linearly to 5° intervals and smoothed using a nine-point cubic over the whole range (*3*). The standard deviations from the curves are not greater then 0.005 microohm cm.

The results for the four systems are given in Tables I-IV (which have been deposited with ADI), and are shown at 290° K. in Figure 1.

LITERATURE CITED

(1) Crisp, R.S., Henry, W.G., Schroeder, P.A., *Phil. Mag.* **10**, 553 (1964).

(2) Henry, W.G., Schroeder, P.A., *Can. J. Phys.* **41**, 1076 (1963).

(3) Guest, P.G., "Numerical Methods of Curve Fitting," p. 358, Cambridge University Press, 1961.

(4) Linde, J.O., *Ann. Phys. Lpz.* **15**, 219 (1932).

RECEIVED for review April 19, 1965. Accepted June 27, 1966. Material supplementary to this article has been deposited as Document number 9050 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Ternary Systems of Sulfur and Sulfur Compounds

ALFRED W. FRANCIS[1]
Socony Mobil Oil Company, Paulsboro, N. J.

New experimental observations are presented for 15 ternary systems of elemental sulfur, mostly near its melting point, 113° C.; 52 systems of sulfuric acid of various strengths including oleum and sulfur trioxide; 43 systems of methyl sulfate, 16 systems of ethyl sulfate, and ten systems of other sulfur compounds, a total of 102 (because 34 are in two categories). Sulfur was found completely unselective between any two hydrocarbons, even when liquid or in solution. The distortion of phase diagrams resulting from high reactivity of sulfuric acid or oleum with organic compounds was minimized by rapid observation and by dilution with alkyl sulfates or methanesulfuric acid. These reagents mix even with oleum, without evolution of appreciable amounts of heat, and so are probably true diluents. Yet a few systems show decided distortion because of the resulting quaternary systems. This is readily detected by the shapes. The unusual phase relations between sulfuric acid, sulfur trioxide, chlorosulfonic acid, hydrogen chloride, and water are shown in two graphs. Eleven systems of methyl sulfate and nine of ethyl sulfate, which do not have sulfuric acid as a component, contained usual features including isooptics, isopycnics, solutropes, and three liquid phases, but no island curves.

THIS is the seventh in a series of twelve papers presenting 1070 ternary systems mostly involving two liquid phases. Those involving sulfuric acid are necessarily approximate because of reaction. Means of minimizing the effects are presented.

SULFUR

Liquid sulfur was considered as a possible solvent for selective extraction of hydrocarbons since above the melting point, 113° C., it is miscible in all proportions with bicyclic hydrocarbons such as naphthalene, biphenyl, tetralin, 1- and 2-methylnaphthalene, and also with phenanthrene and fluorene (*1*). Its CST's with benzene, toluene, and *o*- and *p*-xylenes (*1*) are not excessively high; while the mutual miscibilities of sulfur with nonaromatic hydrocarbons are very low until it begins to react with them at about 135° C. Twenty-five ternary systems of sulfur have been published (mostly compiled in *8* pp. 187, 218), many of them involving an aromatic amine. Those with liquid ammonia (*5*; graphs 7, 29-33) show a deep purple color in the ammonia-rich layer. Two quaternary systems, with water, sulfur, hexane, and aniline or phenol (*12*) separate into four liquid layers at about 96° C.

Fifteen new ternary systems of elemental sulfur are presented in Figure 1, most of them at or near the melting point, so as to have two liquid phases. Systems were made up by weight with sulfur and a liquid not miscible with it near its melting point; and then titrated with the other component as shown in the graphs. Tie lines were observed by adjusting the compositions near 113° C. with substantial volumes of each liquid layer in equilibrium. The layers were separated and cooled to crystallize out the sulfur. The refractive indices from both layers and that of the original hydrocarbon mixture always agreed within 0.001. To the two layers of the systems of graphs 11 and 12, in which crystallization of naphthalene would prevent that procedure, a small addendum of naphthalene, added to the two liquid layers, was found to be distributed less than 5% to the sulfur layer.

