ACKNOWLEDGMENT

The author expresses his gratitude to Wai-Ching Wong, Department of Mathematics, University of Rochester, for the calculation of all values of R_D used in this work.

LITERATURE CITED

(1) Christopher, P.M., J. Chem. Eng. Data 5, 568 (1960).
(2) Christopher, P.M., Tully, T.J., *J. Am. Chem. Soc.* **80**, 6516 (1958).
(3) Green, M., Robinson, P. H., *J. Phys. Chem.* **57**, 938 (1953).
(4) Quane, D., Bottei, R.S., *Chem. Rev.* **63**, 403 (1963).
(5) Vogel, A.I., Cresswell, W.T., Jeffery, G.H., Leicester, J., *J. Chem. Soc.* **1952**, p. 514.
(6) Vogel, A.I., Cresswell, W.T., Leicester, J., *J. Phys. Chem.* **58**, 174 (1954).

RECEIVED for review July 2, 1964. Accepted September 8, 1964.

Ternary Systems of Liquid Sulfur Dioxide

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

This paper presents in a concise arrangement experimental graphs of 15 aqueous and 60 nonaqueous systems of liquid sulfur dioxide under pressure and usually at room temperature. They are ternary except the last five which have an extra component as a diluent. Most of the systems show two liquid phases. The graphs include the usual types and also some special features—such as isopycnics, iso-optics, solutropes, island curves, and separate binodal curves. Some of these graphs are pertinent to solvent extraction with mixtures including sulfur dioxide.

APPLICATION of liquid sulfur dioxide for solvent extraction of hydrocarbon oils was demonstrated over 50 years ago by Edeleanu (2). During that time, it has been one of the most widely used selective solvents for that purpose. Processes employing it have aided in development of chemical engineering for handling condensed gases of moderate pressure.

Advantages of sulfur dioxide over other selective solvents are low cost, convenient transfer owing to pressure, stability, relative inertness when anhydrous, and easy recovery. The chief limitation of sulfur dioxide is the extreme dependence of solubility on the molecular weights of the hydrocarbons. Those of the gasoline range have high solubility, and those of the lubricating oil range have low solubility. The selectivity of sulfur dioxide for type of hydrocarbon is sometimes masked by the effect of molecular weight. This is especially true for cycloparaffins over paraffins, in which the selectivity is negligible for comparable molecular weight.

Extensive studies of mutual solubilities of sulfur dioxide and hydrocarbons have been made by Seyer and coworkers as cited by Francis (3). The apices of their binary graphs are critical solution temperatures (CST), which summarize the studies. CST of sulfur dioxide have been published also by Leslie (*17*), and by others. Such temperatures are listed (*4*) for 50 hydrocarbons and for 40 nonhydrocarbons.

The CST of sulfur dioxide and water were observed by Terres and Rühl (*21*) as 133°, and by Spall (*20*) as 128°. An early unpublished observation of the present author (1932) had agreed with Terres, and also noted an isopycnic at 129.5° (temperature of equal densities of the layers). Butcher and Hanson (*1*) observed mutual solubilities up to 65°.

The solubility of liquid sulfur dioxide in water, 26%, is much greater than that of water in liquid sulfur dioxide, 1.5%. This is characteristic of many pairs of liquefied gases with less volatile components (*9*). Solubility of sulfur dioxide at low pressures is available (*16, 19*) in aqueous and many other solutions.

Although solvent extraction typically involves a ternary system, only a few such systems with sulfur dioxide have been published. Satterfield and coworkers (*18*) presented eight ternary systems with liquid sulfur dioxide, an aromatic hydrocarbon, and a nonaromatic hydrocarbon (one combination at three temperatures). All were at low temperature, below the boiling point of sulfur dioxide, −10°, and so at atmospheric pressure. They are all graphs of the usual bite type. The only published graphs for systems of sulfur dioxide under pressure and two other pure components are those of propane with propylene (*12*) or with hydrogen cyanide (*11*); and those of carbon dioxide (*9*) with cetane, methylnaphthalene, or octadecane.

