

reached without obtaining crystals. Because of the great viscosity of the triethylamine-rich solutions at low temperatures, it was not possible to obtain a reliable eutectic halt for these solutions.

RESULTS

The results of this investigation are shown in the phase diagram in Figure 1, which provides direct evidence for a 1 to 1 compound of chloroform with triethylamine. This compound melts at 191° K. to form a nonideal mixture of chloroform and triethylamine. The eutectic on the chloroform-rich side is at 0.38 mole fraction of triethylamine and 180° K. The eutectic on the triethylamine-rich side is at 0.78 mole fraction of triethylamine and 142° K. Uncertainties in eutectic composition and temperature are less than ± 0.02 and $\pm 1^\circ$ on the chloroform-rich side and ± 0.03 and $\pm 2^\circ$ on the triethylamine-rich side.

Because of the obvious nonideality of the solutions in

equilibrium with the 1 to 1 compound, no attempt was made to calculate the heat of formation of the compound from its components.

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Ternary Systems of Methanol

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Applications of methanol as a selective solvent or cosolvent for types of hydrocarbon are discussed. These include simple selective extraction of a mixture of paraffin isomers, use of methanol in small percentages to liquefy a low-melting organic crystalline solid such as *o*-nitrobiphenyl which has high selectivity, use of an anhydrous mixture of methanol and hydrogen chloride as a good solvent for cuprous chloride which dissolves light olefins selectively, and use of methanol to extract aromatic hydrocarbon impurities from jet fuels diluted with carbon disulfide. Pertinent to these and to other attempted applications are 150 new observed ternary or quaternary systems of methanol, as well as about the same number of published systems. The new systems are presented in this paper in concise form. Most of them include two or more liquid phases. Some of them show unusual types of graphs. The types include isopycnics, iso-optics, twin density lines, twin index lines, island curves, systems with two separate binodal curves, and those with three liquid phases. A novel type is one in which a twin density line terminates at a side line.

MMETHANOL is generally considered a relatively unselective solvent for different classes of hydrocarbons. For only one pair of hydrocarbon types—branched chain over straight chain paraffins—has pure methanol been recommended (13); and for that pair, only because no solvent has a very high selectivity.

On the other hand, the low cost, high stability, and convenient boiling point, 64.6°C., of methanol seemed to justify strenuous efforts to make it available as a selective solvent by the use of appropriate cosolvents. In many cases, these roles might be considered reversed—i.e., the properties of methanol may be exploited so that the selectivity of the other solvent becomes operable. For example, a low melting solid may be liquefied by solution in small percentages of methanol. These include highly polar organic crystalline solids such as *o*-nitrobiphenyl as well as inorganic salts such as lithium chloride.

In one example of this type (14), methanol seems to be much the best solvent for the purpose. Acid cuprous chloride is known to have a strong affinity for olefins over paraffins. However, the solubility of cuprous chloride in a preferred solution (17) is not over 17%, and this solution absorbs only a maximum of 0.224 mole of ethylene or 0.04 mole of propylene per mole of cuprous chloride in solution (17). Solutions of

cuprous chloride in aqueous ammonia or alkylamines show still lower capacity for olefins.

By contrast, an anhydrous mixture of methanol and hydrogen chloride dissolves up to 34% total cuprous chloride (11, p. 101; 14), as illustrated in graph 40 (in contact with copper turnings to keep it reduced and colorless). The solution is greenish black when a trace of cupric chloride is present. The cuprous chloride in solution absorbs molar amounts of ethylene or propylene (about 100 volumes per volume of solution) reversibly (in contrast to solutions of mercury salts) (3).

