in previous literature (2). On previously reported phase diagrams of ternary molten sulfur systems, the tie lines point directly to the sulfur corner indicating that sulfur has no selectivity for either of the other two components.

The results presented in this paper suggest that molten sulfur may be a useful solvent for the separation of certain mixtures by extraction. On the basis of the limited amount of experimental data available, it is difficult to define exactly the types of mixtures which could be separated by extraction with molten sulfur. Apparently, however, cyclic organic compounds, and in particular aromatic, unsaturated and basic organic compounds, could be removed from saturated open-chain hydrocarbons by solvent extraction with sulfur. For example, continuous countercurrent contact of a naphthalene–normal octadecane mixture with molten sulfur would yield an octadecane phase saturated with sulfur but free of naphthalene and a molten sulfur phase containing dissolved naphthalene and minute quantities of octadecane.

LITERATURE CITED

(1) Bacon, R.F., Fanelli, R., *Ind. Eng. Chem.* **34**, 1043 (1942).
(2) Francis, A.W., J. CHEM. ENG. DATA **11**, 557 (1966).
(3) Wiewiorowski, T.K., Matson, R.F., Hodges, C.T., *Anal. Chem.* **37**, 1080 (1965).

RECEIVED for review August 11, 1967. Accepted September 18, 1967.

Thermal Conductivity of Fluids. Propane

L. T. CARMICHAEL, JOAN JACOBS, and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif. 91109

Measurements of the thermal conductivity of propane were carried out at pressures up to 5000 p.s.i.a. in the temperature interval between 40° and 340° F. The data were obtained with a conductivity cell of spherical section and are in satisfactory agreement with the data of other investigators obtained with instruments of markedly different configuration. The results are presented in graphical and tabular form. So far as can be ascertained, the residual thermal conductivity appears to be a single-valued function of specific weight throughout the range of conditions covered in the investigation except in the critical region. No detailed study of the latter region was made.

AS a result of limited information concerning the thermal conductivity of propane (*11-13, 23, 28-30, 32*), and continuing uncertainty as to the extent to which the residual thermal conductivity can be considered a single-valued function of the specific weight, measurements of the thermal conductivity of propane were made in the temperature interval between 40° and 340° F., at pressures between atmospheric and 5000 p.s.i.a.

Some progress has been made in predicting the thermal conductivity of the lighter hydrocarbons at attenuation (*4, 13, 24, 30*). However, it has not yet proved particularly effective to apply the principles of statistical mechanics to the prediction of the thermal conductivity of the lighter hydrocarbons at pressures markedly above that of the atmosphere. The thermal conductivity in the critical region was not investigated in detail.

EQUIPMENT AND METHODS

A conductivity cell of spherical section was employed in these investigations (*18-20*). This equipment involved a gold-plated sphere approximately 3.5 inches in diameter placed symmetrically within a slightly larger spherical cavity. The radial transport path was approximately 0.020 inch between the inner sphere and the outer shell. The inner sphere was provided with a specially-designed electrical heater that yielded nearly equal flux at all points around the surface of the sphere (*19*). Small thermocouples were employed to establish the temperature of the inner spherical surface of the outer shell. Appropriate corrections were made for the location of the thermocouples within the stainless steel body of the sphere and of the shell (*18*). Dimensions of the spherical cavity and the inner sphere were determined by direct physical measurements, and appropriate corrections for changes in the length of the transport path with changes in temperature and pressure were made. These corrections, for the most part, did not amount to much more than 1.0% in the resulting value of thermal conductivity. To check the over-all performance of the equipment, measurements upon the thermal conductivity of helium and argon at atmospheric pressure (*5, 6, 8*) were made. Comparisons yielded satisfactory agreement with values (*6, 8, 16, 31*) that are known with relatively high accuracy.

At most states, measurements were carried out at four different values of thermal flux. Periods of as much as 8 hours, but mostly approximately 4 hours, were required to achieve a steady state at each level of thermal flux. Values of $(q_m/d\theta)/\Delta t_m$ were established for each thermocouple at each level of flux. Individual corrections for the location of the thermocouples below the surface of the sphere and of the shell were applied after the limiting value at zero flux of the aforementioned derivative was obtained by application of regression analysis to the points as a group.

