Heats and Volumes of Mixing in Several C_{12} Hydrocarbon Systems

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SPECIFICATIONS for kerosine-like fuels for use in rocket engines (*11*) include requirements that the net heat of combustion shall not be below a specified minimum value, and that the API gravity (or density) shall lie within a fairly narrow range. These requirements may restrict the sources of supply to certain geographical areas unless the requirements can be met by blending fuels which do not meet the specifications.

The density of a blend can be calculated by the mixture rule from its composition in terms of the component fuels and the densities of the components, provided there is no change in volume on mixing. Similarly, the heat of combustion per unit weight of a blend can be calculated from the composition of the blend and the heats of combustion of its components, if there is no heat of mixing.

Data in the literature on heats of mixing of hydrocarbons indicate that heat of mixing is practically negligible in comparison with heat of combustion, but no data have been found on heats of mixing of hydrocarbons in kerosines—i.e., hydrocarbons in the C_{12} range. The volume change on mixing of hydrocarbons is usually negligible, but in some systems is 0.5% or more of the total volume. In the literature on volume of mixing, no data on systems of C_{12} hydrocarbons have been found.

In this work, data were obtained on heats and volumes of mixing of kerosines and of typical C_{12} hydrocarbons which are found in kerosines, to determine whether these quantities can be neglected in calculating properties of blends from those of the components.

SYSTEMS INVESTIGATED

Measurements of both heat and volume of mixing were made on two systems, one composed of two kerosines having widely different properties, and one composed of the C_{12} hydrocarbons bicyclohexyl and *n*-dodecane. Measurements of volume of mixing were made on four other binary systems in which one component of each was *n*-dodecane while the other was *n*-heptylcyclopentane, *n*-hexylcyclohexane, *n*-hexylbenzene, and phenylcyclohexane. The bicyclohexyl was a purified sample obtained from the National Advisory Committee for Aeronautics. The other hydrocarbons were prepared and purified in the Molecular Kinetics Section of the National Bureau of Standards (*10*). The pure hydrocarbons and properties are listed in Table I.

The two kerosines were selected from a total of 111 samples of straight-run or blended kerosines studied in an investigation of heats of combustion and other properties (*4*). The heats of combustion, aniline points, API gravities, and hydrogen contents of these kerosines (Table II) were near the lower and upper limits, respectively, of the ranges of values of these properties for the 111 fuels.

APPARATUS AND METHODS

Density. The densities of the various mixtures were measured by techniques described previously (*9*). The temperature bath was maintained at 25.00° ± 0.001° C. Pycnometers of 10- and 50-ml. volume were calibrated using air-free distilled water.

The samples were mixed by weight, in approximately 10% steps, using 80-ml. weighing bottles. In calculating the composition of a mixture from the weights of its components no corrections for air buoyancy were made, since such corrections would not significantly affect the values obtained for the weight fractions of the components. However, all other weighings were corrected to vacuum.

Heat of Mixing. The measurements of heat of mixing were made by means of a Bunsen-type calorimeter in which the calorimetric medium is diphenyl ether (m.p. 26.9° C.). This calorimeter and the method of making measurements of heat of mixing have been described (*5, 6*). Briefly, the method is as follows: A measured quantity of one component of the system under investigation is placed in a mixing vessel in the calorimeter. This mixing vessel is provided with a valve which is connected to a buret containing a quantity of the second component of the system. By means of the valve and buret, measured volumes of the second component are added to the material in the mixing chamber in successive experiments, and the thermal effect of each such addition is measured by the calorimeter. The present measurements differed from earlier ones (*6*) principally in these respects:

A larger mixing vessel (45 ml.) was used.

The liquid in the mixing vessel was stirred with a manually operated stirrer.

In the present experiments the amount of the first component placed in the mixing vessel was 12 ml. (9 grams), and the volumes of the second component added in successive experiments were 2, 3, 5, and 9 ml. The buret was read directly to 0.01 ml., and by interpolation to 0.001 ml.

The first component, after being placed in the mixing vessel, was degassed by repeated freezing and evacuation. The second component was likewise degassed and was introduced into the evacuated buret, avoiding any formation of air bubbles in the tubing between the buret and mixing vessel. After the buret was filled, air was admitted above the liquid surface, so that the liquid in the buret was at atmospheric pressure, while the pressure in the mixing vessel was equal to the vapor pressure of the liquid in it—i.e., nearly zero. The kerosines were degassed in such a manner as to avoid loss of lighter components.