In every case tried, all of the tie lines were found to be isologous, pointing directly toward the sulfur corner. This would indicate no selectivity for any hydrocarbon over another one. The proportions of the two hydrocarbons in the extract layer were the same as those of the same two hydrocarbons in the raffinate layer. A corollary is that the plait point in the graph is at the point of contact of the tangent to the binodal curve which passes through the sulfur corner. Thus in graph 11, which illustrates two systems including cetane and decane, respectively, both plait points are at 32% naphthalene and the apices of the curve are at 48% naphthalene.

---

[1] Present address, Mobil Chemical Company, Metuchen, N. J.

Isologous tie lines occur also in the published graphs of sulfur with aromatic amines (compiled in *9*). Attention was called (*8*, p. 88) to inaccuracies in these graphs, since they show angular intersections of binodal curves, especially those having islands, which are shown in the shapes of lenses.

The anomaly of complete lack of selectivity of a solvent for a miscible component (naphthalene) over an immiscible component (decane,) is rare but not unique. It occurs also using *tert*-amyl alcohol with respect to glycerol over water and using diethylene glycol for thiophene over benzene (*8*, p. 36).

Systems of liquid sulfur dioxide have been presented extensively (*2*), and will not be considered here.

SULFURIC ACID

In spite of the importance of sulfuric acid, relatively few of its ternary systems have been published (compiled in *9*, pp. 188, 219) before the present series, probably because of its reactivity with most organic compounds. This uncertainty persists in some of the new systems presented here; but it is minimized by rapid observations.

Certain reagents, including methanesulfonic acid (graphs 36, 57, and 58), and methyl and ethyl sulfates (graphs 37 to 43, 55, 62, 64, and 65) mix with sulfuric acid or even oleum without appreciable evolution of heat. They can be considered as true diluents for sulfuric acid, (*10*, *11*) as contrasted with water and alcohols, which evolve considerable heat and change the character of the acid. These diluents have helped greatly to obtain some measure of accuracy in the presence of such a violent reagent as sulfuric acid. The reaction noted in graph 63 takes place only where there is a limited concentration of such a diluent. Liquid sulfur dioxide serves similarly as a diluent for oleum above 25% sulfur trioxide, but not much lower because it does not mix with sulfuric acid (*2*, graphs 16, 55, 59, and 60). Nitrobenzene and other nitro compounds serve to dilute sulfuric acid of strength about 80 to 95%, but not oleum, which sulfonates it. The lower percentage is limited by miscibility. Although the highest grade of chemicals available was used, the chief uncertainty in observations in this investigation was due to reaction rather than to impurities in the reagents.

For convenience many of the new systems of sulfuric acid are plotted in Figures 3 or 4 instead of Figure 2,