As a result of the change in average temperature of the phases with some local convection possible, there was a significant variation in the apparent thermal conductivity with flux, and the onset of gross convection could be easily established by rapid increase in the apparent thermal conductivity with a small increase in the radial temperature gradient. Measurements were made under such conditions that gross convection in the transport path was not experienced. In the above-described regression analysis, the authors assumed that the change in the apparent thermal conductivity or of the derivative, $(q_m/d\theta)/\Delta t_m$, was linear

Table I. Thermal Conductivity of Helium from Several Sources

Date	Pressure, P.S.I.A.	Temp., ° F.	Thermal Conductivity, B.t.u./(Hr.)(Ft.)(° F.) Authors	Keyes[a]	Hilsenrath, Touloukian[b]	Wilson[a]	Powell, Ho, Liley[a]
			ATMOSPHERIC PRESSURE				
1961	16.3	40	0.08204	0.08273	0.08257		0.08165
1959	15.0	100	0.08853	0.08864	0.08854	0.0890	0.08750
1960	18.9	100	0.08854				
1961	16.6	100	0.08859				
1964	18.1	100	0.08824				
1962[c]	17.7	130	0.09169	0.09150	0.09135		0.09064
1963[c]	16.4	130	0.09130				
1964[c]	17.3	130	0.09094				
1966	17.2	130	0.09132				
	16.9	130	0.09102				
	17.3	130	0.09090				
1959	17.7	220	0.09947	0.09960	0.09941		0.09878
1960	18.8	220	0.09946				
1959[c]	15.0	340	0.10954	0.10957	0.10936		0.11003
1960[c]	18.4	340	0.10927				
Average deviation[d]				0.00028	0.00016	0.00052	0.00066

[a] Statistical mechanical calculations and experimental data (*8*, *16*, *31*). [b] A critical review (*6*). [c] Average value for given year. [d] Average deviation expressed as:

$$s' = \sum_{1}^{N_p} \frac{|\,(k_e)_{\text{av}} - k_r|}{N_p}$$

with thermal flux and was equal for all of the thermocouples.

To establish that no unexpected variation in the performance of the instrument was experienced, measurements upon the thermal conductivity of helium at a pressure of approximately 17.1 p.s.i.a. at a temperature of 130° F. were carried out at three different intervals during the experimental program involved in the measurement of the thermal conductivity of propane. Variation in the behavior of the instruments throughout the experimental program was not more than 0.1%. As has been experienced in the utilization of this instrument with other materials (*2*, *3*), numerous extended evacuations and subsequent fillings with helium were required to eliminate the last traces of propane from the instrument. The diffusion of propane from the small interstices of the seals associated with the instrument was the primary problem in obtaining a pure sample of helium. The values of the thermal conductivity of helium as a function of time are in Table I. The corresponding values recommended by Hilsenrath and Touloukian (*6*) and other investigators (*8*, *16*, *31*) are included for comparison.

MATERIALS

The propane (Phillips Petroleum Co.) was research grade material with a reported purity of 0.9992 mole fraction. Furthermore, the vapor pressure of this material at a temperature of 100° F. did not change by more than 0.53 p.s.i., with an increase in quality from 0.10 to 0.80. The results of these measurements show that the propane employed did not contain more than 0.0008 mole fraction of impurities. The probable impurity was propene with traces of other paraffinic and olefinic hydrocarbons involving one or two carbon atoms per molecule.

EXPERIMENTAL RESULTS

Figure 1 shows the effect of thermal flux upon the quantity $(q_m/d\theta)/\Delta t_m$ for each of the six thermocouples used in determining the temperature of the outer surface of the inner sphere and the inner surface of the outer shell. After correction for the position of the thermocouples, the apparent thermal conductivity was calculated for each of the experimental points as shown in the lower part of the figure. The data of Figure 1 were obtained at a pressure of 1003 p.s.i.a. and an average temperature of 100° F.

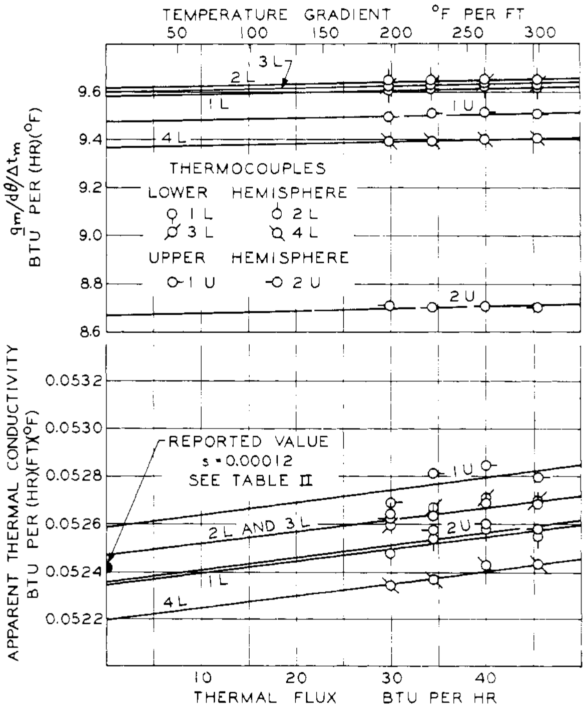

Figure 1. Effect of thermal flux upon apparent thermal conductivity at 100° F. and 1003 p.s.i.a.

