	81
100	.6112	30	32	38	44	50	55	61	72	84
110	.5859	32	34	40	46	53	58	65	77	89
120	.5626	33	36	42	49	55	61	68	81	94
130	.5411	35	38	44	51	58	64	71	85	98
140	.5212	36	39	46	53	60	67	74	88	102
150	.5027	38	41	48	55	62	70	77	91	106

VI. THERMAL CONDUCTIVITY

The data on thermal conductivity of petroleum liquids, given in Table 10, were calculated from the following equation:

$$K = \frac{0.813}{d} [1 - 0.0003(t - 32)] \quad (4)$$

in which K = thermal conductivity in Btu. per hr., sq. ft., and °F. per in., d = specific gravity of liquid at 60°/60° F., and t = temperature in °F. This equation is based on experimental results obtained at atmospheric pressure on a total of 18 petroleum oils by 7 different observers as indicated in second part of Table 10.

Equation (4) is fairly consistent with most of the available experimental data on petroleum oils as shown by the percentage differences between observed and calculated values. The data in the first part of Table 10 are applicable to petroleum products at atmospheric pressure with an estimated accuracy of about 10 per cent. The data are probably too low at high pressures, although Bridgman found the thermal conductivity increased only about 2 per cent per 100 atmospheres at temperatures below 200° F.

The data given in Table 10 for paraffin wax are those selected from a critical review of the results of various observers (for references, see International Critical Tables, Vol. V). Differences in the results for paraffin waxes of different melting points are comparable with the differences found by various observers for waxes of the same melting point. The thermal conductivity of paraffin wax decreases slightly with increased temperature, about 0.1 per cent per °F. and probably decreases rapidly near the melting point, becoming equal to that for petroleum liquids of corresponding gravity at temperatures above the melting point.

The data given in the first part of Table 10 for asphalt are based on the only experimental results found in the literature on asphalt practically free from mineral matter, namely, those obtained by Max Jacob. Considerably higher values were found by Griffiths and by Poensgen for materials which probably contained different amounts of mineral matter although no quantitative data on the mineral content are given by these observers.

Example.—The opposite faces of a slab of petroleum asphalt, 3 inches thick, are maintained at 32° and 77° F., respectively. What is the heat flow per day through each square foot of the slab? The result is obtained as follows: $1.2 \times 24 \times 1 \times \frac{45}{3} = 432$ Btu.

TABLE 10.—*Thermal conductivity of petroleum products*

Temperature	Liquids of various gravities						Solids	
	Degrees A. P. I. at 60° F.						Amorphous	Crystalline
	10	20	30	40	50	60	Asphalt	Paraffin wax
	Specific gravity at 60°/60° F.							
	1.0000	0.9340	0.8762	0.8251	0.7796	0.7389		
Units: Btu. per hr., sq. ft., and °F. per in.								
°F.							1.2	1.6
0	0.82	0.88	0.94	1.00	1.05	1.11	(For temperature range, 32° F. to melting point.)	
200	.77	.83	.88	.94	.99	1.05		
400	.72	.77	.83	.88	.93	0.98		
600	.67	.72	.77	.82				
800	.63	.67	.71					
Units: Cal. per sec., cm ² , and °C. per cm								
°C.							0.00040	0.00056
0	0.00028	0.00030	0.00032	0.00034	0.00036	0.00038	(For temperature range, 0°C. to melting point.)	
100	.00027	.00028	.00030	.00032	.00034	.00036		
200	.00025	.00027	.00029	.00030	.00032	.00034		
300	.00024	.00025	.00027	.00028				
400	.00022	.00024	.00025					

Experimental data on petroleum oils compared with equation (10)

Observer	Number of—		Range		Difference in per cent obs.—calc.		Reference
	Oils	Observations	Sp. gr.	Temp. °F.	Average	Maximum	
Bridgman-----	1	2	(0.81)	86-167	±3	+5	(1)
Van Dusen-----	5	8	0.86-0.95	80-200	±3	+6	(2)
Ernst-----	1	1	(0.90)	162-194	-3	-3	(3)
Graetz-----	1	4	0.788	32-115	±6	+13	(4)
Weber-----	2	12	0.78-0.87	32-95	±8	+16	(5)
Kaye and Higgins-----	4	39	0.81-0.90	68-400	±8	+18	(6)
Davis-----	4	23	0.81-0.92	54-167	-8	-27	(7)

Experimental data on bituminous substances

Observer	Material described as—	Specific gravity	Temp. °F.	Thermal conductivity		Reference
				Btu. in. hr. ft. ² °F.	Cal. cm sec. cm ² °C.	
Jacob-----	Bitumen-----	1.05	68	1.16	0.000400	(8)
		1.05	176	1.19	.000411	(8)
Griffiths-----	{ Bitumen used for cementing cork (2 different samples).	{ Not stated.	86	2.9	.0010	(9)
		{ Not stated.	86	4.4	.0015	(9)
Poensgen-----	Asphalt used for road-making.	2.12	50	4.5	.00156	(10)
		2.12	59	4.7	.00161	(10)
		2.12	68	4.8	.00167	(10)
		2.12	86	5.2	.00178	(10)

1 Proc. Am. Academy Arts and Sciences, 59, p. 141; 1923.
 2 Bureau of Standards (unpublished).
 3 Sitzungberichte Akademie Wissenschaften, Wien, 111, p. 922; 1902.
 4 Annalen der Physik, 25, p. 337; 1885.
 5 Annalen der Physik, 11, p. 1047; 1903.
 6 Proc. Royal Soc., London, 117, p. 459; 1928.
 7 Philosophical Magazine, 47, p. 1057; 1924.
 8 Zeitschrift für Technische Physik, 7, p. 475; 1926.
 9 Proceedings IV International Congress of Refrigeration, London, 1, p. 365; 1924.
 10 Zeitschrift des Vereines Deutscher Ingenieure, 56, p. 1653; 1912.

VII. SPECIFIC HEAT

The data on specific heat of petroleum oils, given in Tables 12 and 13, were calculated from the equation

$$c = \frac{1}{\sqrt{d}}(0.388 + 0.00045t) \quad (5)$$

in which c = specific heat in Btu. per pound per °F., or calories per gram per °C., d = specific gravity at 60°/60° F., and t = temperature in °F.

This equation is based on over 100 measurements made by the electric heating method at the Bureau of Standards, within the temperature interval 32° to 400° F., on 30 petroleum oils ranging in specific gravity at 60°/60° F. from 0.75 to 0.96. The experimental results differ from the values calculated from this equation by less than 2 per cent, on the average, and by about 4 per cent as a maximum. The results on oils from mixed base crudes are in excellent agreement with the calculated values, whereas the results on oils from paraffin base crudes are systematically higher by about 2 per cent, on the average, and the results on oils from naphthene base crudes are systematically lower by about 2 per cent than the values calculated from the equation. The magnitudes of these systematic differences are consistent with specific heat data on pure hydrocarbons of the paraffin and naphthene series (see reference 13, to Table 11).

The bureau's data when extrapolated above 400° F. by means of the equation, are consistent within about 5 per cent with apparently the only published experimental data extending over the temperature interval 400° to 750° F., namely, those of Fortsch and Whitman, Zeitfuchs, and Karawajeff.

A brief summary of all the specific heat data on petroleum oils found in the literature is given in Table 11, which shows that the data obtained by 16 groups of observers by 5 different methods agree within 5 per cent on the average with values calculated from the above equation. A critical study of these data has indicated that differences between observed and calculated values greater than 5 per cent were not caused by differences in hydrocarbon contents, but were probably caused by one or more of the following:

- (a) Evaporation or condensation (volatile products).
- (b) Solidification or liquefaction (distillates containing wax).
- (c) Foreign materials, such as water, sulphur, etc. (crudes).
- (d) Incorrect evaluation of heat leakage.
- (e) Incorrect evaluation of heat capacity of calorimeter or container.
- (f) Incorrect temperature measurements.

The specific heat chart prepared by W. R. Eckhart and published in *Mechanical Engineering*, 47, p. 539; 1925, gives values at 60° F. which are in good agreement with the values given in Table 12. Eckhart's values at higher temperatures, however, are considerably larger, amounting to over 30 per cent at the highest temperatures.

