# Direct Determination of Enthalpy Data for *n*-Heptane by Flow Calorimetry

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**Enthalpies of *n*-heptane were measured by a flow calorimeter at temperatures between 275° and 600°F and pressures up to 1500 psia. The measurements covered the liquid, vapor, vapor-liquid, and critical regions. The experimental results were compared with values calculated by the equations of state of Benedict-Webb-Rubin and Starling and Kwok, by the generalized correlation of Lydersen et al., and with the data of Gilliland and Parekh, Wilson et al., and Lenoir et al.**

In 1950 Stuart et al. (*11*) presented a pressure–enthalpy diagram of *n*-heptane, calculated from PVT data. In 1951 Benedict, Webb, and Rubin (*3, 4*) calculated values for the BWR equation-of-state constants, based on available PVT data for *n*-heptane. Enthalpy values could then be readily calculated from this equation. Recently, Starling and Kwok (*9, 10*) proposed a new equation of state, which is a modification of the BWR equation, and calculated the values of its constants for *n*-heptane, from limited experimental enthalpy data in the vapor region obtained by Gilliland and Parekh (*5*) and available PVT data.

In 1971 Wilson et al. (*14, 15*) measured the enthalpy of *n*-heptane over wide ranges of pressures (50-2500 psia) and temperatures (−100° to 600°F), and Lenoir et al. (*6, 7*) reported enthalpy data for *n*-heptane in the gas phase from 360° to 600°F and up to 100 psia. From their results, Wilson et al. (*14, 15*) and Lenoir et al. (*6, 7*) indicated that the values of enthalpy for *n*-heptane presented in the API Data Book (*2*) and the API Project 44 tabulations (*1*) may be somewhat low at high temperatures and in the ideal gas state.

This paper reports *direct measurements* by flow calorimetry of enthalpies of *n*-heptane in the liquid, vapor, vapor-liquid, and critical regions in the temperature range 275–600°F and pressures up to 1500 psia.

The experimental results were compared with values calculated by the equations of state for *n*-heptane of BWR (*3, 4*) and Starling and Kwok (*9, 10*), by the generalized correlation of Lydersen et al. (*8, 16*) and with the data of Gilliland and Parekh (*5*), Wilson et al. (*14, 15*), and Lenoir et al. (*6, 7*).

## Experimental

The flow calorimeter utilized in this work, as well as the experimental procedure followed, have been described previously (*12*). The *n*-heptane was from Fisher Scientific Co., lot 785040 with certified spectroanalysis. Evaluation of the apparatus performance has been discussed in the previous article (*12*), an error analysis indicating the overall possible error on the measured enthalpy values to be ±1.1 Btu/lbm.

## Results

From the isobaric lines constructed on a $H$ vs. $T$ plot, a $P$ vs. $H$ chart was constructed by cross-plotting, with isotherms being drawn. (Two large-scale graphs containing all data obtained have been deposited with the ACS Microfilm Depository Service.)

The enthalpy data obtained are presented in Table I. (A more detailed version of Table I, containing also the weights of heptane samples and condensed freon-11 and the different corrections applied to obtain the enthalpy values, has been deposited with the ACS Microfilm Depository Service.) These corrections have been discussed in the previous article (*12*). Multiple runs at the same conditions indicated an experimental reproducibility of about 1%.

Plotting the $P$ vs. $H$ and $H$ vs. $T$ diagrams provided rough estimates of the critical temperature and pressure, which were compatible with the precise values reported by API (*1*), namely 512.6°F and 396.8 psia. As indicated in Table II, our estimated values of vapor pressures and heats of vaporization were in agreement with those of API (*2*).

## Discussion of Results

Experimental results obtained in this work were compared with values calculated by three methods of prediction of enthalpy variation with pressure, namely, those of Lydersen et al. (*8, 16*), BWR (*3, 4*), and Starling and Kwok (*9, 10*). To cover the liquid, vapor, and critical regions, the comparison in Table III was made for the isotherms corresponding to temperatures of 400°, 500°, 512.6°, and 550°F. The ideal gas enthalpies utilized were those from API (*1, 13*). The analytical formulation by Yen and Alexander (*16*) of the generalized method of Lydersen was the one used in the calculations.