Ethyl and higher alcohols form similar complexes with cuprous chloride, with somewhat lower solubilities, and lower capacities for olefins; but they are unsatisfactory as selective solvents because the alcohol dissolves too much propane or ethane. Even methanol dissolves small amounts of propane. Glycols, ethoxyethanol, and especially hydroxypropionitrile (with hydrogen chloride) dissolve even larger concentrations of cuprous chloride than does methanol (graphs 41, 42), but these solutions absorb very little olefin. A small percentage of a glycol in a methanol solution greatly diminishes solution of propane. Solubility relations with some of these solvents are illustrated in graphs 40 to 45. CuHCl_2 , a crystalline solid which is soluble in hydroxy compounds, is selected for plotting. However, the solid-solid relations of graph 43 were not in-

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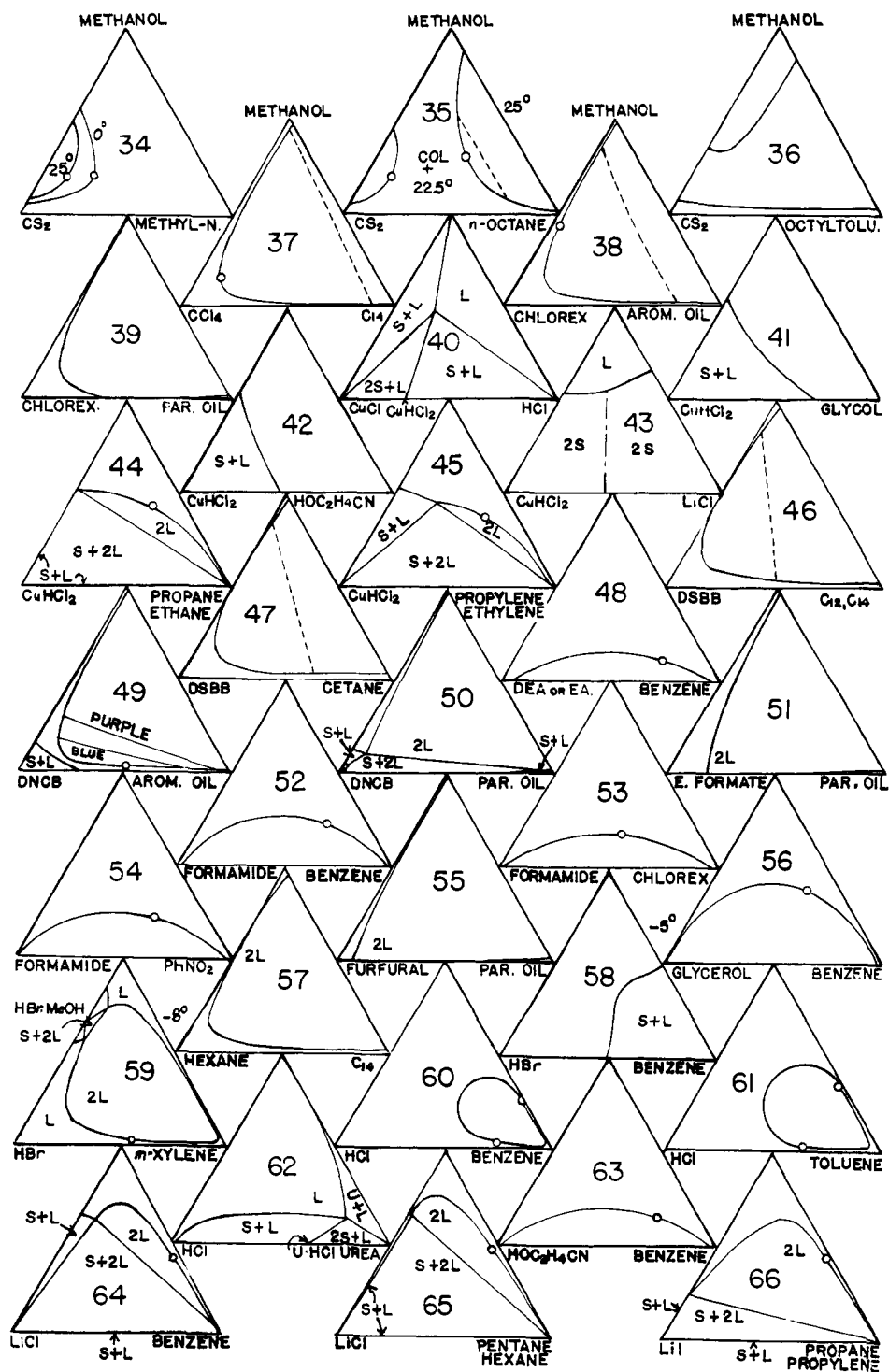


Figure 1. (continued)