The results of measurements are calculated as follows: The observed change in reading of the calorimeter capillary in each experiment is multiplied by the calibration factor, 4.145 joules per cm. (*5*), to obtain the observed thermal effect. This was corrected for (1) thermal leakage, (2) the work done by the atmosphere in forcing the liquid through the valve into the evacuated mixing vessel, (3) the change in internal energy of the liquid in going from the buret at atmospheric pressure to nearly zero pressure in the mixing vessel, and (4) the energy of condensation of vapor in the mixing vessel due to the decrease in vapor volume and change in vapor density when liquid is introduced into the mixing vessel. Correction 1 for thermal leakage was usually less than 10% of the heat measured, which is about 2 joules per experiment. Corrections 2 and 3 amounted to approximately −0.10 and +0.03 joule per ml. of liquid added. Correction 4, which depends upon vapor pressure, vapor density, and energy of vaporization, was negligible for the two pure compounds whose vapor pressure at 26.9° is of the order of 0.1 mm. of mercury, but amounted to about 0.01 joule per ml. of liquid added for the kerosines. The thermal effects of stirring the liquid in the mixing vessel and of opening and closing the valve to admit liquid were negligible.

The volume of liquid measured by the buret at about 25.5° C. on the average was corrected to 26.9° by means of the appropriate coefficients of expansion. Results were calculated in terms of joules per milliliter of mixtures, joules per gram of mixture, and in the case of the two pure compounds, joules per mole of mixture.

Table I. Physical Properties of Hydrocarbons (*10*)

Hydrocarbon	Boiling Point, ° C.	Melting Point, ° C.	Density, G./Ml. d^{20}	Density, G./Ml. d^{25a}	n_D^{25}
n-Dodecane	216.26	−9.71	0.74901	0.74535	1.41955
n-Heptylcyclopentane	223.92	−61.04	0.80132	0.79778	1.43993
n-Hexylcyclohexane	224.78	−47.51	0.80817	0.80452	1.44459
n-Hexylbenzene	225.77	−63.5	0.85802	0.85428	1.48445
Bicyclohexyl	239.04	+3.63	0.88619	0.88249	1.47768
Phenylcyclohexane	240.12	+6.99	0.94272	0.93874	1.52393

[a] These values were obtained in an investigation of the properties of the pure hydrocarbons (*10*). The specific volumes given in Table III correspond to the slightly different values of d^{25} obtained in this work.

Table II. Properties of Two Kerosines (*4*)

No.	Aniline Point, *A*, ° F.	API Gravity, *G*	*A* × *G*	Hydrogen Content, Wt. %	Hydrocarbon Type Analysis, Volume % Paraffin	Naphthene	Aromatic	Olefin	Net Heat of Combustion,[a] B.t.u./Lb.
62	129.40	35.70	4620	12.95	0.0	77.1	22.2	0.7	18410
72	189.88	51.87	9849	15.15	81.5	15.8	1.0	1.7	18915

[a] Heat of combustion at constant pressure to gaseous H_2O, SO_2, and CO_2.

The result of an experiment calculated as described above is, strictly speaking, the intrinsic energy of mixing at constant pressure. This is practically equal to the heat (or enthalpy) of mixing at constant pressure, and is called heat of mixing in this article.

RESULTS

Changes in Specific Volume. The results of measurements of specific volume are given in Table III, and shown graphically in Figures 1 and 2. The symbols used are:

w, x = mass fraction or mole fraction, respectively, of component 2 in the mixture
V_s = observed specific volume at 25° C., in g./ml.
V_{s0} = specific volume corresponding to zero volume of mixing
ΔV_s = $V_s - V_{s0}$

If there is no change in volume on mixing, the specific volume of the mixture can be calculated from the equation:

$$V_{s0} = (1 - w)\,V_{1s} + w\,V_{2s}$$

where V_{1s} and V_{2s} are the specific volumes of components 1 and 2, respectively, or from equivalent equations in terms of volume fractions or mole fractions.