Table II. Experimental Conditions

Pressure, P.S.I.A.	Number Flux Values	Maximum Flux, B.t.u./Hr.	Number of Points	Gradient,[a] °F.$^{-1}$	Standard Error of Estimate,[b] B.t.u./(Hr.)(°F.)	Thermal Conductivity, B.t.u./(Hr.)(Ft.)(°F.)	Standard Deviation,[c] B.t.u./(Hr.)(Ft.)(°F.)
				40° F.			
17	4	11.20	24	0.00077	0.00311	0.009189	0.000021
1012	4	42.58	24	−0.00018	0.01814	0.061637	0.000413
1909	4	46.15	24	−0.00125	0.02446	0.064752	0.000720
2936	4	47.08	24	−0.00042	0.01266	0.067115	0.001109
3885	4	45.72	24	−0.00082	0.00579	0.069173	0.001814
4479	4	42.99	24	−0.00054	0.00681	0.070526	0.002264
				100° F.			
17	4	13.40	24	0.00583	0.00320	0.010119	0.000037
1003	4	45.51	24	0.00083	0.00545	0.052419	0.000124
1934	4	46.42	24	0.00099[d] −0.00111[e]	0.00782	0.056004	0.000750
2888	4	41.93	24	0.00020	0.00007	0.058629	0.000924
3916	3	35.57	18	0.00124	0.01139	0.060961	0.001422
5026	4	42.77	24	0.00054	0.00852	0.063753	0.002043
				160° F.			
17	3	12.05	18	−0.00147	0.00364	0.013527	0.000031
310	4	17.61	24	0.00132	0.01048	0.015222	0.000036
988	4	39.73	24	−0.00051	0.00863	0.044622	0.000142
2001	4	44.90	24	0.00020	0.01820	0.049411	0.000437
				220° F.			
17	4	17.83	24	0.00419	0.00326	0.015647	0.000041
412	4	17.63	24	−0.00736	0.05172	0.018216	0.000063
606	3	17.98	18	0.01110[d] 0.02874[e]	0.00451	0.020653	0.000417
814	4	33.44	24	0.02127[d] 0.06315[e]	0.03222	0.038412	0.002109
1195	4	36.36	24	0.00995[d] 0.03485[e]	0.01620	0.036405	0.001476
1945	4	36.86	24	0.00124[d] −0.00030[e]	0.00260	0.043438	0.000542
2975	3	38.81	18	0.00102	0.00328	0.047262	0.000823
3934	4	39.11	24	0.00027[d] −0.00063[e]	0.00472	0.050514	0.001288
4943	4	39.46	24	−0.00239[d] −0.00554[e]	0.00843	0.053680	0.001954
				280° F.			
18	4	17.94	24	0.00326	0.02561	0.018378	0.000046
1076	4	24.62	24	0.02141[d] 0.06675[e]	0.03420	0.030712	0.000494
2025	4	40.10	24	0.00404[d] 0.00796[e]	0.02806	0.038835	0.000204
				340° F.			
18	4	19.56	24	0.00375	0.00824	0.021160	0.000026
1032	4	30.14	24	0.00332	0.00576	0.027140	0.000089
2031	3	30.25	18	0.00332[d] 0.00867[e]	0.00878	0.036410	0.000110
2964	4	30.88	24	0.00105[d] −0.00152[e]	0.00779	0.041185	0.000774
4265	3	33.79	18	0.00027[d] −0.00302[e]	0.01269	0.045127	0.001228

[a] Average value of $d[(q_m/d\theta)/\Delta t_m]/d(q_m/d\theta)$ for all thermocouple measurements, which corresponds to the average slope of the straight line shown in Figure 1. [b] Standard error of estimate of $[(q_m/d\theta)/\Delta t_m]_e$ from the linear regression analysis of the data from each of the several thermocouples:

$$\sigma = \left[\left\{\sum_1^{N_p}\left[\left(\frac{q_m/d\theta}{\Delta t_m}\right)_e - \left(\frac{q_m/d\theta}{\Delta t_m}\right)_s\right]^2\right\}/(N_p - 1)\right]^{1/2}$$

[c] Standard deviation from area-weighted average of the indication of the six thermocouples at zero flux:

$$s = \left[\sum_1^{N_p} (k'_{\text{av}} - k')^2/N_p\right]^{1/2}$$

[d] Average value of gradient of thermocouples in lower hemisphere. [e] Average value of gradient of thermocouples in upper hemisphere.