Abbreviation	Name	Graphs	Abbreviation	Name	Graphs
C ₁₁ F ₂₀	Perfluoromethyldecalin	114	HBr	Anhydrous hydrogen bromide	58, 59
CETANE	n-Hexadecane	47, 125	HBr·MeOH	Postulated formula of complex	59
CHLOREX	2,2'-Dichloroethyl ether	38, 39, 53	HCl	Anhydrous hydrogen chloride	60, 61, 62
CORYTON	A paraffinic gas oil	32, 118 (6, Table II)	HOC ₂ H ₄ CN	2-Hydroxypropionitrile	42, 63
CuHCl ₂	Postulated formula of cuprous hydro- gen chloride	40-45	LUBE OIL	Lubricating oil	24, 78, 107 (6; 8, Table I)
2,4-DMP	2,4-Dimethylpentane	109	MALEIC ANH	Maleic anhydride	67, 68
DEA	Diethanolamine	48, 128	MeOH	Methanol	15, 16, 17, 132
DNCB	2,4-Dinitrochlorobenzene	49, 50	MeC ₆ H ₁₁	Methylcyclohexane	19, 85
DSBB	m-Di-sec-butylbenzene	4, 17, 31, 46, 47, 77, 82, 116, 122, 125	METHYL-N	1-Methylnaphthalene	10, 34, 69-75, 92, 100, 108, 117-121, 123, 126, 127
EA	Ethanolamine	48	METHYLNAPH.	1-Methylnaphthalene	3, 129-132
EF or E. FORMATE	Ethyl formate	51, 129	NB	Nitrobenzene	130
G or GLYCOL	Ethylene glycol	41, 126, 127	NITROBENZ.	Nitrobenzene	76-81, 122-124
H	n-Heptane	109	OCTYLTOLU.	n-Octyltoluene	36, 91
HEAVY OIL	(Properties not available)	33	ONBP	o-Nitrobiphenyl	11, 82-87, 125