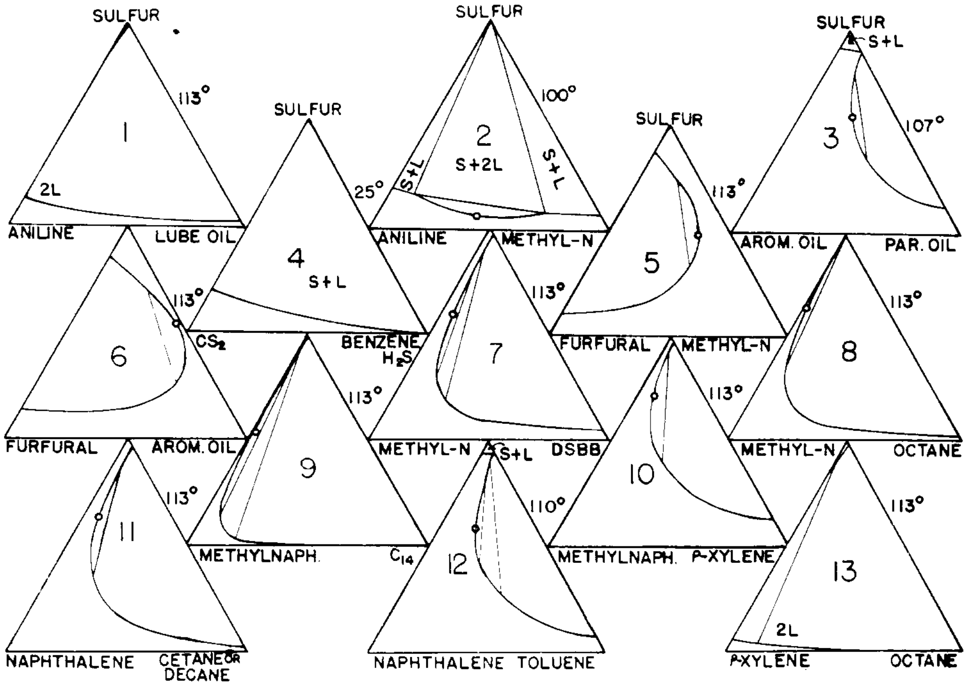


Figure 1. Sulfur systems

One hundred and two systems are presented on 78 independent triangular graphs. The component represented by the top corner in each figure is sulfur for the first 13 graphs, sulfuric acid of some strength in graphs 14 to 28, methyl sulfate in graphs 29 to 53, ethyl sulfate in graphs 54 to 68. The percentage of sulfuric acid (remainder water) is shown either above the top corner or by a number inside the top corner, except in graph 28, where it is pure sulfur trioxide. In graphs 46 to 53 and 67 and 68, an asterisk inside the top corner indicates a mixed component as follows:

Graph	
46	90% methyl sulfate, 10% methanesulfonic acid
47	90% methyl sulfate, 10% of 16% oleum
48	75% methyl sulfate, 25% of 30% oleum
49	65% methyl sulfate, 35% of 96.8% of H_2SO_4
50	65% methyl sulfate, 35% of 16% oleum
51	65% methyl sulfate, 35% of 30% oleum
52	90% methyl sulfate, 10% of $NaHSO_4$
53	54% methyl sulfate, 46% of 100% H_2SO_4
67	90% ethyl sulfate, 10% of methanesulfonic acid
68	70% ethyl sulfate, 30% of 30% oleum.

Other components are shown by names, formulas, or abbreviations under the appropriate corners. Two or more names in the same location indicate alternative components (two or more systems), graphs 4, 23, 37, 39, 40, 42, 43, 50, 51, 66.

Circles on binodal curves are plait points. The temperature of each isotherm is 25° C. except when indicated otherwise above the right side line, graphs 1–13, 41–43, 47, 72, 45.

The straight dashed line in graph 29 is an isopycnic connecting compositions having the same density. Tie lines marked with colors, graphs 24, 29, 46, 57, 72, 76, connect compositions having equal refractive indices. Emulsions along these lines exhibit the colors named, and those with neighboring compositions exhibit others colors in the opalescent spectrum. Tie lines parallel with a base line, in graphs 20, 23, 60 are marked solutropes. Other tie lines are omitted to avoid confusion, except in graphs 27, 28. Three liquid phases are shown in graphs 47, 58, and 67.

in order to have more space to characterize the sulfuric acid used. Altogether, 52 new systems of sulfuric acid (including oleum and sulfur trioxide) are presented.