TABLE 11.—Data of various observers on specific heat of petroleum oils compared with Bureau of Standards data as expressed by equation (5)

Observer	Method	Number of—		Range		Difference in per cent Obs.—Calc.		Probable cause of large differences	Reference
		Oils	Observations	Sp. gr. 60°/60° F.	Temp. °F.	Average	Maximum		
Siivola	I	1	4	0. 826	32-205	-1. 0	-2. 0		(1)
Regnault	C	1	3	0. 891	41-68	-1. 1	-1. 8		(2)
Regnault	M	1	2	0. 891	60-210	-1. 6	-2. 1		(3)
Rey	M	1	4	0. 81	18-244	± 1. 7	+4. 0		(4)
Karawajeff	I	8	45	0. 82-0. 92	32-756	± 1. 8	+4. 2		(5)
Regnault	M	1	1	0. 891	64-433	-1. 9	-1. 9		(6)
Kuklin	C	5	30	0. 75-0. 87	60-104	± 2. 0	-5. 6	(a)	(7)
Davis	M	4	4	0. 81-0. 92	68-212	± 2. 8	-4. 5		(8)
Brame	X	12	12	0. 72-0. 93	54-77	± 2. 8	-5. 7		(9)
Fortsch and Whitman	E	14	132	0. 74-1. 00	35-554	± 3. 0	+14. 3	(d) (e)	(10)
Scheller and Georghiu	B	11	11	0. 72-0. 92	60-68	± 3. 2	+4. 8		(11)
Graefe	B	8	8	0. 71-0. 89	60-77	± 3. 5	-8. 6	(c)	(12)
Bushong and Knight	B	22	64	0. 71-0. 99	52-176	± 3. 7	-9. 8	(d)	(13)
Mabery and Goldstein	I	8	8	0. 79-0. 96	32-122	± 4. 0	-7. 7	(b) (c)	(14)
Zeitfuchs	M	5	28	0. 78-1. 02	77-712	± 4. 6	+10. 2	(a) (f)	(15)
Leslie and Geniesse	E	6	30	0. 89-0. 92	100-300	± 4. 8	-15. 7	(f)	(16)
Syniewski	X	7	7	0. 74-0. 82	68-104	+8. 3	+14. 3	(a)	(17)
Heinlein	E	5	23	0. 74-0. 91	77-200	+12. 0	+22. 3	(d) (e)	(18)
<p>(Specific gravity of oil or temperature of experiment not stated; differences estimated by assuming approximate specific gravity or temperature consistent with general description)</p>									
Wales	M	12	12		68	< 5			(19)
Redwood	X	9	9	0. 64-0. 89		< 5			(20)
Kuklin	M	2	8	0. 74-0. 76		< 5			(7)
Mabery and Goldstein	I	2	2		32-122	< 5			(14)
Bailey and Edwards	E	1	6		122-437	< 5			(21)
Pagliani	M	1	3		64-200	< 5			(22)
Marden and Dover	M	1	1		77-86	< 5			(23)
Sherman, Danziger, and Kohnstamm	X	1	1	0. 817		< 5			(24)
Schmitz	X	7	7	0. 86-0. 95		> 5		(b)	(25)
Sullivan, McGill, and French	E	2	2			> 5		(d) (e)	(26)

METHODS: B=bomb calorimeter (heat supplied to oil from combustion of naphthalene, benzoic acid, etc.); C=cooling method (see Preston's "Theory of Heat," p. 244; 1919 ed.); E=electric heating method; I=ice calorimeter; M=method of mixtures; and X=method not stated.

¹ Oversikt av Finska Vetenskaps-Societetens Forhandlingar, 56, No. 8, p. 7; 1913-14.

² Annales de Chimie et Physique, 9, p. 349; 1843.

³ Annales de Chimie et Physique, 73, p. 5; 1840.

⁴ Annales des Mines, 8, p. 68; 1925.

⁵ Petroleum Zeitschrift, 9, p. 1114; 1914.

⁶ Mémoires de l'Académie des Sciences, France, 26, p. 262; 1862.

⁷ Berichte der Deutschen Chemischen Gesellschaft, 16, p. 949; 1883.

⁸ Philosophical Magazine, 47, p. 1057; 1924.

⁹ B. Redwood's "Treatise on Petroleum," I, p. 222; 1913.

¹⁰ Industrial and Engineering Chemistry, 18, p. 795; 1926.

¹¹ Petroleum Zeitschrift, 8, p. 533; 1913.

¹² Petroleum Zeitschrift, 2, p. 521; 1907.

¹³ Ind. & Eng. Chem., 12, p. 1197; 1920.

¹⁴ Proc. Am. Acad. Arts & Sci., 37, p. 539; 1913.

¹⁵ Ind. & Eng. Chem., 18, p. 79; 1926.

¹⁶ Ind. & Eng. Chem., 16, p. 582; 1924.

¹⁷ Zeitschrift für Angewandte Chemie, 11, p. 621; 1898.

¹⁸ Der Motorwagen, p. 75; Feb. 10, 1926.

¹⁹ Ind. & Eng. Chem., 6, p. 727; 1914.

²⁰ I. I. Redwood's, Mineral Oils and Their By-Products, p. 200; 1897.

²¹ Ind. & Eng. Chem., 12, p. 892; 1920.

²² Atti della reale accademia delle scienze di Torino, 17, p. 97; 1881.

²³ Ind. Eng. Chem., 9, p. 860; 1917.

²⁴ J. Am. Chem. Soc., 24, p. 269; 1902.

²⁵ Les Matières Grasses, Jan. No. 58, p. 3005; 1913.

²⁶ Ind. & Eng. Chem., 19, p. 1040; 1927.

1. SPECIFIC HEAT OF PETROLEUM OILS OF VARIOUS GRAVITIES IN BTU./LB. °F. OR CAL./G. °C.

The data given in Table 12 represent average values based on measurements described on page 26. The estimated accuracy of the tabulated data as true specific heats at a constant pressure of 1 atmosphere is 5 per cent. The data are probably somewhat too low for pressures much above 100 lbs./in.² The data do not take into account such quantities as latent heat of fusion, latent heat of vaporization, and heat of reaction (cracking).

Since the relation between true specific heat and temperature is linear, the mean specific heat between any two temperatures is equal to the true specific heat at the mean temperature.

Example.—What are the true specific heats of a 30° A. P. I. oil (a) at 100° F., (b) at 500° F., and (c) what is the mean specific heat between 100° and 500° F.? The following values are obtained from Table 12: (a) true specific heat at 100° F.=0.463; (b) true specific heat at 500° F.=0.655; (c) mean specific heat between 100° and 500° F.=0.559.

2. SPECIFIC HEAT OF PETROLEUM VAPORS

There are in the literature practically no data on the specific heat of petroleum vapors. Approximate values for the specific heat at constant pressure (moderate pressures) may be obtained from the relation

$$\frac{dL}{dt} = C_g - C_l$$

in which L =latent heat of vaporization, t =temperature, C_g =specific heat of gaseous phase at constant pressure, and C_l =specific heat of liquid phase.

Evaluating the rate of change of latent heat of vaporization with temperature $\frac{dL}{dt}$, from equation (6) given in Section VIII, gives

$$C_g = C_l - \frac{0.09}{d}$$

where d =specific gravity at 60°/60° F. of the liquid corresponding to the condensed vapor.

Example.—What is the specific heat at a constant pressure of one atmosphere of 60° A. P. I. gasoline vapor at 400° F.? An approximate value may be obtained as follows:

$$C_g = 0.661 - \frac{0.09}{0.7389} = 0.54 \text{ Btu./lb. °F.}$$

NOTE ADDED TO PROOF.—The recent experimental values obtained by Bahlke and Kay (Ind. & Eng. Chem., 21, p. 942; 1929) agree with values calculated as outlined above within about 3 per cent on the average.

TABLE 12.—Specific heat of petroleum oils of various gravities in Btu./lb.°F. or cal./g °C.

Temp. °F.	Degrees A. P. I. at 60° F.								Temp. °F.
	10	20	30	40	50	60	70	80	
	Specific gravity at 60°/60° F.								
	1.0000	0.9340	0.8762	0.8251	0.7796	0.7389	0.7022	0.6680	
0	0.388	0.401	0.415	0.427	0.439	0.451	0.463	0.474	0
20	.397	.411	.424	.437	.450	.462	.474	.485	20
40	.406	.420	.434	.447	.460	.472	.485	.496	40
60	.415	.429	.443	.457	.470	.483	.495	.507	60
80	.424	.439	.453	.467	.480	.493	.506	.518	80
100	.433	.448	.463	.477	.490	.504	.517	.529	100
120	.442	.457	.472	.487	.501	.514	.527	.540	120
140	.451	.467	.482	.497	.511	.525	.538	.551	140
160	.460	.476	.491	.506	.521	.535	.549	.562	160
180	.469	.485	.501	.516	.531	.546	.560	.573	180
200	.478	.495	.511	.526	.541	.556	.570	.584	200
220	.487	.504	.520	.536	.552	.567	.581	-----	220
240	.496	.513	.530	.546	.562	.577	.592	-----	240
260	.505	.523	.540	.556	.572	.588	.603	-----	260
280	.514	.532	.549	.566	.582	.598	.613	-----	280
300	.523	.541	.559	.576	.592	.609	.624	-----	300
320	.532	.550	.568	.586	.603	.619	-----	-----	320
340	.541	.560	.578	.596	.613	.629	-----	-----	340
360	.550	.569	.588	.606	.623	.640	-----	-----	360
380	.559	.578	.597	.615	.633	.650	-----	-----	380
400	.568	.588	.607	.625	.643	.661	-----	-----	400
420	.577	.597	.616	.635	.653	-----	-----	-----	420
440	.586	.606	.626	.645	.664	-----	-----	-----	440
460	.595	.616	.636	.655	.674	-----	-----	-----	460
480	.604	.625	.645	.665	.684	-----	-----	-----	480
500	.613	.634	.655	.675	.694	-----	-----	-----	500
520	.622	.644	.665	.685	-----	-----	-----	-----	520
540	.631	.653	.674	.695	-----	-----	-----	-----	540
560	.640	.662	.684	.705	-----	-----	-----	-----	560
580	.649	.672	.693	.715	-----	-----	-----	-----	580
600	.658	.681	.703	.724	-----	-----	-----	-----	600
620	.667	.690	.713	-----	-----	-----	-----	-----	620
640	.676	.699	.722	-----	-----	-----	-----	-----	640
660	.685	.709	.732	-----	-----	-----	-----	-----	660
680	.694	.718	.741	-----	-----	-----	-----	-----	680
700	.703	.727	.751	-----	-----	-----	-----	-----	700
720	.712	.737	.761	-----	-----	-----	-----	-----	720
740	.721	.746	.770	-----	-----	-----	-----	-----	740
760	.730	.755	.780	-----	-----	-----	-----	-----	760
780	.739	.765	.790	-----	-----	-----	-----	-----	780
800	.748	.774	.799	-----	-----	-----	-----	-----	800

3. SPECIFIC HEAT OF PETROLEUM OILS OF VARIOUS GRAVITIES IN BTU./GAL. °F.

The data given in Table 13 represent average values based on measurements described on page 26. For statements regarding the estimated accuracy and the limitations of the tabulated data, see page 28. The unit of mass used in Table 13 is 1 gallon of oil at 60° F.