The values of enthalpy departure for the BWR equation of state (*3, 4*), namely:

$$\begin{aligned}(H - H^{\circ}) = {} & (B_0RT - 2A_0 - 4C_0/T^2)\rho + \\ & (1/2)(2bRT - 3a)\rho^2 + (6/5)(a\alpha\rho^5) + \\ & (c\rho^2/T^2)\{3[1 - \exp(-\gamma\rho^2)]/\gamma\rho^2 - \\ & (1/2 - \gamma\rho^2)\exp(-\gamma\rho^2)\} \qquad (1)\end{aligned}$$

and those for the Starling equation of state (*9, 10*), namely:

$$\begin{aligned}(H - H^{\circ}) = {} & (B_0'RT - 2A_0' - 4C_0'/T^2 + \\ & 5D_0'/T^3 - 6E_0'/T^4)\rho + (1/2)(2b'RT - \\ & 3a' - 4d'/T)\rho^2 + (1/5)\alpha'(6a' + 7d'/T)\rho^5 + \\ & c'/(\gamma'T^2)[3 - (3 + 1/2\,\gamma'\rho^2 - \gamma'^2\rho^4)\exp(-\gamma'\rho^2)] \qquad (2)\end{aligned}$$

were calculated with a digital computer, utilizing density values calculated, respectively, from the BWR (*3, 4*) and Starling (*9, 10*) equations of state for the sake of internal consistency.

Inspection of the results tabulated in Table III reveals excellent agreement between experimental and calculat-

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**Table I. Enthalpy Data of *n*-Heptane**

Datum: $H = 0$, saturated liquid *n*-heptane at 77°F

| Press, psia | Temp, °F | $H$, Btu/lbm (from measurements) | $H$, Btu/lbm (smoothed) | Press, psia | Temp, °F | $H$, Btu/lbm (from measurements) | $H$, Btu/lbm (smoothed) | Press, psia | Temp, °F | $H$, Btu/lbm (from measurements) | $H$, Btu/lbm (smoothed) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 50 | 275.4 | 120.1 | 120.0 | 150 | 276.8 | 119.8 | 121.0 | 230 | 265.4 | 113.5 | 113.5 |
| | 296.1 | 220.2 | 220.2 | | 301.6 | 136.6 | 137.5 | | 309.0 | 143.5 | 142.5 |
| | 448.9 | 345.9 | 343.0 | | 354.7 | 172.7 | 173.0 | | 373.7 | 186.5 | 186.5 |
| | 512.9 | 385.4 | 382.5 | | 400.2 | 283.1 | 283.1 | | 404.1 | 207.9 | 208.0 |
| | 555.6 | 411.9 | 410.0 | | 434.0 | 320.6 | 322.0 | | 446.2 | 283.7 | 283.7 |
| | 603.1 | 442.8 | 441.0 | | 455.9 | 336.0 | 336.0 | | 468.0 | 334.4 | 336.0 |
| | | | | | 502.4 | 367.4 | 367.0 | | 486.4 | 347.9 | 348.0 |
| 90 | 349.2 | 260.8 | 260.0 | | 503.2 | 366.4 | 367.2 | | 547.8 | 389.6 | 391.5 |
| | 395.5 | 308.7 | 307.0 | | 555.0 | 401.3 | 402.0 | | 622.2 | 441.8 | 444.0 |
| | 453.9 | 345.5 | 342.5 | | 589.4 | 426.0 | 425.5 | | | | |
| | 508.1 | 379.4 | 377.0 | | 627.5 | 453.3 | 452.0 | 350 | 401.3 | 204.1 | 206.0 |
| | 586.4 | 428.7 | 428.0 | | | | | | 454.6 | 245.3 | 248.5 |
| | | | | | | | | | 497.7 | 313.0 | 313.0 |
| | | | | | | | | | 503.3 | 341.3 | 341.0 |
| | | | | | | | | | 521.7 | 361.6 | 360.0 |
| | | | | | | | | | 531.8 | 365.7 | 367.0 |
| | | | | | | | | | 605.4 | 422.2 | 424.0 |
| 397 | 301.9 | 138.6 | 138.0 | 450 | 447.1 | 240.1 | 242.0 | 800 | 406.5 | 160.9 | 160.0 |
| | 353.2 | 171.8 | 172.0 | | 499.2 | 286.8 | 286.5 | | 507.3 | 288.4 | 288.4 |
| | 372.0 | 184.3 | 185.0 | | 515.6 | 302.2 | 304.5 | | 549.2 | 324.5 | 324.0 |
| | 486.1 | 274.5 | 276.0 | | 557.4 | 367.9 | 372.5 | | 603.4 | 376.6 | 377.0 |
| | 502.6 | 288.8 | 292.0 | | 602.7 | 413.6 | 413.0 | | | | |
| | 511.1 | 302.7 | 305.0 | | | | | 1000 | 457.1 | 248.1 | 248.0 |
| | 511.8 | 304.5 | 308.0 | 500 | 290.8 | 129.0 | 130.0 | | 521.3 | 298.1 | 298.0 |
| | 515.2 | 329.5 | 332.0 | | 407.1 | 207.7 | 210.0 | | 589.4 | 357.3 | 356.0 |
| | 517.0 | 334.7 | 337.0 | | 499.1 | 279.7 | 285.5 | | | | |
| | 568.0 | 389.5 | 390.0 | | 541.2 | 335.6 | 337.0 | 1500 | 408.6 | 210.5 | 210.5 |
| | 597.1 | 410.7 | 413.0 | | 587.1 | 391.3 | 392.0 | | 467.5 | 254.6 | 255.0 |
| | 598.2 | 415.8 | 414.5 | | | | | | 524.1 | 298.4 | 297.5 |
| | | | | 600 | 417.8 | 220.5 | 219.0 | | 594.3 | 354.7 | 353.5 |
| 400 | 353.8 | 172.5 | 172.5 | | 508.2 | 292.0 | 291.5 | | 619.8 | 373.4 | 375.0 |
| | 399.1 | 206.2 | 204.5 | | 548.0 | 331.3 | 332.0 | | | | |
| | | | | | 597.4 | 387.7 | 388.5 | | | | |