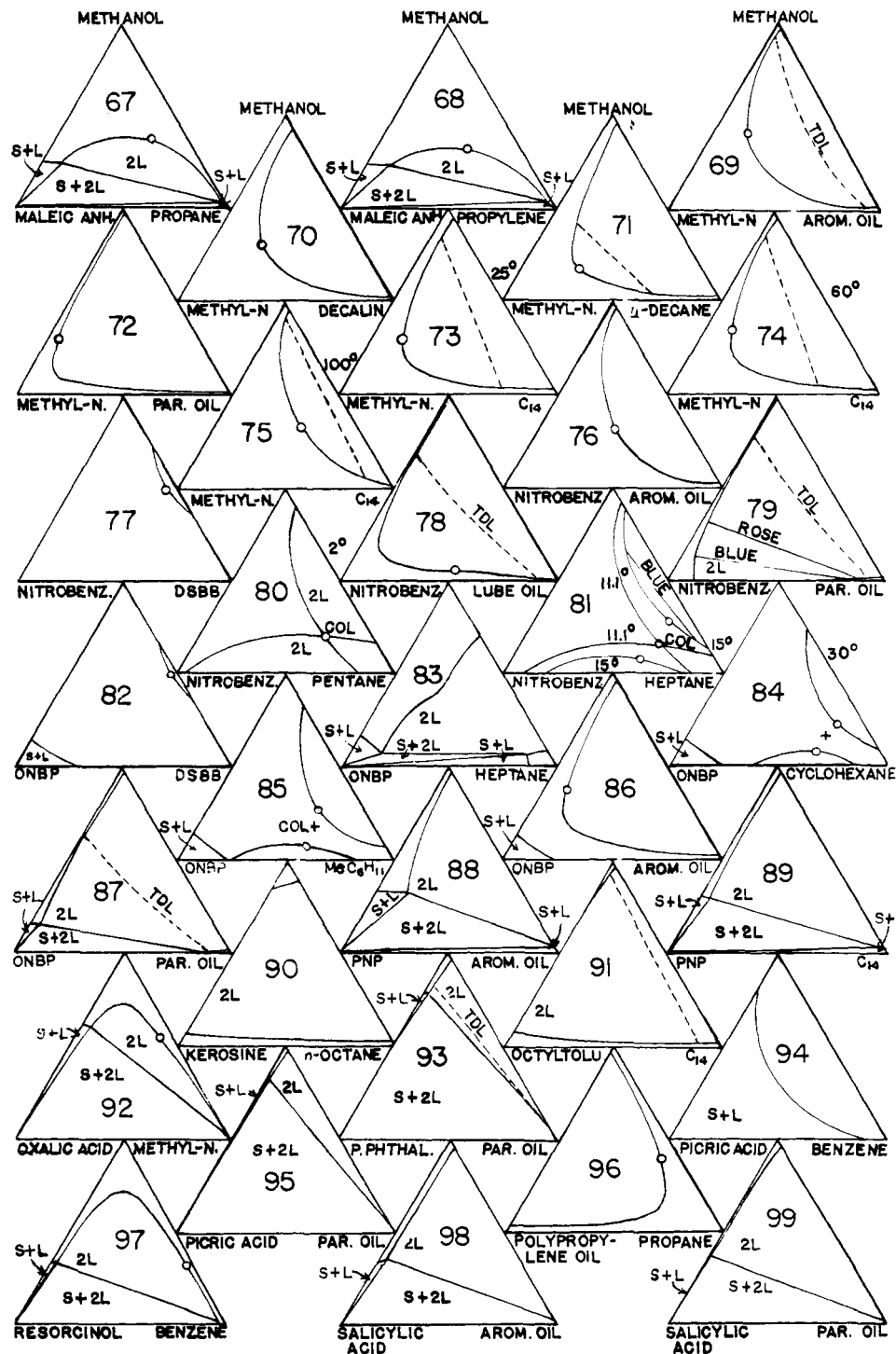


Figure 1. (continued)

Abbreviation	Name	Graphs
PAR OIL	Paraffinic lubricating oil	39, 50, 51, 55, 72, 79, 87, 93, 95, 99, 117, 124, 129 (5; 6, Table I)
PNP	<i>p</i> -Nitrophenol	88, 89
POLYPROPYLENE OIL	(Properties not available)	96
P. PHTHAL	Phenyl phthalate or phthalic acid, diphenyl ester	93
S-BUTYL-B	<i>sec</i> -Butylbenzene	25-27, 115
RESOR	Resorcinol	132
TCAA	Trichloroacetic acid	107
TFAA	Trifluoroacetic acid	108
TETRA	Tetralin	111, 113
TRIPTANE	Trimethylbenzene	109
U·2AcOH	Urea acetate	18
U·HCl	Urea monochloride	62
W	Water	3, 122, 123, 124

When two or more substances are shown with a plus sign or bracket, or by a diluent of the methanol, they are plotted as a single component, graphs 114 to 132. Otherwise, they are alternative components, and the different systems are shown by the same graph, 7-9, 20, 22, 26, 30, 44-46, 48, 65, 66, 102, 109. The temperature is 25° C. unless otherwise indicated above the right side line, graphs 19, 58, 59, 74, 75, 80, 84, 107, 121, 131, 132, or on a curve, graphs 34, 81.

A circle on a binodal curve is a plait point. Curves without plait points are either band-type curves or phase boundaries of liquid and solid. The latter are indicated by L, S + L, S + 2L, 2S + L (sometimes R for resorcinol or U for urea) in certain areas or in adjacent areas with arrows. A straight dashed line is an isopycnic or tie line connecting compositions of two liquids of equal density in equilibrium (26 graphs). A curved dashed line with TDL (16