Example.—How much heat is required to produce a change of 1° F. in the temperature of a gallon of 30° A. P. I. oil (both referred to 60° F.): (a) When oil is at 100° F.; (b) when oil is at 500° F.? The following values are obtained from Table 12: (a) 3.38 Btu. at 100° F.; (b) 4.78 Btu. at 500° F.

4. SPECIFIC HEAT OF PETROLEUM ASPHALT

Measurements of specific heat by the method of mixtures have been made at the Bureau of Standards on one sample of petroleum asphalt having the following characteristics: Specific gravity at 77° F., 1.044; melting point (ball and ring method), 125° F.; loss after five hours at 325° F., 0.1 per cent; penetration at 77° F., 67 before heating, 60 after heating; soluble in carbon disulphide, 99.6 per cent; ash, 0.1 per cent. No evidence was found of any irregularity in the specific heat between -100° and +300° F., which indicates that petroleum asphalt may be regarded thermally as a subcooled liquid with no heat of transformation from liquid to apparent solid. The measurements on this sample agree within 2 per cent with the data given in the 10° A. P. I. columns of Tables 12 and 13, which indicates that the data in these columns are probably applicable to petroleum asphalts and to the bitumen content of natural asphalts. This indication is confirmed by the measurements of Zeitfuchs (see reference 15 on page 27) on a California asphalt, 70 penetration, specific gravity 1.013, and by the measurements of A. W. Dow (Municipal Engineering, **27**, p. 22; 1904) on the following refined natural asphalts: Trinidad, Maracaibo, Cuban, and Bermudez.

In many practical applications, petroleum asphalt is mixed with various amounts of solids, such as sand, crushed rock, etc. The specific heat of such mixtures may be obtained from the equation

$$C_m = 0.01[(100-x)C_a + xC_s] \quad (5a)$$

in which x = per cent, by weight, of solids, C = specific heat, and the subscripts, a , s , and m refer to asphalt, solid, and mixture, respectively. The relation, $C_s = 0.18 + 0.00006t$ ° F., may be used for the solid constituents. (See International Critical Tables, Vol. II, pp. 55, 63, and 128 for experimental data.) Values for C_a may be taken from 10° A. P. I. column of Table 12.

Example.—What is the specific heat at 60° F. of bituminous material containing by weight 15 per cent asphalt and 85 per cent solid materials? Table 12 and the above relations give $C_m = 0.01(15 \times 0.415) + (85 \times 0.184) = 0.22$.

Kinoshita (Gesundheits-Ingenieur, **39**, p. 497; 1916) obtained 0.22 for the mean specific heat between 32° and 68° F. of an "asphalt" of specific gravity 2.10. No further description of the material is given. The values for specific heat and specific gravity are consistent with the data in the above example.

TABLE 13.—Specific heat of petroleum oils of various gravities in Btu./gal. °F.

Temp. °F.	Degrees A. P. I. at 60° F.								Temp. °F.
	10	20	30	40	50	60	70	80	
	Specific gravity at 60°/60° F.								
	1.0000	0.9340	0.8762	0.8251	0.7796	0.7389	0.7022	0.6690	
0	3.23	3.13	3.03	2.94	2.86	2.78	2.71	2.65	0
20	3.31	3.20	3.10	3.01	2.92	2.85	2.77	2.71	20
40	3.38	3.26	3.17	3.07	2.99	2.91	2.84	2.77	40
60	3.46	3.33	3.24	3.14	3.06	2.97	2.90	2.83	60
80	3.53	3.41	3.31	3.21	3.12	3.04	2.96	2.89	80
100	3.61	3.49	3.38	3.28	3.19	3.10	3.02	2.95	100
120	3.69	3.56	3.45	3.35	3.25	3.17	3.09	3.01	120
140	3.76	3.63	3.52	3.41	3.32	3.23	3.15	3.08	140
160	3.84	3.71	3.59	3.48	3.39	3.30	3.21	3.14	160
180	3.91	3.78	3.66	3.55	3.45	3.36	3.28	3.20	180
200	3.99	3.85	3.73	3.62	3.52	3.43	3.34	3.26	200
220	4.06	3.92	3.80	3.69	3.58	3.49	3.40	-----	220
240	4.14	4.00	3.87	3.75	3.65	3.55	3.46	-----	240
260	4.21	4.07	3.94	3.82	3.72	3.62	3.53	-----	260
280	4.29	4.14	4.01	3.89	3.78	3.68	3.59	-----	280
300	4.36	4.21	4.08	3.96	3.86	3.75	3.65	-----	300
320	4.44	4.29	4.15	4.03	3.93	3.81	-----	-----	320
340	4.51	4.36	4.22	4.09	3.99	3.88	-----	-----	340
360	4.59	4.43	4.29	4.16	4.06	3.94	-----	-----	360
380	4.66	4.50	4.36	4.23	4.12	4.01	-----	-----	380
400	4.74	4.58	4.43	4.30	4.19	4.07	-----	-----	400
420	4.81	4.65	4.50	4.37	4.26	-----	-----	-----	420
440	4.89	4.72	4.57	4.44	4.32	-----	-----	-----	440
460	4.96	4.79	4.64	4.50	4.39	-----	-----	-----	460
480	5.04	4.87	4.71	4.57	4.46	-----	-----	-----	480
500	5.11	4.94	4.78	4.64	4.52	-----	-----	-----	-----
520	5.19	5.01	4.85	4.71	-----	-----	-----	-----	-----
540	5.26	5.08	4.92	4.78	-----	-----	-----	-----	-----
560	5.34	5.16	4.99	4.84	-----	-----	-----	-----	-----
580	5.41	5.23	5.06	4.91	-----	-----	-----	-----	-----
600	5.49	5.30	5.13	4.98	-----	-----	-----	-----	-----
620	5.56	5.37	5.20	-----	-----	-----	-----	-----	-----
640	5.64	5.45	5.27	-----	-----	-----	-----	-----	-----
660	5.71	5.52	5.34	-----	-----	-----	-----	-----	-----
680	5.79	5.59	5.41	-----	-----	-----	-----	-----	-----
700	5.86	5.66	5.49	-----	-----	-----	-----	-----	-----
720	5.94	5.74	5.56	-----	-----	-----	-----	-----	-----
740	6.01	5.81	5.63	-----	-----	-----	-----	-----	-----
760	6.09	5.88	5.70	-----	-----	-----	-----	-----	-----
780	6.16	5.95	5.77	-----	-----	-----	-----	-----	-----
800	6.24	6.03	5.84	-----	-----	-----	-----	-----	-----

VIII. LATENT HEAT OF VAPORIZATION

The data on latent heat of vaporization of petroleum oils, given in Table 15, were calculated from the equation

$$L = \frac{1}{d}(110.9 - 0.09t) \quad (6)$$

in which L = latent heat of vaporization in Btu./lb., d = specific gravity of liquid at 60°/60° F., and t = temperature in °F. This equation is based on calorimetric measurements found in the literature on latent heat of vaporization of petroleum distillates, all of which are enumerated briefly in the first part of Table 14.

All of these measurements were made at atmospheric pressure, except for those of Rey, which extended to a pressure of 7 atmospheres. In the experiments of Syniewski, Ormandy and Craven, Regnault, and Kuklin, petroleum vapors were condensed in a water calorimeter. Their results yielded, therefore, values of total heat of vaporization from liquid at room temperature to vapor at 1 atmosphere pressure. These observed values were reduced to latent heats of vaporization for the purpose of comparison (Table 14), by means of the data on specific heat of liquid given in the previous section. The values of latent heat so obtained differ somewhat from those reported by the various authors, because, in one case, an arbitrary value for specific heat was used and, in other cases, the increase of specific heat with temperature was neglected.

Equation (6) is fairly consistent with most of the available experimental data on petroleum distillates as shown by the percentage differences between observed and calculated values. The results obtained by Heinlein are obviously inconsistent with the results of other observers. This was probably caused, in part at least, by the fact that there was good opportunity for reflux condensation in Heinlein's experiments.

Equation (6) yields values which differ less than 10 per cent, on the average, from experimental results obtained at 1 atmosphere pressure on the following hydrocarbons: *n*-hexane, 4-methylheptane, cyclohexane, and methylcyclohexane (Mathews, *J. Am. Chem. Soc.*, **48**, p. 562; 1926); *n*-hexane, *n*-heptane, *n*-octane, hexamethylene, dimethylpentamethylene, methylhexamethylene, and dimethylhexamethylene (Mabery and Goldstein, *Proc. Amer. Acad. Arts and Sci.*, **37**, p. 549; 1902); *n*-decane (Louguinine, *Ann. Chim. phys.*, **13**, p. 289; 1898).