The empirical equations for ΔV_s given at the bottom of Table III, are equivalent to the equation

$$\Delta V/V = Aw(1-w)$$

for the mixture of kerosines, and to

$$\Delta V/V = Bx(1-x)$$

for the mixtures of pure compounds where $\Delta V/V$ is the change in volume on mixing per unit volume of the unmixed components, and A and B are empirical constants.

Component 2 is kerosine NBS No. 72 for the mixture of the two kerosines, and *n*-dodecane for the mixtures of pure compounds. For *n*-heptylcyclopentane–*n*-dodecane and phenylcyclohexane–*n*-dodecane the observed values of ΔV_s are zero within the limits of experimental error.

In Figures 1 and 2 the values of ΔV_s are plotted against composition terms of mass fraction of kerosine NBS No. 72 in the case of the kerosines, and in terms of mole fraction of *n*-dodecane for the mixtures of pure compounds. The curves represent values calculated from the equations given in the footnotes to Table III. One observed value of ΔV_s, 124×10^{-5} ml. per gram for phenylcyclohexane–*n*-dodecane is omitted from the plotted points in Figure 2.

The maximum calculated values of ΔV_s (Table IV.) do not exceed about 0.1%. For any of these systems, therefore,

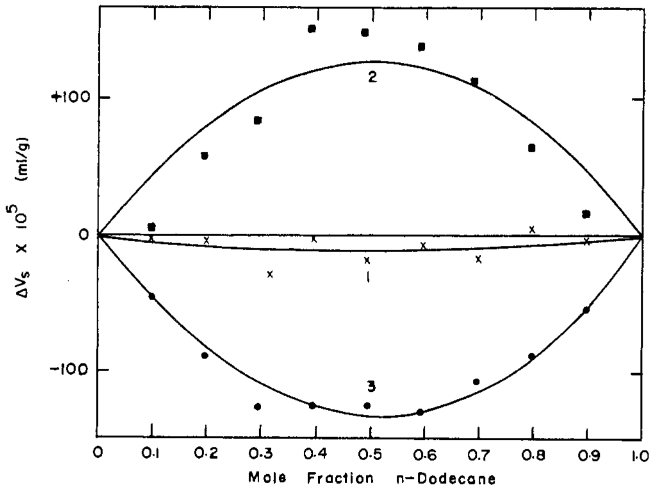

Figure 1. Change in specific volume on mixing
1. *n*-Hexylcyclohexane and *n*-dodecane
2. *n*-Hexylbenzene and *n*-dodecane
3. Bicyclohexyl and *n*-dodecane

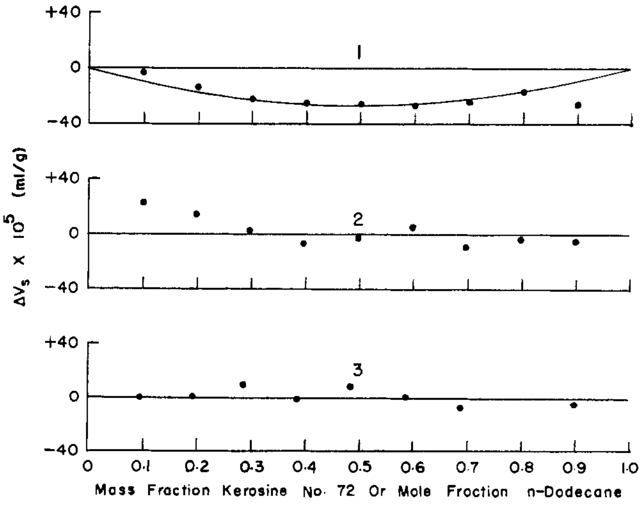

Figure 2. Change in specific volume on mixing
1. Kerosines NBS 62 and NBS 72
2. *n*-Heptylcyclopentane and *n*-dodecane
3. Phenylcyclohexane and *n*-dodecane