This paper presents 75 ternary sulfur dioxide systems (further data may be obtained from the author). These all involve a liquid phase rich in sulfur dioxide under pressure, and at room temperature unless otherwise indicated. Most of them show two liquid phases, although a few have as one component a fairly soluble solid such as urea; some of these show only a solid-liquid equilibrium (graphs 11, 19, 33, 35). The purpose of this research was to find combinations of solvents suitable for concentrating benzene or other aromatics or olefins from more saturated hydrocarbons.

---

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

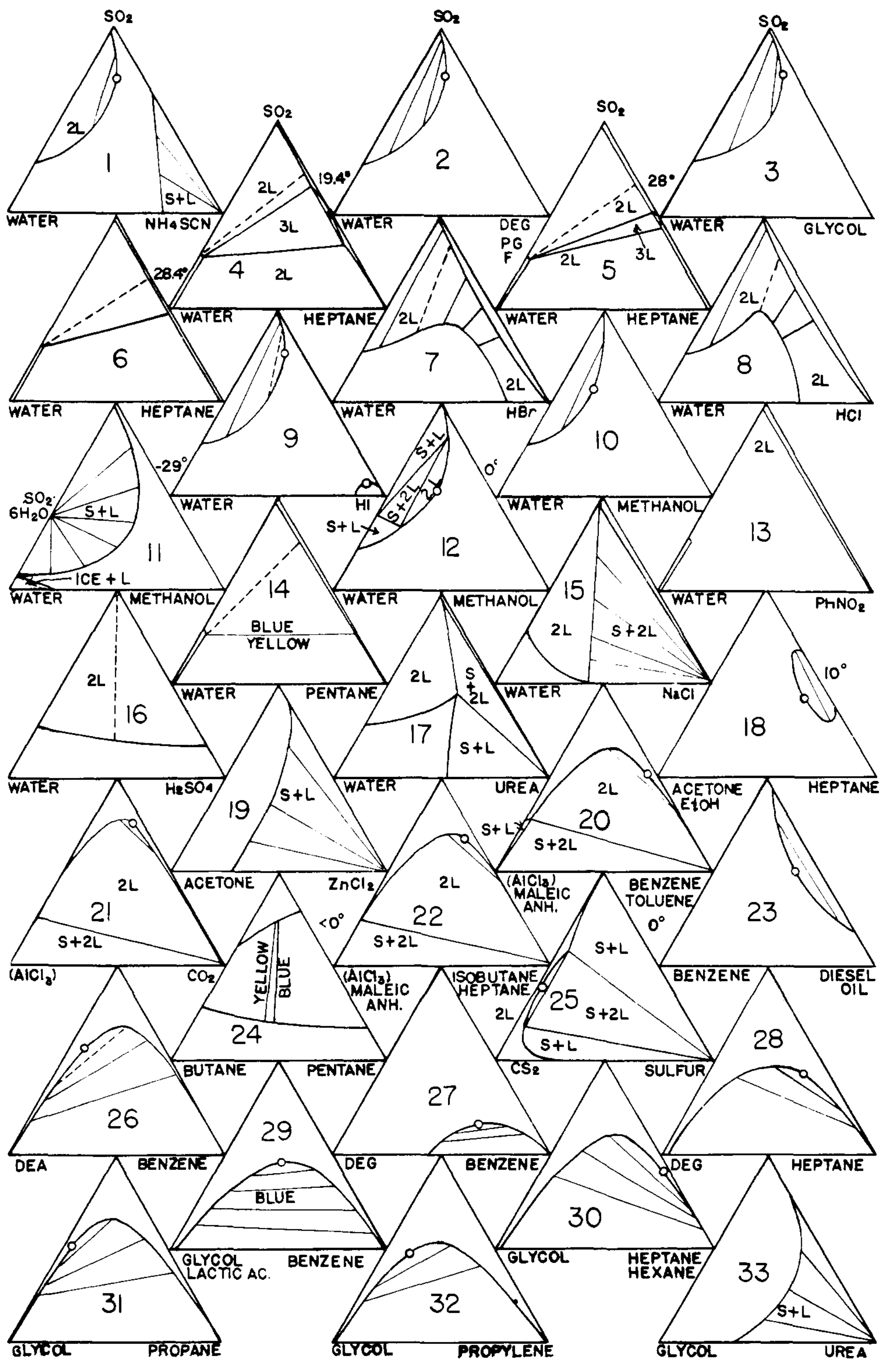

Figure 1. Ternary sulfur dioxide systems

Top corner sulfur dioxide (pure except in the last two graphs) in each of 66 independent triangular graphs. All plots are in weight percentages. Other components are indicated by name of formula or abbreviation *under* the appropriate corner. Graphs are arranged alphabetically for each of two groups, aqueous systems (graphs 1–17) and nonaqueous ternary systems (graphs 18–61). The last five graphs show quaternary systems (see below). So is graph 55, but it is not complex because the oleum is almost entirely in the lower layer (left side). The fourth component in them is assigned so as to minimize fuzziness (*6*, *13*, Chapter 8). Two or three substances named in the same small triangle indicate alternative components, i.e., different systems. Thus graph 2 shows that sulfur dioxide and water are homogenized by addition of about equal weight percentages of diethylene glycol, propylene glycol, or formamide, respectively. Temperatures are room temperature (at autogenous pressure) except when another temperature is marked near the right side line, graphs 4–6, 11, 12, 18, 24, 25, 48, 49, 61, or on a curve, 50.

AC	Acid	29, 40, 41, 42, 54, 56
ANH	Anhydride	20, 22
AROM	Aromatic	51 (Table I)
$C_{11}F_{20}$	Perfluoromethylnaphthalene	49
$C_{19}F_{36}$	Perfluoranonylnaphthalene	49, 57
DEA	Diethanolamine	26
DEG	Diethylene glycol	2, 27, 28
F	Formamide	2
FREON 114	$(CClF_2)_2$	43