In spite of dilution and rapid observation the shapes of the phase boundaries in graphs 25, 26, 61, 62 indicate a reaction. The shapes are typical of some quaternary systems. The reverse curves are attributed to the presence of isopropylsulfuric acid or benzene sulfonic acid, respectively, resulting from the reaction with sulfuric acid. The reverse curves do not usually eliminate the plait points; and large parts of the phase boundaries are substantially the same as in the original (no reaction) binodal curves. But the pan handles in the phase boundaries of graphs 25, 26, and 62, and the hump in graph 61 have no relation to the binodal curves; and tie lines connecting compositions of the phases would not terminate on the phase boundaries shown. In graphs 61 and 62 these entire regions show structural colors, as marked. The order of colors in the two cases is reversed because of different extents of reaction, and the colors vary with time. In graph 63 the extent of reaction is so great that no attempt is made to approximate the complete phase boundary.

Graphs 14 and 15 are almost identical except for the position of the plait point. Acetic acid is distributed mostly to the aqueous layer, and acetone to the hydrocarbon layer. With stronger acid, graph 18, the distribution of acetic acid is more even. Graphs 14, 15, 19, and some others, though quaternary, can be treated as ternary because the solubilities of both water and sulfuric acid in hydrocarbons are negligible.

The relations between the components, sulfuric acid, sulfur trioxide, hydrogen chloride, water, and chlorosulfonic acid shown in graphs 27 and 28, are of special interest. The upper quarter of graph 28 is equivalent to graph 27, reversed. The almost complete insolubility of both water and sulfuric acid in liquid hydrogen chloride; and that of hydrogen chloride in 100% sulfuric acid, even under high pressure is striking. These relations are indicated by