Table III. Changes in Specific Volume on Mixing

Fraction of Component 2,	Specific Volume, Ml./G.			
			$\Delta V_s \times 10^5$	
	V_s	V_{s0}^a	Obsd.	Calcd.[b]
w	Kerosines NBS 62(1) and NBS 72(2)[b]			
0.0000	1.30916	1.30916	0	0
0.1000	1.29742	1.29745	−3	−10
0.2000	1.28559	1.28573	−14	−18
0.3000	1.27380	1.27402	−22	−23
0.4000	1.26205	1.26230	−25	−26
0.4999	1.25034	1.25060	−26	−27
0.6001	1.23859	1.23886	−27	−25
0.7000	1.22692	1.22716	−24	−22
0.8000	1.21526	1.21544	−18	−16
0.9000	1.20347	1.20373	−26	−9
1.0000	1.19201	1.19201	0	0
x	*n*-Heptylcyclopentane(1) and *n*-dodecane(2)			
0.0000	1.25345	1.25345	0	
0.0991	1.26253	1.26230	+23	
0.1981	1.27125	1.27112	+13	
0.2975	1.27997	1.27995	+2	
0.3970	1.28869	1.28877	−8	
0.4971	1.29759	1.29762	−3	
0.5970	1.30649	1.30644	+5	
0.6971	1.31516	1.31525	−9	
0.7982	1.32408	1.32412	−4	
0.8988	1.33289	1.33294	−5	
1.0000	1.34178	1.34178	0	
x	*n*-Hexylcyclohexane(1) and *n*-Dodecane(2)[c]			
0.0000	1.24285	1.24285	0	0
0.0989	1.25272	1.25274	−2	−4
0.1981	1.26258	1.26264	−6	−7
0.3160	1.27408	1.27437	−29	−10
0.3971	1.28241	1.28242	−1	−11
0.4967	1.29212	1.29229	−17	−12
0.5972	1.30215	1.30222	−7	−11
0.6976	1.31194	1.31211	−17	−10
0.7979	1.32202	1.32197	+5	−8
0.8985	1.33181	1.33185	−4	−4
1.0000	1.34178	1.34178	0	0
x	*n*-Hexylbenzene(1) and *n*-Dodecane(2)[d]			
0.0000	1.17066	1.17066	0	0
0.0963	1.18793	1.18787	+6	+41
0.1928	1.20553	1.20495	+58	+75
0.2898	1.22282	1.22198	+84	+101
0.3884	1.24062	1.23911	+151	+118
0.4879	1.25770	1.25622	+148	+126
0.5904	1.27507	1.27369	+138	+123
0.6897	1.29157	1.29044	+113	+111
0.7919	1.30815	1.30750	+65	+86
0.8947	1.32471	1.32453	+18	+52
1.0000	1.34178	1.34178	0	0
x	Bicyclohexyl(1) and *n*-Dodecane(2)[e]			
0.0000	1.13326	1.13326	0	0
0.0980	1.15367	1.15413	−46	−44
0.1962	1.17408	1.17496	−88	−80
0.2950	1.19455	1.19582	−127	−107
0.3942	1.21539	1.21665	−126	−125
0.4941	1.23629	1.23754	−125	−133
0.5942	1.25707	1.25837	−130	−130
0.6951	1.27818	1.27924	−106	−117
0.7970	1.29936	1.30024	−88	−90
0.8973	1.32029	1.32082	−53	−52
1.0000	1.34178	1.34178	0	0
x	Phenylcyclohexane(1) and *n*-Dodecane(2)			
0.0000	1.06536	1.06536	0	
0.0956	1.09327	1.09327	0	
0.1904	1.12064	1.12064	0	
0.2874	1.14841	1.14831	+10	
0.3854	1.17588	1.17589	−1	
0.4848	1.20366	1.20359	+7	
0.5850	1.23113	1.23112	+1	
0.6869	1.25875	1.25882	−7	
0.7898	1.28765	1.28641	(+124)[f]	
0.8942	1.31403	1.31408	−5	
1.0000	1.34178	1.34178	0	

[a] Calculated on assumption of zero volume of mixing.

[b] Calculated $\Delta V_s \times 10^5 = -85w(1 - w)[1.30916(1 - w) + 1.19201w]$.

[c] Calculated $\Delta V_s \times 10^5 = -36x(1 - x)\dfrac{209.18\,(1 - x) + 228.54x}{168.31\,(1 - x) + 170.33x}$.

[d] Calculated $\Delta V_s \times 10^5 = 400x(1 - x)\dfrac{189.95\,(1 - x) + 228.54x}{162.26\,(1 - x) + 170.33x}$.