In addition to being in general accord with the available experimental results on petroleum distillates and individual petroleum hydrocarbons, equation (6) is in fair agreement with about the only existing evidence on the magnitude of the variation of latent heat with temperature or pressure over a considerable range below the critical point as shown by the second part of Table 14.

There are in the literature numerous values for the latent heat of vaporization of petroleum distillates, some of which were calculated by means of Trouton's rule from measurements of "apparent" molecular weight and "average" boiling point of the distillates, while others were obtained from data on pure substances by means of Trouton's or Hildebrand's rule. The values so obtained are uniformly higher than those found by calorimetric measurements on petroleum distillates, amounting in some cases to nearly 100 per cent. Probably the major reasons for the higher values are (1) that Trouton's and Hildebrand's rules are not applicable to complete vaporization of mixtures with a wide range of boiling points, and (2) that the "apparent" molecular weights of the heavier distillates are too low.

TABLE 14.—Comparison of observed and calculated values of latent heat of vaporization of petroleum distillates and pure hydrocarbons

Observer	Method	Range		Number of—		Difference in per cent obs.-calc.		Reference
		Sp. gr. 60°/60° F.	Temp. ° F.	Oils	Observations	Average	Maximum	
Syniewski	Mixtures	0. 74–0. 83	212–470	7	7	±2	–6	(1)
Gurwitsch	Not stated	. 64–. 81	104–348	6	6	–4	–9	(2)
Ormandy and Craven	Mixtures	. 70–. 75	232–250	3	11	±4	–10	(3)
Leslie, Geniesse, Legatski and Jagrawski.	Electric heating	. 68–. 82	152–576	17	17	±6	+10	(4)
Regnault	Mixtures	. 89	536	1	2	+7	+10	(5)
Rey	Not stated	. 81	347–527	1	6	+9	+16	(6)
Kuklin	Mixtures	. 74–. 76	200–235	2	8	+12	+19	(7)
Redwood	Not stated	. 64–. 81	70–260	4	4	±19	–39	(8)
Heinlein	Electric heating	. 74–. 91	194–345	5	23	+40	+70	(9)

Temperature		Pressure atmos.	Latent heat		Difference in per cent obs.-calc.	Pressure atmos.	Latent heat		Difference in per cent obs.-calc.	Temp. ° C.
° C.	° F.		Observations ¹⁰	Calculations			Observations ¹⁰	Calculations		
(Normal pentane)										
0	32	0. 24	168	171	–2	0. 06	164	163	+1	0
20	68	. 55	160	166	–4	. 16	158	158	0	20
40	104	1. 12	152	161	–6	. 36	152	153	–1	40
60	140	2. 11	144	156	–8	. 75	145	148	–2	60
80	176	3. 60	136	151	–11	1. 40	140	143	–2	80
100	212	5. 80	126	145	–15	2. 42	132	138	–4	100
120	248	8. 87	116	140	–21	3. 92	125	133	–6	120
140	284	13. 0	102	135	–32	6. 06	115	129	–12	140
160	320	18. 5	85	130	–53	8. 94	104	124	–19	160
180	356	25. 5	63	125	–98	12. 7	92	119	–29	180
(Normal heptane)										
0	32	0. 015	162	157	+3	0. 004	161	153	+5	0
20	68	. 05	158	152	+3	. 014	156	148	+5	20
40	104	. 12	154	148	+4	. 04	150	144	+4	40
60	140	. 27	149	143	+4	. 10	145	139	+4	60
80	176	. 56	143	138	+3	. 23	139	134	+4	80
100	212	1. 05	136	133	+2	. 46	134	130	+3	100
120	248	1. 80	129	129	0	. 85	129	125	+3	120
140	284	2. 92	121	124	–2	1. 47	123	121	+2	140
160	320	4. 54	113	119	–5	2. 38	117	116	+1	160
180	356	6. 70	105	115	–9	3. 65	110	112	–2	180
200	392	9. 56	96	110	–15	5. 39	101	107	–6	200
220	428	13. 3	84	105	–25	7. 73	94	102	–9	220
240	464	18. 1	67	100	–49	10. 8	83	98	–18	240
260	500	24. 3	39	96	–146	14. 7	70	93	–33	260
280	536	-----	-----	-----	-----	19. 7	51	89	–75	280

¹ Zeitschrift für Angewante Chemie, 11, p. 621; 1898.

² "Wissenschaftliche Grundlagen der Erdölverarbeitung," 2d ed., p. 144; 1924 (J. Springer, Berlin).

³ J. Inst. Petroleum Technologists, 9, p. 368; 1923.

⁴ Ind. & Eng. Chem., 18, p. 45; 1926.

⁵ Mémoires de l'Académie Sciences, France, 26, p. 913; 1862.

⁶ Annales des Mines, 8, p. 53; 1925.

⁷ Berichte der Deutschen Chemischen Gesellschaft, 16, p. 949; 1883.

⁸ "Mineral Oils and Their By-Products" p. 200; 1897 (E. and F. N. Spon (Ltd.), London).

⁹ Der Motorwagen, p. 395, June 30, 1926.

¹⁰ Observed values in Btu./lb. obtained from experimental data on vapor pressure and specific volume by means of Clapeyron equation. (Young, Proc., Royal Dublin Soc., 12, p. 374; 1910; also Mills, J. Am. Chem. Soc., 31, p. 1099; 1909.)

VIII. LATENT HEAT OF VAPORIZATION—Continued

The experimental basis for the data given in Table 15 is described on the preceding pages. The following equation

$$L(\text{Btu./lb.}) = \frac{1}{d} (110.9 - 0.09t)$$

was found to represent satisfactorily most of the experimental results available on petroleum distillates. This equation yields the following convenient relation

$$L(\text{Btu./lb.}) \times \text{density (lbs./gal.)} = 8.33722 Ld = 925 - 0.75t(\text{Btu./gal.}) \quad (7)$$

which indicates that the latent heat of vaporization per unit volume of liquid (60° F.) is dependent only on the temperature of vaporization. Thus, the values given in the second column of Table 15 are applicable to any petroleum oil, regardless of gravity. The values given in the other columns are applicable, in general, to all cases of vaporization of petroleum products in which the temperature of vaporization and the gravity of the condensate are known.

The estimated accuracy of the data in Table 15 is 10 per cent, when vaporization occurs at sensibly constant temperature and at pressures below 50 lbs./in.², without chemical change. The tabulated values are probably too low by more than this amount for petroleum products containing large quantities of the lower members of the aromatic series and too high for vaporization at high pressures, as is illustrated in Table 14.

Example 1.—What is the difference between the latent heats of vaporization of a 50° and a 70° A. P. I. gasoline, assuming complete vaporization occurs at 140° F. in the intake system of an internal-combustion engine? According to Table 15, on a weight basis the difference in latent heats amounts to 140—126=14 Btu./lb. or about 10 per cent, while on a volume basis both gasolines require 820 Btu./gal.

Example 2.—How much latent heat is required to vaporize or condense various petroleum products at the average temperatures indicated below?

Product	Gravity, °A. P. I.	Average tempera- ture °F.	Latent heat from Table 15	
			Btu./lb.	Btu./gal.
Gasoline.....	60	280	116	715
Naphtha.....	50	340	103	670
Kerosene.....	40	440	86	595
Fuel oil.....	30	580	67	490

TABLE 15.—Latent heat of vaporization of petroleum oils

Temp. ° F.	Latent heat 10°-80° A. P. I. oils Btu./gal.	Latent heat of oils of various gravities in Btu./lb.						Temp. ° F.	
		Degrees A. P. I. at 60° F.							
		20	30	40	50	60	70		80
		Specific gravity at 60°/60° F.							
		0.9340	0.8762	0.8251	0.7796	0.7389	0.7022	0.6690	
0	925				142	150	158	166	0
20	910				140	148	155	163	20
40	895				138	145	153	160	40
60	880				135	143	150	158	60
80	865				133	140	148	155	80
100	850			123	131	138	145	152	100
120	835			121	128	135	143	150	120
140	820			119	126	133	140	147	140
160	805			117	124	131	137	144	160
180	790			115	121	128	135	142	180
200	775		106	113	119	126	132	139	200
220	760		104	110	117	123	130		220
240	745		102	108	115	121	127		240
260	730		100	106	112	118	125		260
280	715		98	104	110	116	122		280
300	700	90	96	102	108	113	119		300
320	685	88	94	99	105	111			320
340	670	86	92	97	103	109			340
360	655	84	90	95	101	106			360
380	640	82	88	93	98	104			380
400	625	80	85	91	96	101			400
420	610	78	83	89	94				420
440	595	76	81	86	91				440
460	580	74	79	84	89				460
480	565	73	77	82	87				480
500	550	71	75	80	85				
520	535	69	73	78					
540	520	67	71	75					
560	505	65	69	73					
580	490	63	67	71					
600	475	61	65	69					
620	460	59	63						
640	445	57	61						
660	430	55	59						
680	415	53	57						
700	400	51	55						
720	385	49	53						
740	370	47	51						
760	355	45	48						
780	340	44	46						
800	325	42	44						

IX. HEAT CONTENT

Calculations of the quantities of heat involved in the heating and cooling of fluids are very simple when use is made of the thermodynamic function called heat content (also called total heat and enthalpy). For this reason, data on specific and latent heats have been combined to yield the heat content data given in Tables 16 and 17. Strictly speaking, the data in these tables represent heat content at 1 atmosphere pressure, since they are based on measurements made at atmospheric pressure. The magnitude of the change of heat content with pressure (temperature constant) is small, however, being comparable with the estimated accuracy of these data in general for pressures below 1,000 lbs./in.².