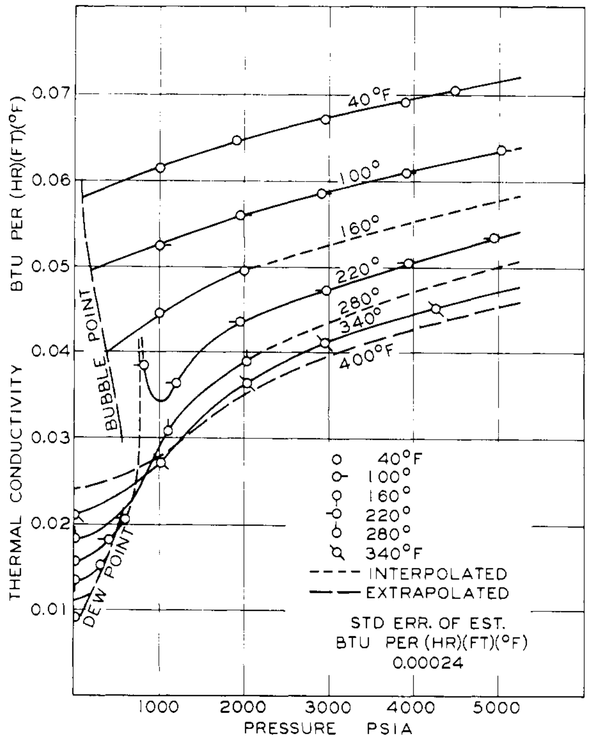

Figure 2. Effect of pressure upon the thermal conductivity of propane

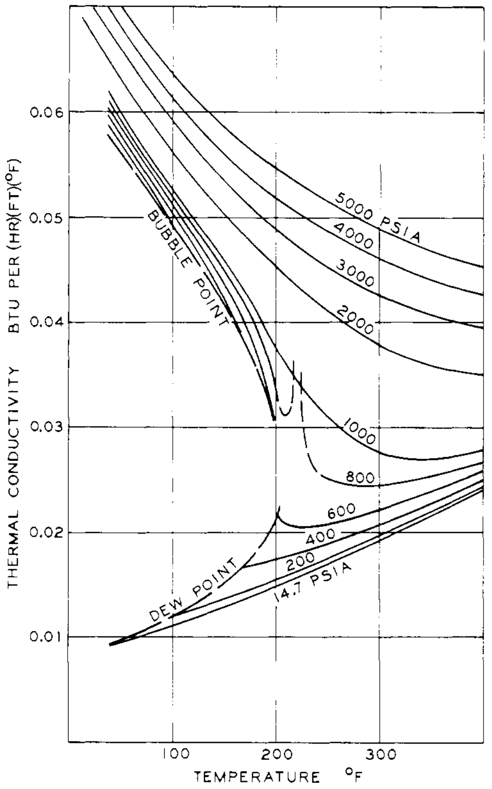

Figure 3. Influence of temperature upon the thermal conductivity of propane

The thermocouples were calibrated individually by comparison with the indications of a strain-free, platinum resistance thermometer recently calibrated by the National Bureau of Standards. The actual temperature of the outer surface of the outer shell was established from the indications of a similar strain-free, platinum resistance thermometer, which was compared periodically with the indications of the above-mentioned instrument calibrated at the National Bureau of Standards. The temperature relative to the international scale was known within 0.01° F. By extrapolating to zero thermal flux, the actual temperature of the transport path corresponded to that of the bath within the uncertainties of extrapolation involved.

Pressures were measured by means of a balance involving a piston-cylinder combination (*17, 21*), which was connected to the equipment through an oil-mercury filled, stainless-steel, aneroid-type diaphragm. Pressures were known within 0.2 p.s.i. or 0.1%, whichever was the larger measure of uncertainty. The pressure balance was calibrated periodically against the vapor pressure of carbon dioxide at the ice point (*7, 9, 10*).

The behavior in Figure 1 is typical of the experimental results obtained. At pressures well above 2000 p.s.i.a., sufficient elastic deformation of the spherical shell was experienced to yield a small eccentricity of the inner sphere with respect to the spherical cavity and thus resulted in a larger difference in the behavior of the thermocouples in the upper and lower part of the sphere.

A review of this situation (*2*) indicates that deviation in measurements from the upper or the lower hemisphere may be taken into account by a spatial average of the local values reported. Because of this small eccentricity at the higher pressures, the standard deviation of the experimental measurements at a given state is somewhat larger than that shown in Figure 1, when the data of both hemispheres were included. An analysis of the results indicates that this predictable difference in the length of the transport path of the upper and lower hemispheres did not introduce more than 0.1% added uncertainty in the behavior in the two hemispheres.

Table II presents values of the thermal conductivity of propane as determined from the experimental measurements after extrapolation to zero thermal flux, and the standard error of estimate of $(q_m/d\theta)/\Delta t_m$ for all the experimental measurements at each state are included. The average value of $(q_m/d\theta)/\Delta t_m$ at zero flux for all thermocouples has been recorded to make the standard error of estimate more meaningful. The gradient, which is the average value of the slope of the curves as shown in Figure 1, is recorded as a part of the table.