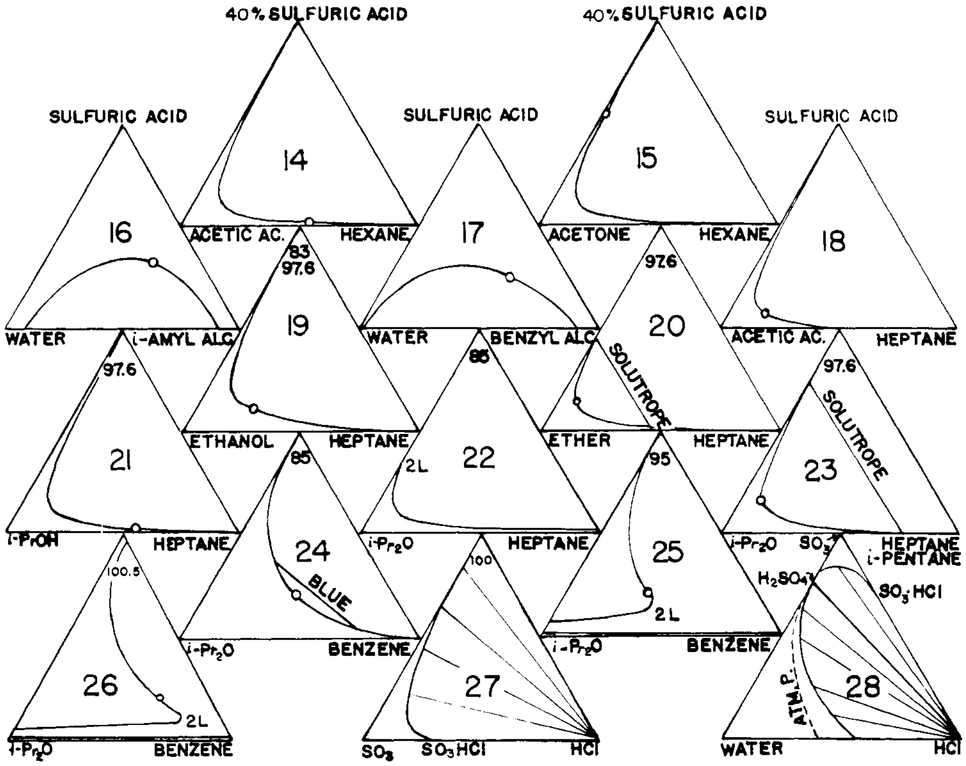


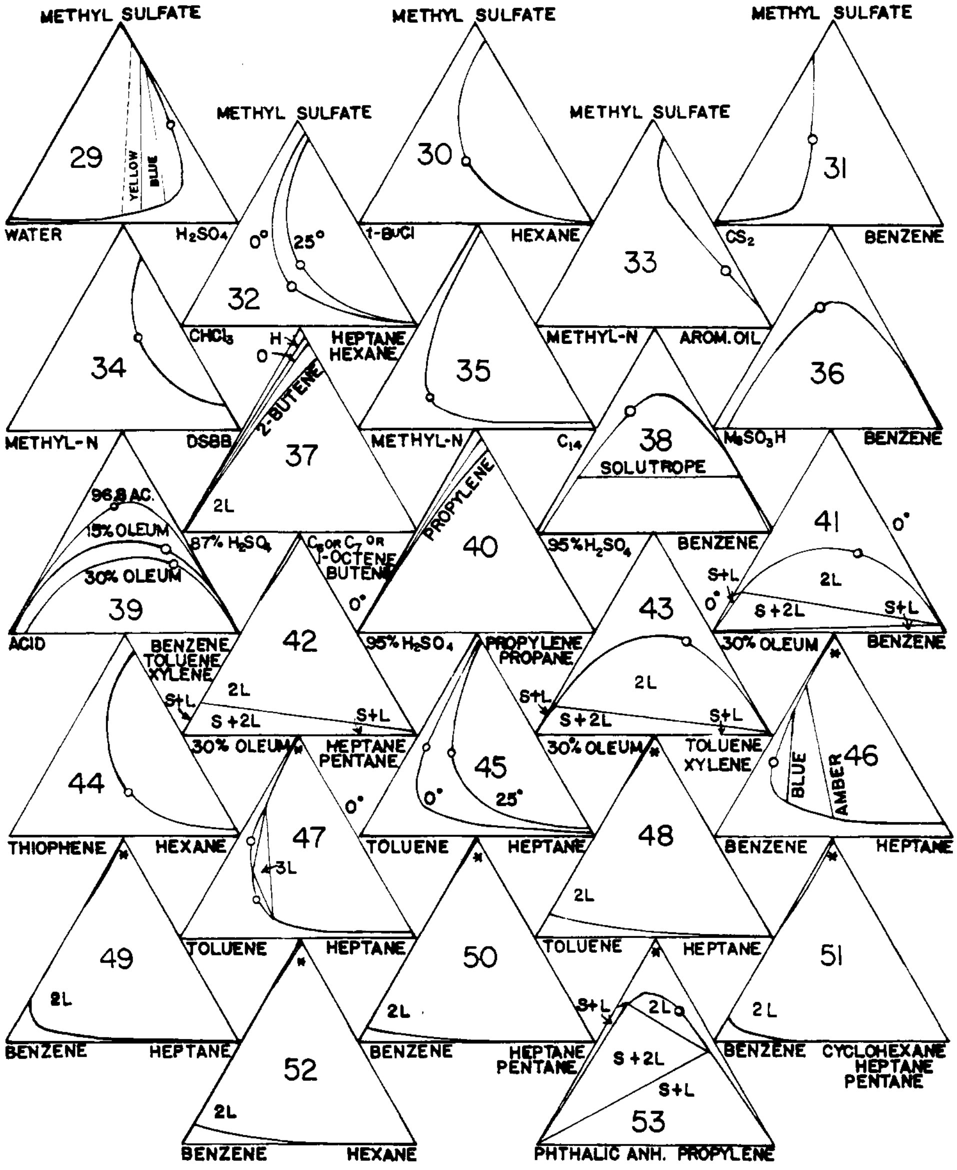
Figure 2. Sulfuric acid systems

Abbreviation	Name	Graphs
AC	Acid	14, 18, 39
ACID	Sulfuric acid (3 strengths shown)	39
ALC	Alcohol	16, 17
ANH	Anhydride	53
AROM. OIL	Aromatic oil (see 2 or 3, Table I)	3, 6, 33
t-BuCl	*tert*-Butyl chloride	30
C_6	*n*-Hexane	37
C_7	*n*-Heptane	37
C_{14}	*n*-Tetradecane	9, 35, 59, 76
$C_{11}F_{20}$	Perfluoro-1-methylnaphthalene	72
$C_{19}F_{36}$	Perfluoro-1-nonylnaphthalene	72
CETANE	*n*-Hexadecane	71
2,4-DMP	2,4-Dimethylpentane	66
DMSO	Dimethylsulfoxide	70, 71
DSBB	*m*-Di-sec-butylbenzene	7, 34
EDF	Ethylene diformate	78

the tie lines shown. The observations were made in a visual autocalve (7).

ALKYL SULFATES

Figures 3 and 4 present eleven additional systems of methyl sulfate and nine of ethyl sulfate beside 39 systems involving sulfuric acid also as a component (e.g. nine in graph 39). These were observed by simple titration of two components with the third, as in earlier papers of this series (3, 4, 6). In graphs involving a liquefied gas as a component, graphs 37, 40, 65, and 74, the titration was necessarily in sealed glass tubes (2, 5). The mixed components at the top corner in graphs 46 to 53 and 67 and 68, indicated by asterisks, are listed in the legend. The 50 graphs of Figures 3 and 4 include three with iso-optics (in addition to those mentioned with sulfuric acid). Systems of seven other sulfur compounds are shown in the last ten graphs.



* SEE LEGEND

Figure 3. Methyl sulfate systems

ETHANOL	Ethyl alconol	19
ETHER	Ethyl ether	20
H	Hexane or heptane	37
IBS	Isopropylbenzene sulfonate	73
i-PENTANE	Isopentane	23
i-PrOH	Isopropyl alcohol	21
i-Pr_2O	Di-isopropyl ether	22 to 26 ·
LUBE OIL	A clean lubrication oil stock (see 2 or 3, Table I)	1
METHYL-N or METHYLNAPH	1-Methylnaphthalene	2, 5, 7, 8, 9, 10, 33, 34, 35, 59, 71, 76