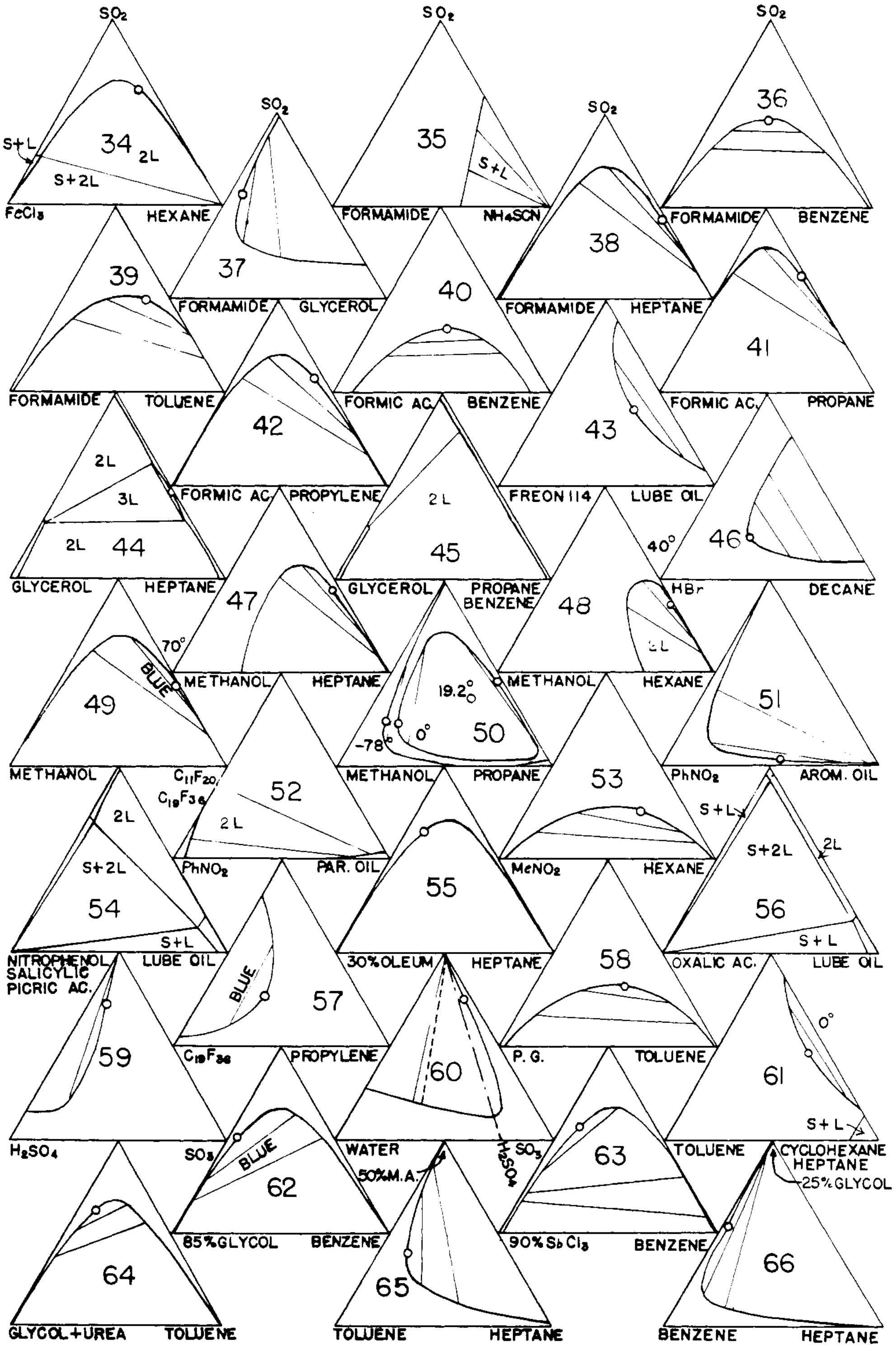

Figure 1. (*Continued*)

GLYCOL	Ethylene glycol	3, 29–33, 62, 64
HBr	Hydrogen bromide (not aqeuous hydrobromic acid)	7, 46
HCl	Hydrogen chloride	8
HI	Hydrogen iodide	9
LUBE OIL	Lubricating oil (A clean charge stock for studies of solvent extraction)	43, 54, 56 (Table I)
MA	Maleic anhydride	65
PAR	Paraffinic	52 (Table I)
PG	Propylene glycol	2

Graph 60 is a combination of graphs 16 and 59.

In graph 61, the short line at the right is the solubility curve of solid cyclohexane (but not of solid heptane).

In graph 62, the diluent in the left component is water.

In graph 63, with 90% antimony chloride, the other 10% can be water or concentrated hydrochloric acid, (two systems).

In graph 64, the left component is half glycol and half urea.

In graph 65, the top corner is 50% SO_2 and 50% MA.

In graph 66, the top corner is 25% ethylene glycol.

In certain areas, L is a liquid phase and S a solid phase (not sulfur, except in graph 25).

Small circles on phase boundary curves are plait points.

A dashed tie line (graphs 4–9, 14, 16, 26, 60) indicates an isopycnic with two liquid phases of equal density in equilibrium (*6, 13*, pp. 46–9).

A color—e.g., Blue—on a tie line (graphs 14, 24, 29, 49, 57) indicates an iso-optic. Other colors were observed on adjacent tie lines. (*6, 8, 13*, pp. 46–9).