The experimental measurements shown in Table II are depicted in Figure 2 where the effect of pressure upon the thermal conductivity of propane is presented. Each of the points shown in Figure 2 represents an average of some 24 experimental measurements carried out at four different values of thermal flux. The standard error of estimate of the experimental measurements from the smooth values shown in Figure 2 and in Table III was 0.00024 B.t.u. per (hour)(foot)(° F.). Experimental indication of some anomalous behavior in the critical region is shown by a single point at 220° F. and 860 p.s.i. Because of uncertainty as to the actual behavior in this region, the dew point and bubble point have not been extended to the critical state. It is not certain whether the anomalous behavior is an actual transport property of the system or results from convection of other unexpected behavior encountered during measurements in the critical region.

The influence of temperature upon the thermal con-

Table III. Thermal Conductivity of Propane

Pressure, P.S.I.A.	Temperature, ° F. 40	100	160	220	280	340	400[a]
	(79)[b]	(188.7)	(383.8)				
Dew Point	0.00943	0.01184	0.01639				
Bubble Point	0.05789	0.04939	0.04002				
Attenuation	0.00912[c]	0.01110	0.01331	0.01564	0.01834	0.02113	0.02410
14.7	0.00919[d]	0.01114	0.01334	0.01568	0.01835	0.02114	0.02410
200	0.05850	0.04945	0.01413	0.01642	0.01890	0.02150	0.02435
400	0.05930	0.05025	0.04027	0.01811	0.02010	0.02240	0.02492
600	0.06008	0.05104	0.04205	0.02059	0.02169	0.02369	0.02571
800	0.06085	0.05183	0.04340	0.04002	0.02455	0.02524	0.02670
1000	0.06160	0.05260	0.04465	0.03426	0.02892	0.02697	0.02787
1500	0.06328	0.05445	0.04728	0.04022	0.03531	0.03261	0.03151
2000	0.06475	0.05613	0.04935	0.04351	0.03870	0.03626	0.03496
2500	0.06610	0.05760	0.05100[e]	0.04569	0.04140[e]	0.03905	0.03740
3000	0.06735	0.05887	0.05255	0.04731	0.04361	0.04129	0.03961
3500	0.06846	0.06008	0.05380	0.04880	0.04542	0.04290	0.04132
4000	0.06950	0.06119	0.05505	0.05030	0.04703	0.04440	0.04221
4500	0.07052[e]	0.06223	0.05640	0.05182	0.04852	0.04578[e]	0.04400
5000	0.07152	0.06333	0.05779	0.05332	0.04990	0.04710	0.04530
σ[f]	0.00012	0.00049	0.00013	0.00024	0.00008	0.00008	. . .

[a] Values for this temperature extrapolated. [b] Vapor pressure of propane expressed in p.s.i.a. [c] Extrapolated. [d] Thermal conductivity expressed in B.t.u./(hr.)(ft.)(° F.). [e] Values at this temperature and higher pressures interpolated. [f] Standard error of estimate, σ, expressed in B.t.u./(hr.)(ft.)(° F.):

$$\sigma = \left[\left\{ \sum_{1}^{N_p} (k_e - k_s)^2 \right\} / (N_p - 1) \right]^{1/2}$$

ductivity of propane, as established from the current experimental investigation, is shown in Figure 3. The rapid change in the thermal conductivity under isobaric conditions with change in temperature near the critical state follows the behavior shown in Figure 2.

The residual thermal conductivity as used in this investigation represents the difference between the thermal conductivity at a particular pressure and that at attenuation for the same temperature. This quantity is often known as a "thermal conductivity excess." Abas-Zade (*1*) predicted that the residual thermal conductivity would be a single-valued function of specific weight. Owens and Thodos (*15*) and Schaefer and Thodos (*22*) confirmed this prediction for a number of gases. More recently, Michels (*14*) and Sengers (*25-27*) have reviewed the thermal conductivity excess for a large number of compounds and have submitted substantial evidence that the single-valued relationship of the residual thermal conductivity to specific weight was not valid in the critical region.

The residual thermal conductivity of propane is presented as a function of specific weight for the current experimental data shown in Figure 4. In evaluating the standard deviation of the single-valued curve showing the thermal conductivity excess as a function of specific weight, two points were omitted since they were in the so-called critical region. The data for lower specific weights are shown on an enlarged scale in an insert on the same diagram.

Since there are more experimental data near atmospheric pressure than at more elevated pressures, a comparison of present measurements with those of other investigators is presented. Figure 5 presents current experimental data obtained at pressures near atmospheric corrected for the effect of pressure to attenuation. The same correction has been applied to each of the other sets of measurements at atmospheric pressure. The standard error of estimate of the current experimental data from the smooth curve shown in Figure 5 was 0.00019 B.t.u. per (hour)(foot)(° F.).