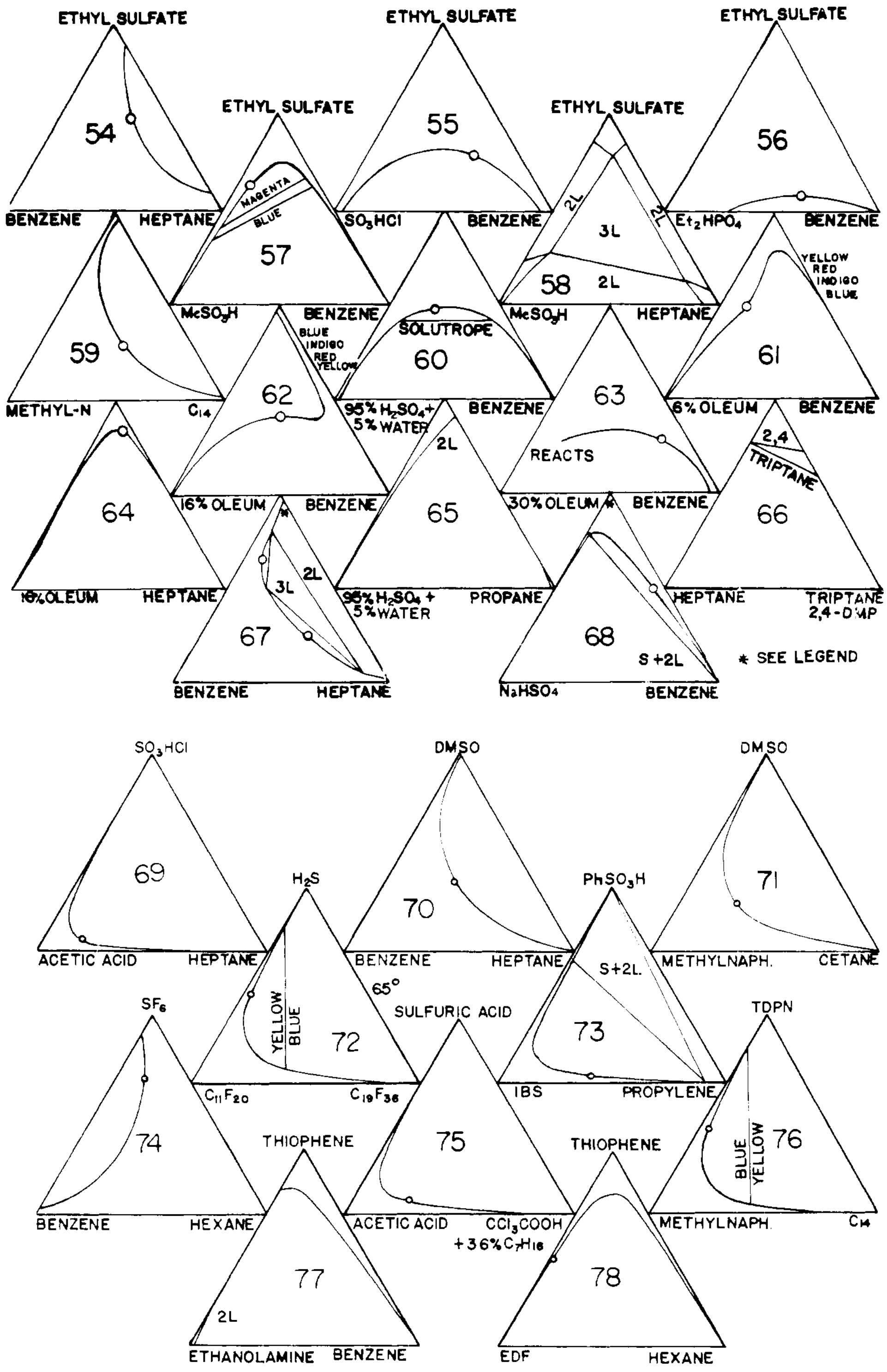


Figure 4. Ethyl sulfate and other systems

$MeSO_3H$	Methanesulfonic acid	36, 57, 58
O	1-Octene	37
OLEUM	Fuming sulfuric acid	39, 41, 42, 43, 61, 62, 63, 64
$PhSO_3H$	Benzene sulfonic acid	73
PAR. OIL	Paraffinic oil	3
SF_6	Sulfur hexafluoride	74
SO_3HCl	Chlorosulfonic acid	27, 28, 55, 69
TDPN	Thiodipropionitrile	76
TRIPTANE	Trimethylbutane	66

LITERATURE CITED

(1) Francis, A.W., "Critical Solution Temperatures," *Advan. Chem. Ser.* **31**, 165–6, 169 (1961).
(2) Francis, A.W., J. CHEM. ENG. DATA **10**, 45 (1965).
(3) *Ibid.*, p. 145.
(4) *Ibid.*, p. 260.
(5) *Ibid.*, p. 327.
(6) *Ibid.*, **11**, p. 96.
(7) Francis, A.W., *J. Phys. Chem.* **58**, 1099 (1954).
(8) Francis, A.W., "Liquid-Liquid Equilibriums," pp. 35, 88, 187–8, 218–9, Wiley, New York, 1963.
(9) Francis, A.W., in "Solubilities of Inorganic and Organic Compounds," A. Seidell and W. F. Linke, Eds., Supplement to the 3rd ed., pp. 1066–7, Van Nostrand, Princeton, N. J., 1952.
(10) Francis, A.W., U. S. Patent **2,756,266** (July 24, 1956).
(11) *Ibid.*, **2,776,327** (Jan. 1, 1957).
(12) Mertslin, R.V., Nikurashina, N.I., Gos'kova, I.D., Erofeeva, M.I., *Uchenye Zapiski Saratov Univ.* **71**, 99, 105 (1959); *C.A.* **56**, 2033h, i (1962).