**Table II. Vapor Pressures and Heats of Vaporization of *n*-Heptane**

From API Technical Data Book and estimated from enthalpy measurements

| Vapor press, psia | Temp, °F | Heat of vaporization, Btu/lbm |
|---|---|---|
| 50 | 297 | 119 |
| 90 | 349 | 107 |
| 150 | 400 | 92 |
| 230 | 448 | 73 |
| 350 | 500 | 40 |

ed enthalpy values. Starling's values are the closest to the experimental data, followed by BWR's and Lydersen's, respectively, with an average error of 0.5, 0.5, and 3.25 Btu/lbm in the vapor region, and 1.3, 1.7, and 7.8 Btu/lbm in the liquid region.

In 1942 Gilliland and Parekh (*5*) reported direct measurements of the isothermal enthalpy change accompanying the expansion of *n*-heptane vapor from an elevated pressure to atmospheric pressure. The few experimental isothermal enthalpy change values of Gilliland and Parekh (*5*), as well as those calculated by the equations of state of Starling and Kwok (*9, 10*) and BWR (*3, 4*), were added to the ideal gas enthalpies reported by API (*1, 13*) for comparison with the measurements from this work. This comparison is presented in Table IV, in which the enthalpy values of Gilliland and those calculated by the methods of Starling and BWR show about the same average error, respectively, 0.9, 0.8, and 0.7 Btu/lbm.

In 1972 Wilson and coworkers (*14, 15*) reported experimental isothermal and isobaric enthalpy changes for *n*-heptane over wide ranges of pressures and temperatures. The ideal gas enthalpies of *n*-heptane, as derived from their data (*14, 15*) and from the experimental enthalpy data of Lenoir and coworkers (*6*) in 1971, were slightly higher than those reported in the API Technical Data Book (*2*) and in the API Project 44 tabulations (*1*). These ideal gas enthalpies of Wilson were consistently higher than those of API 44 (*1*); at 340°F the difference is 2.6 Btu/lbm increasing with temperature to become 4.5 Btu/lbm at 600°F.