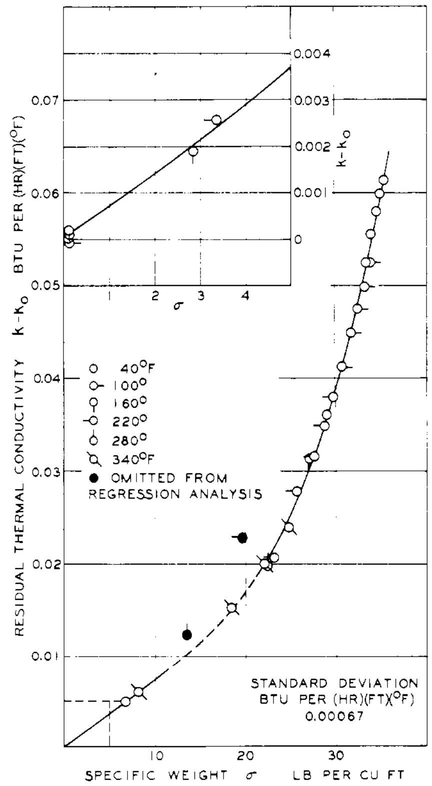

Figure 4. Residual thermal conductivity of propane

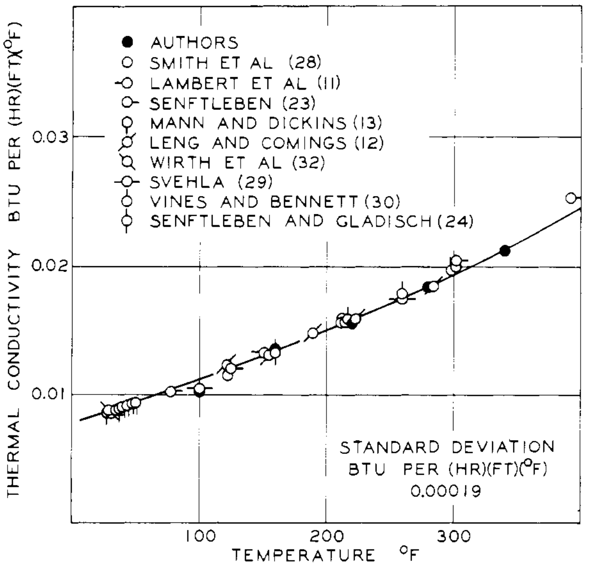

Figure 5. Thermal conductivity of propane at attenuation

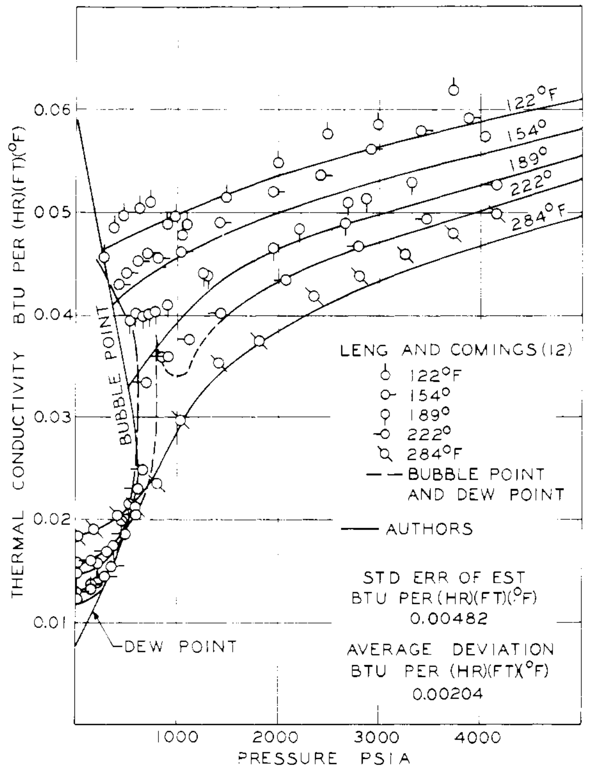

Figure 6. Comparison of results at elevated pressures with data of another investigator

The experimental data at elevated pressures appear to be limited to the measurements of Leng and Comings (*12*). Figure 6 shows the effect of pressure upon the thermal conductivity of propane, and the full curves are interpolated from the current experimental measurements. The experimental data of Leng and Comings (*12*) have been included. A sufficient number of experimental points were available to permit the standard error of estimate of these data from the current measurements to be included on the diagram.