1. HEAT CONTENT OF PETROLEUM LIQUIDS

The experimental basis for the data on heat content of petroleum liquids, given in Table 16, is the same as for the specific heat data described in Section VII. Differences in heat content between 32° F. (or 77° F.) and higher temperatures have been directly measured by numerous observers. The agreement of the observed results and the tabulated values is shown in Table 11.

Following usual practice, the heat content of liquid has been arbitrarily assigned the value zero at 32° F. Thus, for all practical purposes, the heat content of petroleum liquids, H_t is given by the equation

$$H_t = \int_{32}^t c \, dt$$

since the heat equivalent of the external work, $p \, dv$, is so small that it may well be neglected here. Integrating the equation for specific heat, c , given on page 26, and multiplying by $8.33722\bar{d}$ to reduce to a volume basis, gives the following equation for heat content in Btu./gal.

$$H_t = \sqrt{\bar{d}}(3.235t + 0.0001875t^2 - 105.5) \quad (8)$$

in which \bar{d} = specific gravity of liquid at 60°/60° F. and t = temperature in °F. This equation was used to calculate the data given in Table 16.

The estimated accuracy of the data in Table 16 as heat content at 1 atmosphere pressure is 5 per cent. The data are probably too low by more than this amount in the neighborhood of the critical point. The data do not take into account such quantities as latent heats of fusion and vaporization and heats of chemical reaction.

2. HEAT CONTENT OF PETROLEUM VAPORS

The data on heat content of petroleum vapors, given in Table 17, were calculated from the following equation

$$H_v = \sqrt{d}(3.235t + 0.001875t^2 - 105.5) + 925 - 0.75t \quad (9)$$

which represents a combination of heat content of liquid, equation (8), and latent heat of vaporization, equation (7). Thus the data on heat content of vapor represent values above that of the heat content of liquid at 32° F.

The experimental basis for the data in Table 17 is the same as for the specific and latent heat data described in Sections VII and VIII. It may be noted that the heat content of petroleum vapors above that of liquid at room temperature has been directly measured by Syniewski, Ormandy and Craven, Regnault, and Kuklin. (See Table 14 for references.) The results obtained by these observers are consistent with the data in Table 17 within 5 per cent on the average.

Wilson and Barnard (*Ind. & Eng. Chem.*, **13**, p. 912; 1921) determined the heat content of gasoline and kerosene vapor at atmospheric pressure by heating these vapors to temperatures of 550° to 850° F. and measuring the heat given up in changing to liquid at room temperature. Their results agree within 10 per cent with the data given in Table 17. The agreement is within 5 per cent when account is taken of the fact that the specific heat of the saturated vapor is less than that of the liquid (see Sec. VII (2)), and that specific heats of superheated vapors increase less rapidly with temperature, in general, than do those of liquids.

The accuracy of the data in Table 17, estimated solely from the agreement with all of the rather meager experimental data available on petroleum vapors and from known data on the properties of pure substances, is as follows: 5 per cent for vapor saturated at atmospheric pressure or below; 10 per cent for vapor saturated at any temperature and pressure; 15 per cent for vapor at any pressure and superheated by any amount. The data do not take into account heats of chemical reactions.

As pointed out in Sections VII and VIII, the specific heat data are too low and the data on latent heat of vaporization are too high for the higher pressures. There is considerable compensation, therefore, in the resultant values for heat content. There is an analogous compensation in the case of vapors rich in aromatics,

TABLE 16.—Heat content of petroleum liquids of various gravities in Btu./gal.¹

Temp. ° F.	Degrees A. P. I. at 60° F.								Temp. ° F.
	10	20	30	40	50	60	70	80	
	Specific gravity at 60°/60° F.								
	1.0000	0.9340	0.8762	0.8251	0.7796	0.7389	0.7022	0.6690	
0	-105	-102	-99	-96	-93	-91	-88	-86	0
10	-73	-70	-68	-66	-64	-63	-61	-60	10
20	-40	-39	-37	-36	-35	-34	-34	-33	20
32	0	0	0	0	0	0	0	0	32
40	+27	+26	+25	+24	+24	+23	+23	+22	40
50	61	59	57	55	54	52	51	50	50
60	95	92	89	86	84	82	80	78	60
70	130	126	122	118	115	112	109	106	70
80	165	160	155	150	146	142	138	135	80
90	201	194	188	182	177	173	168	164	90
100	237	229	222	215	209	204	198	194	100
110	273	264	256	248	241	235	229	223	110
120	310	300	290	281	273	267	260	253	120
130	347	335	325	315	306	299	291	284	130
140	384	371	360	349	339	331	322	314	140
150	422	408	395	383	372	363	354	345	150
160	460	445	431	418	406	396	386	376	160
170	499	482	467	453	440	429	418	408	170
180	538	520	503	488	475	462	451	440	180
190	577	558	540	524	509	496	484	472	190
200	617	596	577	560	544	530	517	504	200
210	657	635	615	596	580	564	550	537	210
220	697	674	652	633	615	599	584	570	220
230	738	713	691	670	651	634	618	603	230
240	779	753	729	707	688	669	653	637	240
250	820	793	768	745	724	705	688	671	250
260	862	833	807	783	761	741	723	705	260
270	904	874	847	822	799	778	758	740	270
280	947	915	887	861	836	814	794	775	280
290	990	957	927	900	874	851	830	810	290
300	1,034	999	968	939	913	889	866	846	300
310	1,078	1,041	1,009	979	952	926	903	881	310
320	1,122	1,084	1,050	1,019	991	964	940	917	320
330	1,166	1,127	1,092	1,059	1,030	1,002	977	954	330
340	1,211	1,170	1,134	1,100	1,070	1,041	1,015	981	340
350	1,256	1,214	1,176	1,141	1,110	1,080	1,053	1,028	350
360	1,302	1,258	1,219	1,183	1,150	1,119	1,091	1,065	360
370	1,348	1,303	1,262	1,225	1,190	1,159	1,130	1,103	370
380	1,395	1,348	1,306	1,267	1,231	1,199	1,169	1,141	380
390	1,441	1,393	1,349	1,309	1,273	1,239	1,208	1,179	390
400	1,489	1,439	1,393	1,352	1,314	1,280	1,247	1,217	400

¹ The unit used here is 1 gallon of oil at 60° F. See page 36 for statements regarding the experimental basis for these data and their estimated accuracy.

Example.—How much heat is required to raise the temperature of a 30° A. P. I. oil from 70° to 500° F.? The result is obtained from Table 16 as follows:
 Heat content at 500° F. = 1,854 Btu./gal.
 Heat content at 70° F. = 122 Btu./gal.
 Heat required = difference = 1,732 Btu./gal.

TABLE 16.—Heat content of petroleum liquids of various gravities in Btu./gal.—Continued

Temp. ° F.	Degrees A. P. I. at 60° F.								Temp. ° F.
	10	15	20	25	30	35	40	45	
	Specific gravity at 60°/60° F.								
	1.0000	0.9659	0.9340	0.9042	0.8762	0.8498	0.8251	0.8017	
400	1,489	1,463	1,439	1,416	1,393	1,372	1,352	1,333	400
410	1,536	1,510	1,485	1,461	1,438	1,416	1,395	1,375	410
420	1,584	1,557	1,531	1,506	1,483	1,460	1,439	1,418	420
430	1,632	1,604	1,578	1,552	1,528	1,505	1,483	1,461	430
440	1,681	1,652	1,625	1,598	1,573	1,549	1,527	1,505	440
450	1,730	1,700	1,672	1,645	1,619	1,595	1,571	1,549	450
460	1,779	1,749	1,720	1,692	1,666	1,640	1,616	1,593	460
470	1,829	1,798	1,768	1,740	1,712	1,686	1,661	1,638	470
480	1,879	1,847	1,816	1,787	1,759	1,732	1,707	1,683	480
490	1,930	1,897	1,865	1,835	1,806	1,779	1,753	1,728	490
500	1,981	1,947	1,914	1,884	1,854	1,826	1,799	1,774	500
510	2,032	1,997	1,964	1,932	1,902	1,873	1,846	1,820	510
520	2,084	2,048	2,014	1,981	1,950	1,921	1,893	1,866	520
530	2,136	2,099	2,064	2,031	1,999	1,969	1,940	1,912	530
540	2,188	2,151	2,115	2,081	2,048	2,017	1,988	1,959	540
550	2,241	2,203	2,166	2,131	2,097	2,066	2,036	2,007	550
560	2,294	2,255	2,217	2,182	2,147	2,115	2,084	2,054	560
570	2,348	2,308	2,269	2,233	2,197	2,164	2,133	2,102	570
580	2,402	2,361	2,321	2,284	2,248	2,214	2,182	2,150	580
590	2,456	2,414	2,373	2,335	2,299	2,264	2,231	2,199	590
600	2,511	2,467	2,426	2,387	2,350	2,314	2,281	2,248	600
610	2,566	2,521	2,479	2,440	2,402	2,365	2,331	2,297	610
620	2,621	2,576	2,533	2,492	2,454	2,416	2,381	2,347	620
630	2,677	2,631	2,587	2,545	2,506	2,467	2,432	2,397	630
640	2,733	2,686	2,641	2,599	2,558	2,519	2,483	2,447	640
650	2,789	2,741	2,696	2,652	2,611	2,571	2,534	2,497	650
660	2,846	2,797	2,751	2,706	2,665	2,624	2,586	2,548	660
670	2,903	2,854	2,806	2,761	2,718	2,677	2,638	2,600	670
680	2,961	2,911	2,862	2,815	2,772	2,730	2,690	2,651	680
690	3,019	2,968	2,918	2,871	2,826	2,783	2,743	2,703	690
700	3,078	3,025	2,974	2,927	2,881	2,837	2,796	2,756	700
710	3,137	3,083	3,031	2,983	2,936	2,891	2,849	2,809	710
720	3,196	3,141	3,088	3,039	2,991	2,946	2,903	2,862	720
730	3,255	3,199	3,146	3,095	3,047	3,001	2,957	2,915	730
740	3,315	3,258	3,204	3,152	3,103	3,056	3,011	2,969	740
750	3,376	3,318	3,262	3,210	3,159	3,111	3,066	3,023	750
760	3,436	3,377	3,321	3,268	3,216	3,167	3,121	3,078	760
770	3,497	3,437	3,380	3,326	3,273	3,224	3,177	3,131	770
780	3,559	3,498	3,440	3,384	3,331	3,280	3,232	3,186	780
790	3,621	3,558	3,499	3,443	3,389	3,337	3,289	3,242	790
800	3,683	3,619	3,559	3,502	3,447	3,395	3,345	3,297	800