RECEIVED for review May 17, 1965. Accepted August 31, 1965. Division of Physical Chemistry, 150th Meeting, ACS, Atlantic City, N. J., September 1965.

Physical Properties of Decaborane(14) Derivatives

R. W. ATTEBERRY
Chemicals Division, Olin Mathieson Chemical Corp., New Haven, Conn.

Enthalpy and entropy of vaporization for 2-ethyldecaborane(14) are 13.8 kcal. and 28.0 cal. per deg. per mole, respectively. Similar values for 1,2-diethyldecaborane(14) are 18.1 kcal. and 39.0 cal. per deg. per mole. Activation energies for flow are 4.8 kcal. for the monoethyl and 3.0 kcal. for the diethyl derivative. The former demonstrated a distribution of free volumes double that of the latter. These results are interpreted as changes from somewhat associated, spherical molecules for the 2-ethyldecaborane(14) to highly asymmetric, strongly associated 1,2-diethyldecaborane(14) molecules.

PHYSICAL MEASUREMENTS on 2-ethyldecaborane(14), I, and 1,2-diethyldecaborane(14), II, are given in Table I. These materials were prepared by reactions between decaborane(14) and ethyl chloride, catalyzed by anhydrous aluminum trichloride, then purified by reduced pressure fractionation to 99.9% assay of boron, carbon, and hydrogen.

METHODS

Kinematic viscosities were obtained with Cannon-Fenske viscometers operated under high purity nitrogen atmospheres; these values are means of at least 11 determinations and of 0.5% precision. Densities were determined pycnometrically with 0.3% precision. Vapor pressures were determined with the Reid micro vapor pressure apparatus operated under high purity nitrogen atmospheres, with a precision of 0.5%.

THERMODYNAMICS

Enthalpies of vaporization calculated from the Clapeyron-Clausius equation gave values of 13.8 kcal. for I and 18.1 kcal. for II. Moreover, this value for I correctly predicts the extrapolated boiling temperature for I at 217° C. (*1*), and gives $\Delta S_{\text{vap.}}$ = 28.0 cal. per degree per mole.

Table I. Physical Measurements on Decaborane(14) Derivatives

	Temperature, ° C.											
	0	20	30	40	45	50	55	60	65	70	75	80
I. 2-ETHYLDECABORANE(14), $C_2H_5B_{10}H_{13}$												
Kinematic viscosity, centistokes	13.59	7.62	6.10			4.56		3.43				
Density, grams/cc.	0.8296	0.8164	0.8099			0.7967		0.7903				
Absolute viscosity, centipoises	11.28	6.22	4.94			3.63		2.71				
Vapor pressure, mm. of Hg					0.34	0.49	0.68	0.84	1.26	1.67	2.19	
Free volume, $\frac{V_o}{V - V_o}$[a]	5.43	4.94	4.64			4.25		4.08				
II. 1,2-DIETHYLDECABORANE(14), $(C_2H_5)_2B_{10}H_{12}$												
Kinematic viscosity, centistokes	11.80	6.35	5.20	4.19		3.55		3.17				
Density, grams/cc.	0.8410	0.8283	0.8215	0.8150		0.8088		0.8025				
Absolute viscosity, centipoises	9.84	5.26	4.27	3.42		2.87		2.54				
Vapor pressure, mm. of Hg								0.27	0.30	0.49	0.72	1.03
Free volume, $\frac{V_o}{V - V_o}$[a]	2.60	2.43	2.38	2.32		2.24		2.20				

[a] Based upon $d = 0.8$ gram/cc./$B_{10}H_{14}$ (solid).