In 1973 Lenoir and Hipkin (*7*) published additional enthalpy data of *n*-heptane and derived "corrected" ideal gas enthalpies of *n*-heptane, which on the average are 1.9 Btu/lbm lower than their previous values (*6*) used in the comparison by Wilson et al. (*15*).

The derived ideal gas enthalpies of Wilson et al. (*14, 15*) and the "corrected" values presented by Lenoir and Hipkin (*7*) in 1973 are compared with values from API 44 (*1*) in Table V; the estimates of ideal gas enthalpies of *n*-heptane from this work were in agreement with the

**Table III. Comparison of Experimental Enthalpies of *n*-Heptane of This Work with Enthalpies Calculated by Methods of Starling and Kwok (*9*, *10*), BWR (*3*, *4*), and Lydersen et al. (*8*, *16*) in Vapor and Liquid Phases**[a]

Datum: $H = 0$, saturated liquid *n*-heptane at 77°F

| | | 400°F isotherm | | | | 500°F isotherm | | | | 512.6°F isotherm | | | | 550°F isotherm | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *H*, Btu/lbm | | | | | | | | | | | | | | | |
| Region | Press, psia | Exptl | Starling | BWR | Lydersen | Exptl | Starling | BWR | Lydersen | Exptl | Starling | BWR | Lydersen | Exptl | Starling | BWR | Lydersen |
| Vapor | 50 | 312.0 | 311.5 | 311.3 | 311.1 | 373.0 | 372.9 | 372.8 | 372.8 | 382.0 | 380.9 | 380.8 | 380.9 | 405.0 | 405.2 | 405.1 | 405.2 |
| | 100 | 307.0 | 306.7 | 306.2 | 306.5 | 369.0 | 369.4 | 369.2 | 369.8 | 378.5 | 377.5 | 377.4 | 378.0 | 401.5 | 402.1 | 402.1 | 402.6 |
| | 150 | 299.0 | 300.7 | 299.9 | 300.1 | 365.4 | 365.5 | 365.3 | 366.8 | 373.5 | 373.9 | 373.7 | 375.1 | 398.0 | 398.9 | 398.8 | 400.0 |
| | 250 | | | | | 356.0 | 356.0 | 355.7 | 360.7 | 365.0 | 365.0 | 364.7 | 369.4 | 391.0 | 391.4 | 391.3 | 394.9 |
| | 350 | | | | | 337.0 | 337.6 | 338.6 | 352.8 | 351.0 | 350.5 | 350.9 | 362.1 | 381.5 | 381.5 | 381.6 | 388.7 |
| Liquid | 200 | 205.0 | 205.8 | 207.7 | 217.4 | | | | | | | | | | | | |
| | 400 | 204.7 | 205.4 | 207.3 | 214.7 | 289.0 | 289.8 | 289.5 | 293.2 | 312.0 | 316.3 | 309.2 | 303.6 | | | | |
| | 600 | 204.5 | 205.2 | 207.0 | 213.4 | 284.5 | 283.8 | 284.5 | 290.6 | 296.5 | 295.3 | 295.5 | 300.8 | | | | |

[a] The average errors for the three methods of Starling, BWR, and Lydersen are, respectively, in the vapor region, 0.5, 0.5, and 3.25, Btu/lbm and in the liquid region 1.3, 1.7, and 7.8 Btu/lbm.

**Table IV. Comparison of Experimental Enthalpies of *n*-Heptane of Gilliland and Parekh (*5*) and This Work with Enthalpies Calculated by Methods of Starling and Kwok (*9*, *10*) and BWR (*3*, *4*)**

Datum: $H = 0$, saturated liquid *n*-heptane at 77°F

| | | *H*, Btu/lbm | | | |
|---|---|---|---|---|---|
| | | Gilliland, exptl | This work, exptl | Starling, calcd | BWR, calcd |
| $T_r = 1.00$ | $P_r = 0.2$ | 379.5 | 381.0 | 379.0 | 378.9 |
| ($T = 512.6$°F) | $P_r = 0.4$ | 374.1 | 372.5 | 373.3 | 373.1 |
| | $P_r = 1.5$ | 297.2 | 296.0 | 295.5 | 295.7 |
| | $P_r = 2.0$ | 293.0 | 293.0 | 292.2 | 292.9 |
| $T_r = 1.10$ | $P_r = 0.6$ | 436.0 | 435.0 | 434.9 | 434.9 |
| ($T = 610$°F) | $P_r = 0.8$ | 429.7 | 429.5 | 429.5 | 429.7 |
| | $P_r = 1.5$ | 403.7 | 403.5 | 402.6 | 403.2 |
| | $P_r = 3.0$ | 372.9 | 372.0 | 371.0 | 370.4 |
| Average error | | 0.9 | | 0.8 | 0.7 |

values of API 44. In the comparisons in Table V, all ideal gas enthalpies were converted to the datum of $H = 0$, 77°F, and saturated liquid *n*-heptane.