TABLE 17.—Heat content of petroleum vapors in Btu. per gallon of condensed vapor ¹

Temp. ° F.	Degrees A. P. I. at 60° F.							Temp. ° F.
	20	30	40	50	60	70	80	
	Specific gravity at 60°/60° F.							
	0.9340	0.8762	0.8251	0.7796	0.7389	0.7022	0.6690	
0					834	837	839	0
10					855	856	858	10
20					876	876	877	20
32					901	901	901	32
40					918	918	917	40
50				941	940	939	937	50
60				964	962	960	958	60
70				987	984	981	979	70
80				1,011	1,007	1,003	1,000	80
90				1,035	1,030	1,025	1,022	90
100			1,065	1,059	1,054	1,048	1,044	100
110			1,090	1,083	1,078	1,071	1,066	110
120			1,116	1,108	1,102	1,095	1,088	120
130			1,142	1,133	1,126	1,118	1,111	130
140			1,169	1,159	1,151	1,142	1,134	140
150		1,208	1,196	1,185	1,176	1,166	1,157	150
160		1,236	1,223	1,211	1,201	1,191	1,181	160
170		1,264	1,250	1,238	1,226	1,216	1,205	170
180		1,293	1,278	1,265	1,252	1,241	1,230	180
190		1,322	1,306	1,292	1,278	1,266	1,254	190
200	1,371	1,352	1,335	1,319	1,305	1,292	1,279	200
210	1,402	1,382	1,364	1,347	1,332	1,318	1,304	210
220	1,434	1,412	1,393	1,375	1,359	1,344	1,330	220
230	1,466	1,443	1,422	1,404	1,386	1,371	1,356	230
240	1,498	1,474	1,452	1,433	1,414	1,398	1,382	240
250	1,530	1,505	1,482	1,462	1,442	1,425	1,409	250
260	1,563	1,537	1,513	1,491	1,471	1,453	1,435	260
270	1,597	1,569	1,544	1,521	1,500	1,481	1,462	270
280	1,630	1,602	1,576	1,551	1,529	1,509	1,490	280
290	1,664	1,635	1,607	1,582	1,559	1,537	1,518	290
300	1,699	1,668	1,639	1,613	1,589	1,566	1,546	300
310	1,734	1,701	1,671	1,644	1,619	1,595	1,574	310
320	1,769	1,735	1,704	1,676	1,649	1,625	1,602	320
330	1,804	1,769	1,737	1,708	1,680	1,655	1,631	330
340	1,840	1,804	1,770	1,740	1,711	1,685	1,651	340
350	1,876	1,839	1,804	1,772	1,742	1,715	1,690	350
360	1,913	1,874	1,838	1,805	1,774	1,746	1,720	360
370	1,950	1,910	1,872	1,838	1,806	1,777	1,750	370
380	1,988	1,946	1,907	1,871	1,839	1,809	1,781	380
390	2,026	1,982	1,942	1,905	1,872	1,840	1,811	390
400	2,064	2,018	1,977	1,939	1,905	1,872	1,842	400

¹ The unit of mass used here, because of its practical usefulness, is the weight of petroleum vapor which, when condensed, is equal to the weight of a gallon of liquid at 60° F. See page 37 for statements regarding the experimental basis for these data and their estimated accuracy.

Example.—How much heat must be removed in a condenser in order to change vapor at 500° F. into liquid at 80° F., the gravity of the condensate being 50° A. P. I. at 60° F.? The result is obtained as follows:

Heat content of vapor at 500° F. = 2,299 Btu./gal. (from Table 17).

Heat content of liquid at 80° F. = 146 Btu./gal. (from Table 16).

Heat removed = difference = 2,153 Btu./gal.

TABLE 17.—Heat content of petroleum vapors in Btu. per gallon of condensed vapor—Continued

Temp. ° F.	Degrees A. P. I. at 60° F.								Temp. ° F.
	15	20	25	30	35	40	45	50	
	Specific gravity at 60°/60° F.								
	0.9659	0.9340	0.9042	0.8762	0.8498	0.8251	0.8017	0.7796	
400	2, 088	2, 064	2, 041	2, 018	1, 997	1, 977	1, 958	1, 939	400
410	2, 127	2, 102	2, 078	2, 055	2, 033	2, 013	1, 993	1, 974	410
420	2, 167	2, 141	2, 116	2, 093	2, 070	2, 049	2, 028	2, 009	420
430	2, 207	2, 180	2, 154	2, 130	2, 107	2, 085	2, 064	2, 044	430
440	2, 247	2, 220	2, 193	2, 168	2, 144	2, 122	2, 100	2, 079	440
450	2, 288	2, 260	2, 232	2, 207	2, 182	2, 159	2, 136	2, 115	450
460	2, 329	2, 300	2, 272	2, 246	2, 220	2, 196	2, 173	2, 151	460
470	2, 370	2, 340	2, 312	2, 285	2, 258	2, 234	2, 210	2, 187	470
480	2, 412	2, 381	2, 352	2, 324	2, 297	2, 272	2, 248	2, 224	480
490	2, 454	2, 423	2, 393	2, 364	2, 336	2, 310	2, 286	2, 262	490
500	2, 497	2, 464	2, 434	2, 404	2, 376	2, 349	2, 324	2, 299	500
510	2, 540	2, 506	2, 475	2, 445	2, 416	2, 388	2, 362	2, 337	510
520	2, 583	2, 549	2, 516	2, 485	2, 456	2, 428	2, 401	2, 375	520
530	2, 627	2, 592	2, 558	2, 526	2, 496	2, 468	2, 440	2, 413	530
540	2, 671	2, 635	2, 601	2, 568	2, 537	2, 508	2, 479	2, 452	540
550	2, 715	2, 678	2, 644	2, 610	2, 578	2, 549	2, 519	2, 491	550
560	2, 760	2, 722	2, 687	2, 652	2, 620	2, 589	2, 559	2, 530	560
570	2, 805	2, 766	2, 730	2, 695	2, 662	2, 630	2, 600	2, 570	570
580	2, 851	2, 811	2, 774	2, 738	2, 704	2, 672	2, 640	2, 610	580
590	2, 896	2, 856	2, 818	2, 781	2, 746	2, 714	2, 681	2, 651	590
600	2, 942	2, 901	2, 862	2, 825	2, 789	2, 756	2, 723	2, 692	600
610	2, 989	2, 947	2, 907	2, 869	2, 832	2, 798	2, 765	2, 733	610
620	3, 036	2, 993	2, 952	2, 914	2, 876	2, 841	2, 807	2, 774	620
630	3, 083	3, 039	2, 998	2, 958	2, 920	2, 884	2, 850	2, 816	630
640	3, 131	3, 086	3, 044	3, 003	2, 964	2, 928	2, 892	2, 858	640
650	3, 179	3, 133	3, 090	3, 049	3, 009	2, 972	2, 935	2, 900	650
660	3, 227	3, 181	3, 136	3, 095	3, 054	3, 016	2, 978	2, 943	660
670	3, 276	3, 229	3, 183	3, 141	3, 100	3, 061	3, 022	2, 986	670
680	3, 326	3, 277	3, 230	3, 187	3, 145	3, 105	3, 066	3, 030	680
690	3, 375	3, 325	3, 278	3, 234	3, 191	3, 150	3, 111	3, 074	690
700	3, 425	3, 374	3, 327	3, 281	3, 237	3, 196	3, 156	3, 118	700
710	3, 475	3, 424	3, 375	3, 328	3, 284	3, 242	3, 201	3, 162	710
720	3, 526	3, 473	3, 424	3, 376	3, 331	3, 288	3, 247	3, 207	720
730	3, 577	3, 523	3, 473	3, 424	3, 378	3, 334	3, 292	3, 252	730
740	3, 628	3, 574	3, 522	3, 473	3, 426	3, 381	3, 339	3, 297	740
750	3, 680	3, 625	3, 572	3, 522	3, 474	3, 428	3, 385	3, 343	750
760	3, 732	3, 676	3, 623	3, 571	3, 522	3, 476	3, 432	3, 389	760
770	3, 785	3, 727	3, 673	3, 621	3, 571	3, 524	3, 479	3, 435	770
780	3, 838	3, 780	3, 724	3, 671	3, 620	3, 572	3, 526	3, 482	780
790	3, 891	3, 832	3, 775	3, 721	3, 670	3, 621	3, 574	3, 529	790
800	3, 944	3, 884	3, 827	3, 772	3, 720	3, 670	3, 622	3, 576	800

3. HEAT CONTENT OF ASPHALT

The data, given in Table 18, on the heat content of asphalts containing various percentages of mineral matter were calculated from the following equation:

$$H_a = (0.388t + 0.000225t^2 - 12.65) (1 - 0.01x) + (0.18t + 0.00003t^2 - 5.76) 0.01x$$

in which t = temperature in °F. and x = per cent, by weight of mineral matter. This equation was obtained from the integration of equation (5a), using equation (5) for the specific heat of asphalt.