[e] Calculated $\Delta V_s \times 10^5 = -430x(1 - x)\dfrac{188.46\,(1 - x) + 228.54x}{166.30\,(1 - x) + 170.33x}$.

[f] Omitted from Figure 2.

Table IV. Maximum Calculated Values of ΔV_s

Mixture	Max. Value of $\Delta V_s \times 10^5$	
	Ml./g.	%
Kerosines	−27	−0.021
n-Heptylcyclohexane, *n*-dodecane	0	0.000
n-Hexylcyclohexane, *n*-dodecane	−12	−0.009
n-Hexylbenzene, *n*-dodecane	+126	+0.100
Bicyclohexyl, *n*-dodecane	−133	−0.108
Phenylcyclohexane, *n*-dodecane	0	0.000

Table V. Heat of Mixing of Bicyclohexyl and *n*-Dodecane

Mole Fraction *n*-Dodecane	Heat of Mixing, ΔH		
	J/ml.	J./g.	J./mole
0.1198	0.161	0.178	31.2
.2583	.296	.352	58.9
.4124	.357	.436	73.2
.5691	.301	.377	63.6

the composition of a mixture having a specified specific gravity intermediate between those of the components can be calculated with an accuracy sufficient for most purposes, assuming no change in volume on mixing.

However, changes in volume larger than those found here have been reported for other hydrocarbon systems. Wood and his associates have reported maximum volumes of mixing of about 0.66% for the system benzene-cyclohexane at 30° C. (*15*), and about 0.42% for the system benzene–2,2,4-trimethylpentane at 25° C. (*16*). Conolly (*3*) reported maximum volumes of mixing ranging from 0.45% at 16° C. to 1.37% at 60° C., and from 0.60% at 16° C. to 1.50% at 60° C. for the systems *n*-butane–benzene and *n*-butane–cyclohexane, respectively. The assumption of zero volume of mixing may sometimes lead to rather serious errors. However, this assumption is probably a good approximation for mixtures in which the components are petroleum distillates of reasonably similar properties.

Heats of Mixing. The results obtained on mixtures of bicyclohexyl and *n*-dodecane are given in Table V and are shown graphically in Figure 3. The results for the two kerosines are shown in Figure 4.

Although the experimental data on both systems can be represented by smooth curves, as shown in Figures 3 and 4, no simple equation has been found which will satisfactorily represent the heat of mixing as a function of composition.

Table V and Figures 3 and 4 show that the heats of mixing in the two systems studied are small, the maximum value for both systems being about 0.4 joules per gram, which corresponds to about 0.2 B.t.u. per pound of mixture. This is approximately 0.001% of the heat of combustion, and hence the heat of combustion per unit weight of any blend of the two pure compounds, or of the two kerosines can be calculated without appreciable error by means of the mixture rule:

$$Q' = (1 - w)Q_1 + wQ_2$$

where Q', Q_1, and Q_2 are the heats of combustion per unit weight of the blend and of components 1 and 2, respectively, and w is the weight fraction of component 2. The superscript is used to specify that this equation applies only when the heat of mixing is zero. If a blend is made by mixing measured volumes V_1 and V_2 of the components, it may be more convenient to calculate its heat of combustion per unit weight by the mixture rule in the form

$$Q' = \frac{V_1 d_1 Q_1}{V_1 d_1 + V_2 d_2} + \frac{V_2 d_2 Q_2}{V_1 d_1 + V_2 d_2}$$

where d_1 and d_2 are the densities (or specific gravities) of the components 1 and 2 of the blend at the temperature at which the volumes V_1 and V_2 were measured, or to which these volumes are referred. An equivalent expression in terms of the API gravity, G, is obtained by substituting $(G_2 + 131.5)$ for d_1 and $(G_1 + 131.5)$ for d_2. In this case the volumes V_1 and V_2 should be referred to 60° F.

The fact that heat of mixing is negligible in comparison with heat of combustion in the systems studied here does not necessarily mean that this is true for all hydrocarbon systems. In an examination of a considerable amount of data reported in the literature (*1, 2, 7, 8, 12, 13, 14*), however, no case has been found in which heat of mixing in such systems exceeded about 0.03% of heat of combustion. It seems very unlikely that the heat of mixing of two similar petroleum distillates, such as kerosines, would be appreciable in comparison with the heat of combustion.