Lenoir and Hipkin (*7*) reported their enthalpy values on the basis of $H = 0$, $-200$°F, and saturated liquid, and recommended the subtraction of 134.4 or 291.6 Btu/lbm to place their results respectively, on the basis of 75°F, saturated liquid or 75°F, ideal gas state (the latent heat of vaporization of *n*-heptane at 75°F is 157.2 Btu/lbm). The difference in ideal gas enthalpy between 75° and 77°F is equal to 0.2 Btu/lbm, as obtained from the integration of the $C_p^*$ equation of *n*-heptane (*13*), based on API 44 (*1*). The latent heat of vaporization (*1*, *2*) at 77°F being 156.9 Btu/lbm, then a subtraction of 134.9 Btu/lbm would put Lenoir's values on the basis of 77°F, saturated liquid.

Wilson and coworkers (*15*) presented their enthalpy values on the basis of $H = 0$ for liquid *n*-heptane at $-100$°F and 50 psia. Lenoir et al. (*6*) suggested that the change in enthalpy for liquid *n*-heptane is linear with temperature change from 75° to $-200$°F. As a conversion value of 134.4 Btu/lbm is recommended (*7*) for converting the enthalpy values based on the basis $H = 0$, liquid *n*-heptane at $-200$°F to the basis of 75°F, saturated liquid, then a value of 85.5 Btu/lbm is necessary to convert the enthalpies based on liquid heptane at $-100$°F to the basis of $H = 0$, 75°F, and saturated liquid.

The API 44 ideal gas enthalpies in Table V were obtained by integrating the $C_p^*$ equation for *n*-heptane (*13*), based on API 44 (*1*), from 77°F to the desired temperature and adding the latent heat of vaporization of *n*-heptane at 77°F (156.9 Btu/lbm).

Inspection of Table V reveals that the API 44 ideal gas enthalpies (the estimates from this work agree with the values of API 44) and those of Lenoir and Hipkin (*7*) are essentially the same, and Wilson's values are slightly higher than the former's.

Table V also shows the comparison of enthalpy deviations from this work, Lenoir and Hipkin (*7*), Wilson et al. (*15*), Starling and Kwok (*9*, *10*), and BWR (*3*, *4*). Examination of Table V reveals that enthalpy deviation values of this work, Lenoir and Hipkin (*7*), Starling and Kwok (*9*, *10*), and BWR (*3*, *4*) are of the same order of magnitude, considering that the experimental error in this work and the measurements of Lenoir et al. (*6*, *7*) are about the same, i.e., from 1 to 2 Btu/lbm. Wilson's derived ideal gas enthalpies and enthalpy deviations at 50 psia for *n*-heptane are slightly higher than all the others' values.

## Nomenclature

$A_0$, $B_0$, $C_0$, $a$, $b$, $c$, $\alpha$, $\gamma$ = constants in BWR equation of state

$A_0'$, $B_0'$, $C_0'$, $D_0'$, $E_0'$, $a'$, $b'$, $c'$, $d'$, $\alpha'$, $\gamma'$ = constants in Starling equation of state