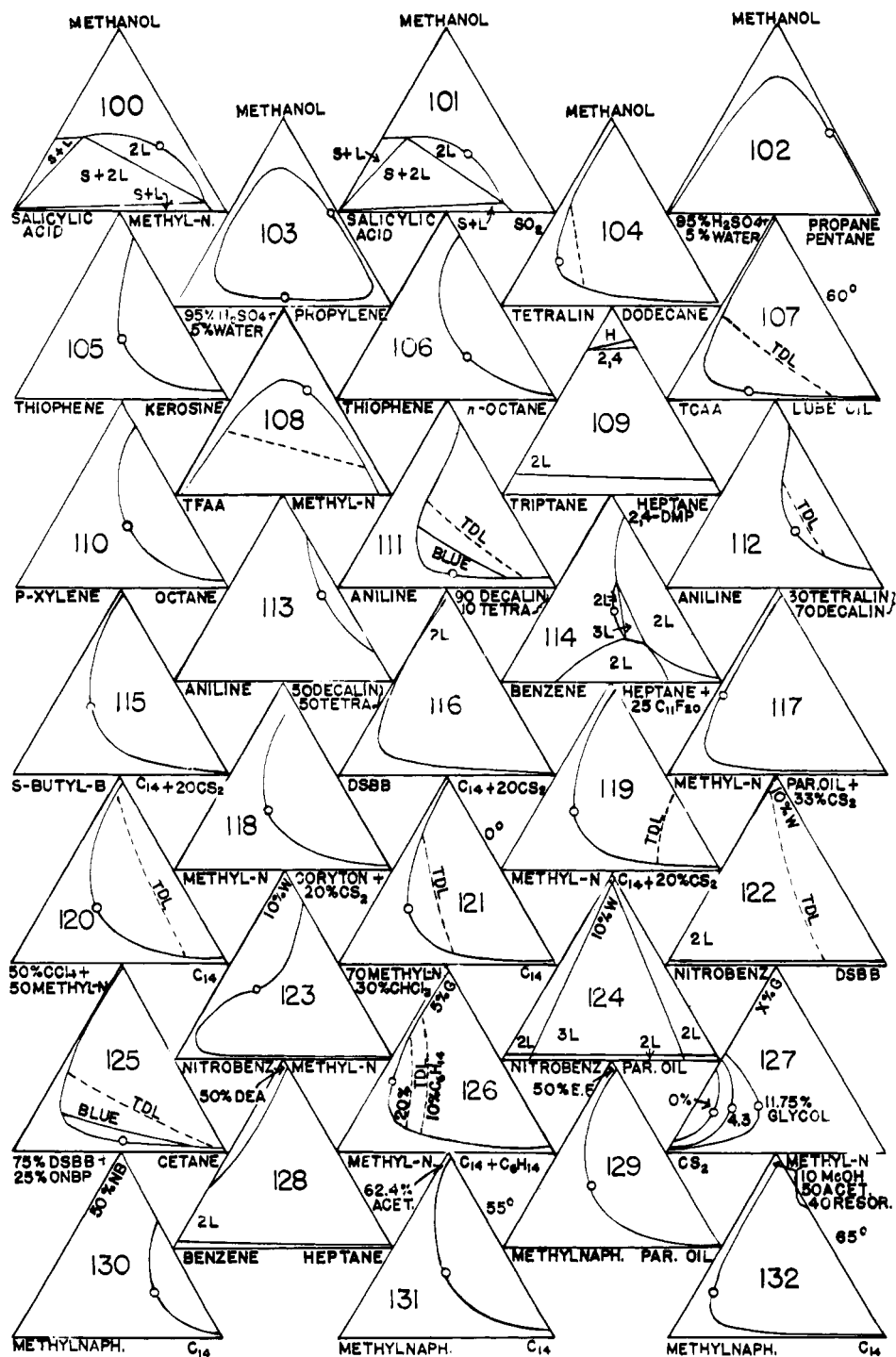


Figure 1. (continued)

graphs) is a twin density line showing the locus of compositions separating into two liquid layers of equal density (in a quaternary system), but not uniform along the line.

Tie lines with the name of a color connect liquid compositions having equal refractive indices or iso-optics (2; 11, pp. 46-9), graphs 19, 49, 81. Other tie lines are omitted. In graphs 24, 79, 111, 125, there are twin index lines. Dot-dashed lines in graphs 5, 6 indicate that compositions to the right of them are observable

only at superatmospheric pressure, including the binodal curves of hydrogen halides (10), sometimes ignored in published graphs.

Graph 43 shows the solubilities in methanol of lithium chloride and of cuprous hydrogen chloride. These two crystalline materials presumably have a eutectic, pictured qualitatively by a dot-dashed line; although it was not investigated because of its extreme sensitivity to air.

vestigated. The liquid solutions are extremely sensitive to oxygen, which turns them black and ruins their absorptive capacity for olefins.