The experimental basis for the data in Table 18 is described in Section VII (4). The tabulated data on heat content of asphalt represent average values which are consistent to about 5 per cent with all of the experimental results at present available, namely, those obtained by the Bureau of Standards and by Zeitfuchs (Ind. Eng. Chem., 18, p. 79; 1926) on petroleum asphalts and by Dow (Municipal Eng., 27, p. 22; 1904) on the following refined natural asphalts: Trinidad, Maracaibo, Cuban, and Bermudez.

The data given in the column marked "0 per cent" are applicable to the bitumen content of natural asphalts and to petroleum asphalts which usually contain only small amounts of mineral matter. The data given in the columns marked "10 per cent" to "80 per cent," inclusive, are applicable to natural asphalts and to mixtures of natural or petroleum asphalts with known amounts of mineral matter. In using these data, it should be noted that the content of mineral matter, as used here, includes the so-called "free-carbon" content of the asphalt.

The values of heat content given in Table 18 are too small for products containing water or wax by amounts which vary in proportion to the quantity of these materials present.

Example.—How much heat is required to raise the temperature of asphalt containing 10 per cent of mineral matter from 60° to 400° F.? The result may be obtained from Table 18 as follows:

Heat content of asphalt at 400° F. = 168 Btu./lb.

Heat content of asphalt at 60° F. = 11 Btu./lb.

Heat required = difference = 157 Btu./lb.

TABLE 18.—Heat content of asphalt in Btu./lb.

Temp. ° F.	Heat content of asphalts containing 0 to 80 per cent mineral matter, by weight								Temp. ° F.
	0	10	20	30	40	50	60	80	
0	-13	-12	-11	-11	-10	-9	-8	-7	0
10	-9	-8	-8	-7	-7	-6	-6	-5	10
20	-5	-5	-4	-4	-4	-3	-3	-3	20
32	0	0	0	0	0	0	0	0	32
40	+3	+3	+3	+3	+2	+2	+2	+2	40
50	7	7	6	6	6	5	5	4	50
60	11	11	10	10	9	8	8	6	60
70	16	15	14	13	12	11	10	9	70
80	20	19	18	17	15	14	13	11	80
90	24	23	21	20	19	17	16	13	90
100	28	27	25	24	22	21	19	16	100
110	33	31	29	27	25	24	22	18	110
120	37	35	33	31	29	27	25	20	120
130	42	39	37	35	32	30	28	23	130
140	46	43	41	38	36	33	30	25	140
150	51	48	45	42	39	36	33	28	150
160	55	52	49	46	43	40	36	30	160
170	60	57	53	50	46	43	39	33	170
180	65	61	57	53	50	46	42	35	180
190	69	65	61	57	53	49	45	37	190
200	74	70	66	61	57	53	48	40	200
210	79	74	70	65	61	56	52	42	210
220	84	79	74	69	64	60	55	45	220
230	89	83	78	73	68	63	58	47	230
240	93	88	83	77	72	66	61	50	240
250	98	93	87	81	75	70	64	52	250
260	103	97	91	85	79	73	67	55	260
270	108	102	96	89	83	77	70	58	270
280	114	107	100	94	87	80	74	60	280
290	119	112	105	98	91	84	77	63	290
300	124	117	109	102	95	87	80	65	300
310	129	122	114	106	99	91	83	68	310
320	135	127	119	111	103	95	87	71	320
330	140	132	123	115	107	98	90	73	330
340	145	137	128	120	111	102	94	76	340
350	151	142	133	124	115	106	97	79	350
360	156	147	138	128	119	110	100	82	360
370	162	152	142	133	123	113	104	84	370
380	167	157	147	137	127	117	107	87	380
390	173	163	152	142	131	121	111	90	390
400	179	168	157	146	136	125	114	93	400
420	190	178	167	155	144	133	121	98	420
440	202	189	177	165	153	140	128	104	440
460	213	200	187	174	161	148	135	109	460
480	225	212	198	184	170	156	143	115	480
500	238	223	208	194	179	165	150	121	500

4. HEAT CONTENT OF PARAFFIN WAX

The data given in Table 19 represent the results of measurements made at the Bureau of Standards on the summation of three quantities—latent heat of fusion, specific heat of solid, and specific heat of liquid, all of which are involved simultaneously and inseparably in temperature changes of a complex material like paraffin wax. The data are given in terms of heat content above that of wax at 32° F.

The data on the effective heat content of wax, when in solution with petroleum oils at temperatures below the melting point of the wax, were obtained by extrapolation of the values at temperatures above the melting point. In other words, the effective heat content when in solution was assumed equal to the heat content of subcooled liquid and the heat of mixing was assumed equal to zero. The data on heat of solution (or of fusion) were obtained as differences between heat content of wax and effective heat content when in solution.

The data in Table 19 are consistent, in general, to about 5 per cent, with the experimental data on the change in heat content of paraffin wax obtained by the following observers:

Author	Reference
Sullivan, McGill, and French.....	Ind. & Eng. Chem., 19 , p. 1040; 1927.
Fortsch and Whitman.....	Ind. & Eng. Chem., 18 , p. 795; 1926.
Bushong and Knight.....	Ind. & Eng. Chem., 12 , p. 1197; 1920.
Kozicki and Pilat.....	Chemische Umschau, Fette, Oele, Wachse, und Harze, p. 71; 1917.
Nernst.....	Annalen der Physik, 36 , p. 413; 1911.
Koref.....	Annalen der Physik, 36 , p. 67, 1911.
Graef.....	"Laboratoriumsbuch für die Braunkohlenteerindustrie," p. 133; 1908.
Battelli.....	Atti del reale istituto Veneto, 3 , p. 1781; 1884-85.
Weber.....	Vierteljahrsschrift der naturforschenden Gesellschaft Zurich, 23 , p. 209; 1878.

The estimated accuracy of most of the data in Table 19 is 5 per cent for paraffin waxes obtained from petroleum. The heat content of waxes at temperatures somewhat below their melting points may be different by more than this amount for waxes of similar melting points due to different concentrations of the lower melting point constituents.

Example.—A wax distillate of gravity equivalent to 30° A. P. I. at 60° F. yields 10 per cent by weight, of paraffin wax of melting point 125° F. when cooled to 15° F. How much refrigeration is required to cool a gallon of this distillate from 90° to 15° F. and crystallize this amount of wax? The result may be obtained from Tables 12 and 19 as follows:

Weight of 1 gallon of 30° A. P. I. distillate=7.30 lbs.

Weight of wax= $7.30 \times 0.10 = 0.730$ lbs.

Weight of remaining oil= $7.30 - 0.73 = 6.57$ lbs.

Heat content of wax in solution at 90° F.=111 Btu./lb.

Heat content of wax at 15° F.= -7 Btu./lb.

Change in heat content of wax, 90° to 15° F.=118 Btu./lb.

Mean specific heat of oil (90° to 15° F.)= 0.440 Btu./lb. ° F.

Heat removed from oil= $0.440 \times 75 \times 6.57 = 217$ Btu.

Heat removed from wax= $118 \times 0.730 = 86$ Btu.

Heat removed from oil and wax= 303 Btu. per gallon of distillate.

TABLE 19.—Heat content and heat of solution of paraffin waxes of melting points 110°, 125°, and 140°F., in Btu./lb.