$C_p^*$ = heat capacity at zero pressure, Btu/lbm °F

$H$ = enthalpy, Btu/lbm

$H^\circ$ = enthalpy corresponding to ideal gas state; btu/lbm

$P$ = pressure, psia or atm

$T$ = absolute temperature, K or °R

$\rho$ = density; g mol/l. or lb mol/ft$^3$

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Table V. Comparison of Experimental Enthalpy Deviations of *n*-Heptane of This Work, Lenoir and Hipkin (*7*), and Wilson et al. (*14, 15*) with Those Calculated by Methods of Starling and Kwok (*9, 10*) and BWR (*3, 4*)

| | Enthalpy, Btu/lbm (Datum: $H = 0$, saturated liquid *n*-heptane) | | | Enthalpy dev ($H° - H$), Btu/lbm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 psi | | | 50 psia | | | | | 100 psia | | | | |
| T, °F | API and this work | Lenoir | Wilson | This work[a] | Lenoir[b] | Wilson[c] | Starling | BWR | This work[a] | Lenoir[b] | Wilson[c] | Starling | BWR |
| 400 | 315.7 | 316.8 | 318.3 | 3.7 | 4.9 | 6.2 | 4.2 | 4.4 | 8.7 | 10.4 | 10.9 | 9.0 | 9.5 |
| 500 | 376.0 | 376.0 | 379.9 | 3 | 4.1 | 5.0 | 3.1 | 3.2 | 7.0 | 8.3 | 8.4 | 6.6 | 6.8 |
| 550 | 408.0 | 408.3 | 412.5 | 3 | 3.7 | 4.0 | 2.8 | 2.9 | 6.5 | 7.3 | 7.0 | 5.9 | 5.9 |

[a] Enthalpy deviation from API ideal gas enthalpy. [b] Enthalpy deviation from Lenoir's ideal gas enthalpy. [c] Enthalpy deviation from Wilson's ideal gas enthalpy.

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Received for review May 31, 1973. Accepted March 25, 1974. Financial support received from the National Research Council of Canada.

**Supplementary Material Available.** The complete Table I and two large-scale graphs containing enthalpy-temperature and pressure-enthalpy data for *n*-heptane will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JCED-74-193.

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# Dielectric Constants, Viscosities, and Related Physical Properties of 10 Liquid Sulfoxides and Sulfones at Several Temperatures

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**Dielectric constants, viscosities, densities, and refractive indices of 10 liquid dialkyl and cyclic sulfoxides and sulfones were measured at several temperatures ranging from 25° to 125°C. The experimental data as functions of temperature were fitted precisely to appropriate equations. Values of activation energies of viscous flow and Kirkwood correlation factors were also calculated. At comparable temperatures, sulfones consistently had higher dielectric constants, densities, viscosities, and activation energies of viscous flow but lower refractive indices than those of corresponding sulfoxides. Kirkwood correlation factors for the sulfones and sulfoxides ranged from 0.69 to 1.48 without any obvious general trend, and the magnitude of these factors implied only slight amounts of net parallel or antiparallel configurations of dipoles in the liquids.**

Sulfoxides and sulfones are recognized as important aprotic compounds having broad liquid ranges, large dipole moments, and moderately high dielectric constants and viscosities. Dimethyl sulfoxide (DMSO) is by far the best known and most widely used sulfoxide (*11, 18*); tetramethylenesulfoxide (TMSO) quite recently has received considerable attention as a ligand in inorganic complexes (*2, 3*). Tetramethylenesulfone or sulfolane ($TMSO_2$) and, to a lesser extent, its 3-methyl and 2,4-dimethyl derivatives ($3MeTMSO_2$ and $2,4MeTMSO_2$) have been used as electrolytic solvents (*6, 20*) and media for several other types of investigations (*4, 21, 34*).

The general objective of this research was to investigate the physical properties of sulfoxides and sulfones as functions of structure and temperature. This study was designed to yield the first values for the dielectric constants, viscosities, densities, activation energies of viscous flow, and Kirkwood correlation factors at several temperatures in the range of 25–125° for five compounds, namely, di-*n*-propyl sulfoxide (DnPSO), di-*n*-butyl sulfoxide (DnBSO), dimethyl sulfone ($DMSO_2$), di-*n*-propyl sulfone ($DnPSO_2$), and di-*n*-butyl sulfone ($DnBSO_2$). Of equal importance, this study was further designed not only to check limited literature data but also to significantly extend knowledge concerning several physical properties of the other five compounds named in the preceding paragraph which heretofore have been studied over considerably narrower ranges of temperature.

## Experimental

The experimental compounds were obtained from Phillips Petroleum Co., Crown Zellerbach Corp., and Aldrich

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