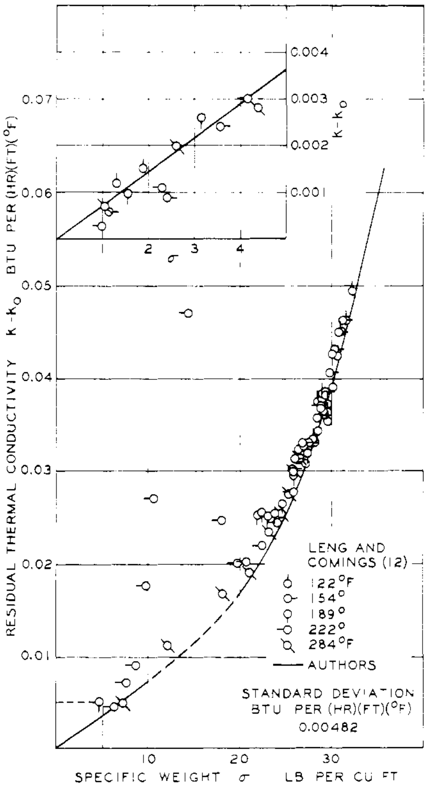

Figure 7. Comparison of residual thermal conductivities from two investigators

Figure 7 presents the residual thermal conductivity of propane utilizing the same experimental data shown in Figure 6 with the full curve being the authors' measurements. This curve has been broken in the region of the critical pressure of propane since the behavior in this region has not been studied in detail. The measurements of the other investigators have been shown as experimental points, and the standard deviation of their data from the smooth values resulting from this study is included. No effort was made to prepare critically-chosen values of the thermal conductivity of propane. Since the number of experimental measurements by others (*4*, *11-13*, *23*, *24*, *28-30*, *32*) is not large, it appears probable that further investigations will be required for critical review to be effective.

ACKNOWLEDGMENT

H. H. Reamer contributed to the supervision of the experimental work and Theresa Hubik to the resolution of the experimental data.

NOMENCLATURE

d = differential operator
k = thermal conductivity, B.t.u./(hr.)(ft.)(° F.)
k_0 = thermal conductivity at attenuation, B.t.u./(hr.)(ft.)(° F.)
k' = thermal conductivity uncorrected for effect of pressure on instrument, B.t.u./(hr.)(ft.)(° F.)
N_p = number of points
$q_m/d\theta$ = measured rate of energy addition, B.t.u./hr.
s = standard deviation defined in Table II
s' = average deviation defined in Table I
Δt_m = measured temperature difference, ° F.
θ = time, hr.
σ = specific weight, lb./cu. ft.
$\underline{\sigma}$ = standard error of estimate defined in Tables II and III
$\sum$ = summation operator

Subscripts

av = average
e = experimental
r = reference
s = smooth

LITERATURE CITED

(1) Abas-Zade, A. K., *Zh. Eksperim. i. Teor. Fiz.* **23**, 60 (1952).
(2) Carmichael, L. T., Berry, Virginia, Sage, B. H., J. CHEM. ENG. DATA **8**, 281 (1963).
(3) Carmichael, L. T., Sage, B. H., *Ibid.*, **9**, 511 (1964).
(4) Galloway, T. R., Sage, B. H., *Ibid.*, **12**, 59 (1967).
(5) Hilsenrath, J., Beckett, C.W., *et al.*, *Natl. Bur. Std. (U. S.) Circ.* No. **564** (1955).
(6) Hilsenrath, J., Touloukian, Y.S., *Trans. Am. Soc. Mech. Engrs.* **76**, 967 (1954).
(7) Keyes, F.G., *Proc. Am. Acad. Arts Sci.* **68**, 505 (1933).
(8) Keyes, F.G., *Trans. Am. Soc. Mech. Engrs.* **73**, 589 (1951).
(9) Keyes, F.G., Brownlee, R.B., "Thermodynamic Properties of Ammonia" Wiley, New York, 1916.
(10) Keyes, F. G., Dewey, Jane, *J. Opt. Soc. Am.* **14**, 491 (1927).
(11) Lambert, J. D., Cotton, K. J., *et al.*, *Proc. Roy. Soc. (London)* **231A**, 280 (1955).
(12) Leng, D. E., Comings, E. W., *Ind. Eng. Chem.* **49**, 2042 (1957).
(13) Mann, W. B., Dickins, B. G., *Proc. Roy. Soc. (London)* **134A**, 77 (1931).
(14) Michels, A., Sengers, J. V., Van der Gulik, P. S., *Physica* **28**, 1201 (1962).
(15) Owens, E. J., Thodos, G. J., *J. Am. Inst. Chem. Engrs.* **3**, 454 (1957).
(16) Powell, R. W., Ho, C. Y., Liley, P. E., *Natl. Bur. Std. (U.S.) Circ.* No. **8** (1966).
(17) Reamer, H. H., Sage, B. H., *Rev. Sci. Instr.* **26**, 592 (1955).
(18) Richter, G. N., Sage, B. H., CHEM. ENG. DATA SER. **2**, 61 (1957).
(19) Richter, G. N., Sage, B. H., J. CHEM. ENG. DATA **4**, 36 (1959).
(20) *Ibid.*, **8**, 221 (1963).
(21) Sage, B. H., Lacey, W. N., *Trans. Am. Inst. Mining Met. Engrs.* **136**, 136 (1940).
(22) Schaefer, C.A., Thodos, G., *Ind. Eng. Chem.* **50**, 1585 (1958).
(23) Senftleben, Hermann, *Z. Angew. Phys.* **17**, 86 (1964).
(24) Senftleben, Hermann, Gladisch, Heinz, *Z. Physik* **125**, 653 (1949).
(25) Sengers, J.V., *Intern. J. Heat Mass Transfer* **8**, 1103 (1965).
(26) Sengers, J.V., *Natl. Bur. Std. (U. S.) Misc. Publ.* **273** (1966).
(27) Sengers, J.V., "Transport Properties of Compressed Gases," *Natl. Bur. Std. (U. S.)*, prepared for proceedings of 4th Tech. Mtg. of Soc. Engrng. Science, 1967.
(28) Smith, W. J. S., Durbin, L. D., Kobayashi, Riki, J. CHEM. ENG. DATA **5**, 316 (1960).
(29) Svehla, R. A., *NASA Tech. Rept.* **R-132** (1962).
(30) Vines, R. G., Bennett, L. A., *J. Chem. Phys.* **22**, 360 (1954).
(31) Wilson, M. P., General Dynamics Corp., GA-1355, TID-4500, 15th Ed., January 1960.
(32) Wirth, H., Klemenc, A., *Monatsh* **83**, 879 (1952).