Temp. °F.	Heat content of wax			Effective heat content of wax in solution			Heat of solution			Temp. °F.
	Melting point			Melting point			Melting point			
	110°	125°	140°	110°	125°	140°	110°	125°	140°	
0	-15	-13	-11	62	65	68	77	78	79	0
5	-13	-11	-9	65	68	71	78	79	80	5
10	-11	-9	-8	67	70	73	78	79	81	10
15	-8	-7	-6	70	73	76	78	80	82	15
20	-6	-5	-4	72	75	78	78	80	82	20
25	-3	-2	-2	75	78	81	78	80	83	25
32	0	0	0	78	81	84	78	81	84	32
35	+1	+1	+1	79	82	85	78	81	84	35
40	4	3	+3	82	85	88	78	82	85	40
45	7	6	5	85	88	91	78	82	86	45
50	10	8	7	87	90	93	77	82	86	50
55	13	11	9	90	93	96	77	82	87	55
60	16	13	11	92	95	98	76	82	87	60
65	19	16	13	95	98	101	76	82	88	65
70	23	19	16	98	101	104	75	82	88	70
75	27	22	19	100	103	107	73	81	88	75
80	32	27	22	103	106	109	71	79	87	80
85	38	31	25	105	108	111	67	77	86	85
90	44	36	29	108	111	114	64	75	85	90
95	51	42	33	111	114	117	60	72	84	95
100	60	49	38	113	116	119	53	67	81	100
105	73	57	43	116	119	122	43	62	79	105
110	119	65	49	119	122	125	0	57	76	110
115	121	76	55	121	124	127	0	48	72	115
120	124	90	62	124	127	130	0	37	68	120
125	127	130	71	127	130	133	0	0	62	125
130	130	133	81	130	133	136	0	0	55	130
135	132	135	94	132	135	138	0	0	44	135
140	135	138	141	135	138	141	0	0	0	140
145	138	141	144	138	141	144	0	0	0	145
150	141	144	147	141	144	147	0	0	0	150
160	146	149	152	146	149	152	0	0	0	160
170	152	155	158	152	155	158	0	0	0	170
180	157	160	163	157	160	163	0	0	0	180
190	163	166	169	163	166	169	0	0	0	190
200	169	172	175	169	172	175	0	0	0	200
220	181	184	187	181	184	187	0	0	0	220
240	193	196	199	193	196	199	0	0	0	240
260	205	208	211	205	208	211	0	0	0	260
280	217	220	223	217	220	223	0	0	0	280
300	230	233	236	230	233	236	0	0	0	300
320	243	246	249	243	246	249	0	0	0	320
340	256	259	262	256	259	262	0	0	0	340
360	269	272	275	269	272	275	0	0	0	360
380	282	285	288	282	285	288	0	0	0	380
400	295	298	301	295	298	301	0	0	0	400

X. CONCLUSION

Many of the thermal properties of petroleum oils appear to vary systematically with temperature and with the density of the oils. Empirical equations have been found which represent with moderate accuracy what appear to be the most reliable experimental data at present available.

Table 20 contains a summary of the empirical equations expressed in engineering units and also metric units. In the various columns are given (1) the property, (2) the units in which the property is expressed, (3) the empirical equation, (4) the density and temperature ranges covered by the experimental data used as a basis for the equations, and (5) the accuracy of the values given by the equations, estimated largely from the agreement with the experimental results. The data given in nearly all of the preceding tables were calculated from these empirical equations.

The present work was undertaken with the object of collecting and correlating the various scattered experimental data on the subject in order to determine wherein the existing data were most deficient. The conclusions as to the data on the various thermal properties may be summarized briefly as follows:

Thermal expansion.—The data given in Tables 1 to 5 supplement similar data given in Bureau of Standards Circular No. 154, National Standard Petroleum Oil Tables. The information now available on thermal expansion appears sufficient to meet most of the requirements of industry. Additional experimental data at high temperatures appear desirable.

Heat of combustion.—The data given in Tables 6, 7, and 8 appear to be sufficient for all practical uses of such data. Heating value determinations on petroleum products as routine tests seem to serve no useful purpose.

Specific volume of vapor.—The data given in Table 9 for products of gravity 50° to 150° A. P. I. appear to be sufficiently reliable for most industrial purposes. The data given for products of gravity 20° to 50° A. P. I. are admittedly approximate and are included mainly for the benefit of those users of petroleum products who have no information at hand as to the source or the volatility of these products. Additional experimental data on molecular weights of products of gravity 10° to 40° A. P. I. appear desirable.

Thermal conductivity.—The data given in Table 10 appear to be sufficient for all practical uses of such data.

Specific heat.—The data given in Tables 12 and 13 appear to be sufficiently reliable for all practical applications wherein only moderate pressures (less than 50 lbs./in.²) are involved. Additional experimental data on petroleum vapors and also on petroleum liquids at high temperatures and pressures are desirable.

Latent heat of vaporization.—The data given in Table 15 are in general accord with the available, somewhat fragmentary, experimental data, the reliability of which appears uncertain. Additional experimental data, particularly at pressures above 1 atmosphere, are desirable.

Heat content.—The data given in Tables 16 to 19 should provide simplicity and convenience in calculations of the quantities of heat involved in the heating and cooling of petroleum products.

TABLE 20.—Empirical equations for thermal properties of petroleum products

Property	Units	Empirical equation	Experimental range		Estimated accuracy, per cent
			d	t	
In engineering units: <i>d</i> = specific gravity at 60°/60° F.; <i>t</i> = temperature in °F.; <i>p</i> = pressure in lbs./in. ² absolute; unit volume of liquid = gallon, measured at 60° F.					
Coefficient of expansion of liquid.	$\frac{1}{V_{60}} \frac{dV}{dt}$	$= A + 2B(t - 60)$ $\log(A \times 10^3) = 0.835 + \frac{0.70}{d}$; $\log(B \times 10^3) = \frac{2.10}{d} - 1.20$	0.51-1.00	32-200	5
Total heat of combustion at constant volume.	Btu./lb. Btu./gal.	$= 22,320 - 3,780d^2$ $= 186,087d - 31,515d^3$	0.51-0.99		1
Specific volume of vapor.	ft. ³ /lb.	$= 0.242(t + 460) \cdot \frac{(1.03 - d)}{d}$			
Thermal conductivity of liquid.	Btu. in. ft. ² hr. °F.	$= \frac{0.813}{d} [1 - 0.0003(t - 32)]$	0.78-0.95	32-400	10
Specific heat of liquid.	Btu./lb. °F.	$= \frac{1}{\sqrt{d}} (0.388 + 0.00045t)$	0.72-0.96	32-750	5
	Btu./gal. °F.	$= \sqrt{d} (3.235 + 0.00375t)$			
Latent heat of vaporization.	Btu./lb.	$= \frac{1}{d} (110.9 - 0.09t)$	0.64-0.91	100-600	10
	Btu./gal.	$= 925 - 0.75t$			
Heat content of liquid.	Btu./gal.	$= \sqrt{d} (3.235t + 0.001875t^2 - 105.5)$	0.72-0.96	32-750	5
Heat content of vapor.	Btu./gal.	$= \sqrt{d} (3.235t + 0.001875t^2 - 105.5) + 925 - 0.75t$	0.64-0.91	100-600	5
In metric units: <i>d</i> = density in g/ml at 15° C.; <i>t</i> = temperature in °C.; <i>p</i> = pressure in atmospheres; unit volume of liquid = milliliter, measured at 15° C.					
Coefficient of expansion of liquid.	$\frac{1}{V_{15}} \frac{dV}{dt}$	$= A + 2B(t - 15)$ $\log(A \times 10^3) = 1.09 + \frac{0.70}{d}$; $\log(B \times 10^3) = \frac{2.10}{d} - 0.69$	0.51-1.00	0-100	5
Total heat of combustion at constant volume.	Cal./g. Cal./ml.	$= 12,400 - 2,100d^2$ $= 12,400d - 2,100d^3$	0.51-0.99		1
	Specific volume of vapor.	l/g.			
Thermal conductivity of liquid.	Cal. cm. cm ² sec. °C.	$= \frac{0.00028}{d} [1 - 0.00054t]$	0.78-0.95	0-200	10
Specific heat of liquid.	Cal./g. °C.	$= \frac{1}{\sqrt{d}} (0.403 + 0.00081t)$	0.72-0.96	0-400	5
	Cal./ml. °C.	$= \sqrt{d} (0.403 + 0.00081t)$			
Latent heat of vaporization.	Cal./g.	$= \frac{1}{d} (60 - 0.09t)$	0.64-0.91	40-300	10
	Cal./ml.	$= 60 - 0.09t$			
Heat content of liquid.	Cal./ml.	$= \sqrt{d} (0.403t + 0.000405t^2)$	0.72-0.96	0-400	5
Heat content of vapor.	Cal./ml.	$= 60 + (0.403\sqrt{d} - 0.09)t + 0.000405\sqrt{d}t^2$	0.64-0.91	40-300	5

It is fully realized that the experimental data on several of the above properties is not as complete as could be desired and that a revision of the tabulated data may be rendered necessary by additional experimental work, such as that recently undertaken on "The Thermodynamic Properties of Petroleum Hydrocarbons," listed as project No. 38 of the American Petroleum Institute Research. Hence, the tables here presented are not to be considered as final, but as best representing our present knowledge.

This publication represents the first attempt apparently ever made to supply the petroleum industry and the users of petroleum products with comprehensive data on the thermal properties of these products in readily useful form somewhat analogous to the tables now available on steam and ammonia. This is indeed surprising when it is recalled that heat is involved, almost without exception, in all of the numerous processes used to convert crude petroleum into its many useful products.

Tables of the properties of steam and ammonia, based largely on the extensive researches of Regnault, were available to mechanical and refrigerating engineers

nearly 50 years ago. Those tables played no small part in the progress and development of these two branches of engineering. The importance of such tables in engineering is reflected by the elaborate researches conducted on steam and ammonia in recent years, primarily to extend the range and accuracy of the tabulated data.

The petroleum industry has been less fortunate. It has had no analogous tables to point the way toward advancement in processes and in design of equipment. If the petroleum industry, in the last 25 years of its astounding growth, had possessed as much information on the thermal properties of its fluids as was made available on steam and ammonia by Regnault in 1862, the economic saving in more efficient methods and apparatus would probably have amounted to an appreciable fraction of the total value of its products.

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