EXPERIMENTAL

Almost all of the observations were made in sealed glass tubes. Reagent grade chemicals were used in all cases. The amount of each reagent was determined by weight. A thick-walled glass tube with a narrow neck was weighed accurately, charged with a liquid or solid reagent, weighed again, and cooled in a dry ice-acetone bath. Dry sulfur dioxide from a lecture bottle was passed in through a capillary funnel and condensed. The tube was sealed while in the cold bath, removed, warmed to room temperature, and weighed again, including the tip pulled off. The tube was shaken vigorously and settled before each observation. If the sulfur dioxide all dissolved, the tube was cooled, opened, more sulfur dioxide was added, and the operation was repeated. If too much sulfur dioxide was present, more of another reagent was added after cooling. In this way each other component, or mixture of two or more components was "titrated," giving the solubility of sulfur dioxide therein. About six to 10 points were established for each phase boundary curve.

When another liquefied gas, propane, propylene, or isobutane was involved, these gases were condensed separately (with intermediate sealing and weighing) in the same way as sulfur dioxide. Sulfur trioxide was introduced in the form of oleum. The temperature was controlled by immersion in a bath of water, ice water, or in a cold acetone bath. Portions of the systems for hydrogen halides (graphs 7, 8, 9) and carbon dioxide (graph 21) were observed in a visual autoclave (*9, 10*).

In a process resulting from this investigation (*15*), the solubilities of light hydrocarbons in sulfur dioxide were diminished and controlled by dilution of the sulfur dioxide with ethylene glycol, formamide, or other diluent almost immiscible with hydrocarbons. The volatility of sulfur dioxide facilitates recycling of this component of the solvent and virtually complete precipitation of the extract, so that the glycol can be recycled without distillation.

DISCUSSION

Graphs of all of the observed ternary systems (Figure 1) are presented in concise form as with the systems of carbon dioxide (*9*) and hydrogen cyanide (*11*). In each triangular graph, the top corner represents sulfur dioxide. Other components are named, or listed in the legend.

Some unusual features are shown in the graphs. One system (graph 50) has an island curve (*10*) surrounding an area with two liquid phases. Propane is miscible with sulfur dioxide at all temperatures above −24°, and with methanol above −35°, while methanol and sulfur dioxide are miscible even at −75°. Yet in the ternary system, two layers are possible up to a ternary CST of 19.2°.

Other graphs of unusual shape are aqueous systems of hydrogen chloride or bromide (graphs 7, 8), which seem to be mergers of two separate binodal curves (graph 9). The aqueous system with methanol is shown at three temperatures. The binodal curve at room temperature (graph 10) is submerged completely at −29° (graph 11) by the curve of equilibrium with crystalline hydrate, perhaps $SO_2 \cdot 6H_2O$. Near 0° (graph 12) the two curves intersect. Within the metastable area an iso-optic line was observed momentarily (not shown to avoid confusion).

The aqueous system with heptane also is shown at three temperatures from the CST of heptane with anhydrous sulfur dioxide, 19.4°, having a three-phase area (graph 4). This contracts to a narrower triangle (graph 5), and then to a limiting line at 28.4°, which is the CST of heptane with sulfur dioxide saturated with water (graph 6). It disappears at higher temperatures, where only two liquid layers are possible.

Table I. Properties of Lube Oils Tested

Property	Aromatic	Lube Oil	Paraffinic Oil
API gravity	22.1	23.8	27.3
Specific gravity	0.918	0.910	0.89
Refractive index	1.5231	1.5076	1.4923
Aniline point	45	72	80
Pour point, ° F.		20	15
Flash, (open cup), ° F.		395	350
Fire, ° F.		455	400
Viscosity, centistokes at 100° F.	51.65	28.65	24
Viscosity, centistokes at 210° F.	6.23	4.51	4.3
Viscosity gravity constant	0.83	0.871	0.875
Color, lovibond	28	18	14

The aqueous system of sulfuric acid (with a minimum solubility of about 17% sulfur dioxide in 94 to 96% sulfuric acid, graph 16) is combined with the system of sulfuric acid and sulfur trioxide (graph 59), and results in a continuous smooth curve (graph 60). Sulfur dioxide is completely miscible with 30% oleum (graph 55). These mixtures permit wide variation in gross concentration of oleum without much loss in reactivity, because the heat of dilution by sulfur dioxide is trivial.