As another result of this research (15), methanol has been used to extract small percentages of aromatic hydrocarbons from jet fuels so as to upgrade them. As in applications of acetonitrile (6, 16), the density difference between solvent and hydrocarbon mixture must be increased by the addition of another liquid of high or very low density, in order to avoid isopycnics (two layers of equal density in equilibrium) (2). Again carbon disulfide is much the most efficient diluent because it is incompletely miscible with methanol and distributes itself mostly to the hydrocarbon layer (Cf. graph 115 with 27; 116 with 46; 117 and 118 with 72; 119 with 30 and 73). Graph 119 is novel in having a twin density line which terminates on a side line instead of at a phase boundary. This could not happen in a ternary system since a tie line would never do so. The anomaly results because the isologous line (straight dashed-dot line) in graph 30, from the methanol corner to the 20% CS₂ point on the base line, intersects the isopycnic.

Isopycnics are not very sensitive to temperature (graphs 73 to 75). A little water or glycol sometimes has an effect on a graph similar to that of lowering the temperature (Cf. graphs 3 and 127 with 34).

Critical solution temperatures (CST) are listed for methanol with 61 hydrocarbons and 80 nonhydrocarbons (including several with > or < signs) (1, 11, pp. 228-9). Many ternary systems including methanol as a component have been published. Illustrated by triangular graphs in Seidell's Solubilities (12) are 40 aqueous and 19 nonaqueous methanol systems. Fourteen others are shown among carbon dioxide systems (9), thirteen others among glycol systems (7, graphs 17-25, 29-31, and 33), and seven among sulfur dioxide systems (5, graphs 10-12 and 47-50). A compilation (11, pp. 169-72, 210-11) refers to at least 36 other aqueous and 40 nonaqueous methanol systems, most of which are illustrated in the original papers with graphs. Yet additional systems are needed to extend the solvent extraction possibilities of methanol.

This paper presents in concise form 150 new ternary or quaternary systems of methanol (Figure 1). In each graph, methanol is represented by the top corner of the triangle. The quaternary systems, graphs 15 to 17 and 111 to 132, also are shown by triangles, with the fourth component assigned as a diluent to one of the other three, selected so as to minimize fuzziness due to that component (11, Chap. 8). The arrangement is alphabetical by classes: aqueous, nonaqueous ternary, quaternary with pure methanol as a component, and those with diluted methanol.

EXPERIMENTAL

As in the paper on acetonitrile systems (6), known mixtures of two miscible components were titrated with the third until the appearance of another liquid phase at the temperature indicated; or two not miscible components were titrated to a single phase, using the best grade of chemicals available. Twenty systems involving liquefied gases, graphs 5, 6, 21, 22, 40, 41, 44, 45, 58-62, 66-68, 96, and 101 to 103, required the titration in a sealed tube, as with the paper on sulfur dioxide

systems (5), using a separate seal with each tentative observation. The temperature of graph 75, above the boiling point of methanol, required sealing in that system also.

DISCUSSION

Seven graphs, 19, 31, 35, 80, 81, 84, and 85, show two separate binodal curves. These each have a col (4) at which the two curves meet at both plait points. The reverse curve of graph 9 is similar to that with mercuric chloride and acetonitrile (6). Those of graphs 15, 111, 112, and 123 are due to the fourth component. Graph 114 seems to violate Schreinemakers' rule (7). Again the fourth component is responsible.

Four other systems have island curves, graphs 59 to 61 and 103. The last name is the triangular island (10, footnote 20). The other three island curves involve hydrogen halides. Graphs 60 and 61 are similar to those reported (10), but in graph 59 the temperature is low enough so that the phase boundary of crystalline HBr·MeOH overlaps the island curve. In fact, at slightly lower temperature it submerges the whole island. In graph 58, the island is submerged by the area for equilibrium with solid benzene. Because of the high pressure and the extreme sensitivity to temperature, the positions of the phase boundaries shown in these two graphs must be considered partly schematic.

Other systems with precision lacking for different reasons are those of antimony chloride, graphs 20, 21. The high concentrations and viscosity in methanol, together with precipitation of butter-like material on dilution (even with methanol) and possible incipient reaction with the olefins, make accurate observations of a phase diagram almost impossible. However, it seemed worthwhile to present the best data available for these systems.

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