RECEIVED for review August 11, 1967. Accepted September 15, 1967. Work supported by the National Science Foundation under Grant GP-2357. This paper was accepted as a contribution to this journal by R.L. Pigford, Editor of *Ind. Eng. Chem. Fundamentals*.

Isopiestic Measurements on the System H_2O–NaCl–Na_2SO_4 at 25° C.

R. F. PLATFORD[1]
Fisheries Research Board of Canada, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada

The mean activity coefficients and the Harned coefficients for the system H_2O–NaCl–Na_2SO_4 have been calculated from isopiestic vapor pressure measurements for ionic strengths up to 6*m*. The results for NaCl in the system agree with those reported using e.m.f. measurements. Values for α_c in Harned's equation were −0.008, −0.010, −0.032, and −0.040 at I = 0.7, 1, 3, and 6, respectively.

TERNARY systems consisting of aqueous NaCl and another salt are important sea water analogs; this paper presents activity coefficients for the system H_2O-NaCl-Na_2SO_4 for comparison with results from the systems H_2O-NaCl-$MgSO_4$ (*5*) and H_2O-NaCl-$MgCl_2$ (*6*).

Activity and osmotic coefficients of pure Na_2SO_4 solutions at 25° C. have been reported for concentrations up to 4*m* (*7*) although the solubility of this salt is reported (*10*) to be only 1.96*m* at 25° C. Anhydrous Na_2SO_4 liberates enough heat on solution in water so that the warm solution is unsaturated, and on cooling to room temperature the solution becomes supersaturated with respect to $Na_2SO_4 \cdot 10H_2O$, which is the stable solid phase at 25° C. The system H_2O-NaCl—Na_2SO_4 is the first ternary system supersaturated with one of its components that has been studied by the isopiestic method.

EXPERIMENTAL

Reagents. Sodium chloride was precipitated with HCl and fused in a platinum dish. Sodium sulfate was recrystallized twice from distilled water and dried at 100° C. to give the anhydrous salt. The solubility of $Na_2SO_4 \cdot 10H_2O$ was determined by evaporating to dryness solutions saturated at 25° C. The mean of seven runs was 1.9503 ± 0.0020*m*.

Method. Solutions were equilibrated in seven silver cups resting in depressions in a gold plated copper block (*5*). The block fitted snugly in a 10-cm. Dry Seal desiccator sealed with a rubber O-ring. The desiccator was evacuated with a water aspirator and rotated for from 4 to 7 days at an angle in a water bath kept at 25° ± 0.005° C.

Solution concentrations were determined by weighing dry pure salts into the cups, adding water, and reweighing at the end of each run. One cup usually contained pure NaCl solution, another contained pure Na_2SO_4 solution, the rest were aqueous mixtures of the two salts.

Solutions were easily supersaturated with Na_2SO_4 by adding an appropriate amount of water to the anhydrous

---

[1] Present address: Canada Centre for Inland Waters, Great Lakes Division, Inland Waters Branch, Department of Energy, Mines and Resources, Burlington, Ontario, Canada