The aluminum chloride systems (graphs 20–22) cannot be observed accurately. A solution in sulfur dioxide may be as high as 80% aluminum chloride; but it is a very viscous tar, probably involving some complex reactions. The tars and also slightly more dilute solutions of aluminum chloride in sulfur dioxide are active catalytically in isomerizing paraffins (*5, 14*). The graphs are included in spite of lack of precision, because of wide interest (but with $AlCl_3$ in parentheses to emphasize this point). They are assumed to be similar to those of maleic anhydride, which show equilibriums with more crystalline phases.

A mixture of butane and pentane can be adjusted in composition to give iso-optics with sulfur dioxide at any temperature below the CST, about 0° (graph 24), all the way down to −78°, though with varying colors (*6–8*).

Although all of the graphs are based on observations, and are as accurate as the data permit, many of the systems were not investigated as thoroughly as would be expected if one or only a few systems were to be studied. When a system was found unsuitable for practical use, the less significant portions of its graph were approximated with the help of published solubilities (*19*) and CST (*3*).

ACKNOWLEDGMENT

The author is indebted to George C. Johnson of the Central Research Laboratory, Socony Mobil Oil Company, Princeton, N. J., for hundreds of informal discussions on the systems of this and subsequent papers in the proposed series. He is also indebted to Wilbur Shea of the File Room of Socony Mobil Oil Company, Paulsboro, N. J., who greatly facilitated access to experimental data from the author's 91 notebooks which were used in this work.

LITERATURE CITED

(1) Butcher, K.L., Hanson, C., *Chem. Ind.* **1957**, 1509.
(2) Edeleanu, L., *Petroleum* **9**, 862; *Bull. Am. Inst. Mining Eng.* **1914**, 2313; *Chem. Abstr.* **8**, 3626 (1914).
(3) Francis, A.W., *Advan. Chem. Ser.* **31**, 1–246 (1961).
(4) *Ibid.*, pp. 167–8.
(5) Francis, A.W., *Ind. Eng. Chem.* **42**, 342 (1950).
(6) *Ibid.*, **45**, 2789 (1953).
(7) Francis, A.W., J. CHEM. ENG. DATA **5**, 534 (1960).
(8) Francis, A.W., *J. Phys. Chem.* **56**, 510 (1952).
(9) *Ibid.*, **58**, 1099 (1954).

(10) *Ibid.*, **62**, 579 (1958).
(11) *Ibid.*, **63**, 753 (1959).
(12) Francis, A.W., "Physical Chemistry of the Hydrocarbons," A. Farkas, Ed., Vol. I, p. 265, Academic Press, New York, 1950.
(13) Francis, A.W., "Liquid-Liquid Equilibriums," Wiley, New York, 1963.
(14) Francis, A.W., U. S. Patent **2,389,250** (November 20, 1945).
(15) Francis, A.W., U. S. Patent **3,003,006** (October 3, 1961).
(16) International Critical Tables, Vol. **III**, McGraw-Hill, New York, 1928.
(17) Leslie, R.T., *J. Res. Natl. Bur. Std.* **13**, 95 (1934).
(18) Satterfield, C.N., Powell, J.H., Jr., Oster, E.A., Jr., Noyes, J.P., *Ind. Eng. Chem.* **47**, 1458 (1955).
(19) Seidell, A., "Solubilities of Inorganic and Metal-Organic Compounds," 3rd ed., Van Nostrand, Princeton, N. J., 1940.
(20) Spall, B.C., *Can. J. Chem. Eng.* **1963**, 79.
(21) Terres, E., Rühl, G., *Z. Angew. Chem.* **47**, 331 (1934); through Landolt Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, Erg. IIIa, 672 (1935).