If both heat of mixing and volume of mixing are negligible, then the heat of combustion per unit volume of a blend can be calculated from the heats of combustion per unit volume of the components by the form

$$\bar{Q}'' = (1 - \phi)\,\bar{Q}_1 + \phi\bar{Q}_2$$

where $\bar{Q}''$, $\bar{Q}_1$, and $\bar{Q}_2$ represent heats of combustion per unit volume and $\phi = V_2/V_1 + V_2$ represents volume fraction of component 2. Here volumes and volume fractions are all referred to the same temperature. The superscript is used to specify that the equation applies only when both heat and volume of mixing are negligible. These conditions are probably fulfilled for blends of petroleum distillates such as kerosines, but volume of mixing is not negligible in some hydrocarbon systems (*3, 15, 16*).

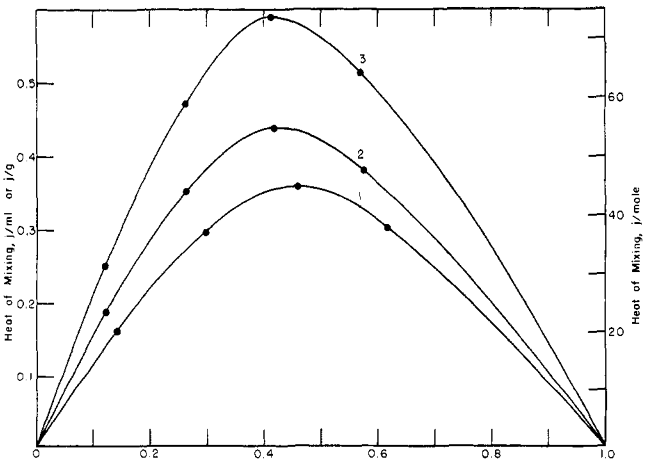

Figure 3. Heat of mixing of biclohexyl and *n*-dodecane

1. Joules per milliliter vs. volume fraction *n*-dodecane
2. Joules per gram vs. mass fraction *n*-dodecane
3. Joules per mole vs. mole fraction *n*-dodecane

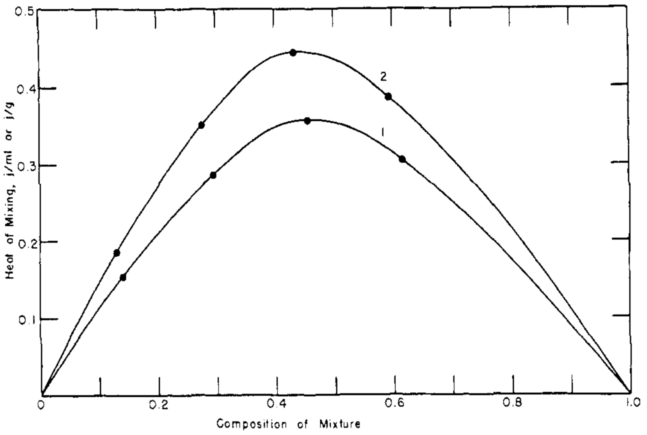

Figure 4. Heat of mixing of two kerosine-like fuels

1. Joules per milliliter vs. volume fraction fuel 72
2. Joules per gram vs. mass fraction fuel 72

The small magnitude of the heat of mixing per mole of bicyclohexyl and *n*-dodecane is somewhat surprising, being less than one third of that of cyclohexane with *n*-hexane (*7, 8*). However, it is well within the range of values reported for other hydrocarbon systems—for example, the maximum values of heat of mixing of *n*-hexane with *n*-hexadecane and of *n*-octane with tetraethylmethane have been reported as about 113 joules per mole (*7, 8*) and −92 joules per mole (*8*), respectively.

Curve 3 of Figure 3 is very similar in form to the corresponding curve for the system cyclohexane–*n*-hexane. If the experimental values for this system as reported by Mathieson and Thynne (*7*) and Mathot (*8*) are multiplied by appropriate constant factors and the resulting values plotted against mole fraction of *n*-hexane, the plotted points lie remarkably close to curve 3.

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