RECEIVED for review May 11, 1964. Accepted October 27, 1964. Presented before the Physical Chemistry Session of the Third Annual New York-North Jersey Metropolitan Regional Meeting of the American Chemical Society, January 27, 1964. The Central Research Division of Socony Mobil Oil Company, in which this investigation was conducted, is now located in Princeton, N. J.

Partial Volumetric Behavior in Hydrocarbon Systems. *n*-Decane and Carbon Dioxide in the Liquid Phase of the *n*-Decane–Carbon Dioxide System

H. H. REAMER and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif.

Partial molal volumes were evaluated for *n*-decane and carbon dioxide from experimental volumetric data for the *n*-decane–carbon dioxide system and corresponding information for the pure components. The evaluation extended to pressures of 10,000 p.s.i.a. in the temperature interval between 40° and 460° F. The internal inconsistency in terms of the standard error of estimate was 0.005 cubic foot per pound-mole. The partial volumes are presented in graphical and tabular form.

INFORMATION concerning the partial volumetric behavior of the components of binary and multicomponent systems helps to determine the heat and work associated with changes in state of these systems. In particular, such partial quantities are of importance in the evaluation of the molecular transport in systems where the concentration of each of the components is significant.

The volumetric and phase behavior of the *n*-decane-carbon dioxide system has been investigated at pressures up to 10,000 p.s.i.a. in the temperature interval between 40° and 460° F. (*9*). The volumetric behavior of carbon dioxide has been reported by several investigators (*2*, *5*, *6*, *7*). In addition, the volumetric behavior of *n*-decane has been studied in some detail (*8*). The related volumetric and phase behavior of other binary systems containing carbon dioxide and a paraffin hydrocarbon has recently been reviewed (*9*).

The partial molal volume (hereafter referred to as partial volume) has been defined (*3*) as

$$\bar{V}_k = \left(\frac{\partial V}{\partial m_k}\right)_{T,P,m_j} \tag{1}$$

From the smooth volumetric data of the *n*-decane–carbon dioxide system (*9*) in the homogeneous region, large-scale diagrams of the isobaric, isothermal change in the molal volume with composition were prepared. The partial volumes of each of the components were reached by graphical application of the following expression (*4*):

$$\bar{V}_k = V + (1 - n_k)\left(\frac{\partial V}{\partial n_k}\right)_{T,P} \tag{2}$$

It was not feasible to employ Equation 2 at small mole fractions of the component in question because of the significant loss of precision which resulted from attempting to utilize graphical operations in these regions. Therefore, in the regions of small mole fractions, the partial volumes were established from

$$\bar{V}_k = \frac{V - n_j \bar{V}_j}{n_k} \tag{3}$$

In a number of cases, the partial volumes of each of the components were established by carrying out graphically the integration indicated in the following expression:

$$\bar{V}_k = V_k^{\circ} - \int_0^{1-n_k} \left(\frac{n_j}{n_k}\right) \left(\frac{\partial \bar{V}_j}{\partial n_j}\right)_{T,P} \mathrm{d}n_j \tag{4}$$

The foregoing expression is based upon the Gibbs-Duhem equation (*1*).

Equations 3 and 4 permit a direct check upon the internal consistency of the calculations. Equation 4 was employed to ascertain the over-all uncertainties in the calculations. The internal consistency of the partial volumetric data is presented in Table I, where the directly calculated values established from Equation 2 are compared with the integrated values obtained from Equation 4. A reasonable sample of the conditions covered in these calculations is set forth in the table. The average standard error of estimate for all the calculations carried out was 0.005 cubic foot per pound-mole. The information presented in Table I is typical of that found throughout the range of conditions for which experimental data are reported.