Yang and Foster who found no plateau but simply observed a curve of decreased slope after the initial region where $C_0/C_i = 1$. This is probably accounted for by a distribution of homologs in the material used by later investigators. On the basis of Yang and Foster's discussion, the concentration C_0 at which this plateau occurs would be taken as the critical micelle concentration of the detergent. However, in view of the fact that micelles of sodium dodecyl sulfate are able to diffuse through Cellophane under certain conditions, this assumption is not always justified. For purpose of comparison all results in Fig. 2 were obtained after a standard time of two days. The concentration C_0 corresponding to the plateau (ca. 0.14%) thus represents not the CMC but the sum of the critical micelle concentration and the concentration of micelles which have diffused in this time. When the concentration of detergent within the dialysis bag exceeds approximately 1.5%, the concentration C_0 increases with increasing C_i until a further plateau is reached at C_i approximately 2.0%. The concentration C_0 at this plateau is approximately 0.27%. This plateau extends to $C_i = 4.0\%$, the highest concentration investigated. It is difficult to understand the significance of this second plateau. The most likely explanation is that it represents the formation of a second type of micelle, this latter being in equilibrium with a different concentration of single ions. (For a comprehensive discussion of the types of micelles postulated from time to time see McBain.[13]) It is interesting to compare this effect with the results of Ekwall and Passinen.[14] These workers studied the solubilization of decanol in sodium oleate and sodium myristyl sulfate and found that the composition of the detergent–alcohol complex was constant as the detergent concentration was increased above the critical micelle concentration until, at considerably higher concentrations, (ca. 5%), the alcohol/detergent ratio increased, again suggesting that the nature of the micelles changes at these higher concentrations.

(13) J. W. McBain, "Colloid Science," D. C. Heath and Co., Boston, Mass., 1950, pp. 255–261.

(14) P. Ekwall and K. Passinen, Acta Chem. Scand., 7, 1098 (1953).

TERNARY SYSTEMS OF LIQUID CARBON DIOXIDE[1]

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Mutual solubilities of liquid carbon dioxide with each of 261 other substances are reported. Nearly half of these are miscible with carbon dioxide. Some relations to structure are noted. Density observations show contractions of ten to fifteen per cent on mixing.

Triangular graphs are presented for 464 ternary systems involving liquid carbon dioxide. These are of many different types, some of them novel. They include those with three separate binodal curves (and three plait points) and several with a binodal band across two sides of the triangle and a separate binodal curve on the third side. Another system has three plait points although one pair of components is miscible.

Carbon dioxide has a strong homogenizing action upon pairs of other liquids at moderate concentrations, but a precipitating action at higher concentrations. In contrast to most solvents it has a selectivity against dicyclic hydrocarbons. Cosolvents were found necessary to make these unusual properties effective in solvent extraction of hydrocarbon mixtures.

The large collection of unusual graphs provides experimental evidence on methods of merging of binodal curves. External contact of convex curves always occurs at both plait points.

No ternary systems of liquid carbon dioxide have been published. Miscibility relations of this condensed gas with other liquids have now been studied in an investigation of its possibilities for use in solvent extraction.[2] Cosolvents are necessary to make its unusual properties available for that purpose.

Several ternary systems with two separate binodal curves were presented in a recent paper.[3] Graphs with three such curves are suggested in many physical chemistry textbooks, but no actual example is recorded in the chemical literature. For this type two incompletely miscible liquids must become homogenized by addition of a third liquid which is not miscible with either of the other two; and this effect must occur with all three pairs.

This would not normally be expected.[4] Liquid carbon dioxide yields many such systems.

Ternary diagrams were observed for 464 systems involving carbon dioxide at or near room temperature. Several of these are of novel types including 21 systems with graphs showing three separate binodal curves, and 38 showing a binodal band across two sides of the triangle and a separate binodal curve on the third side. There are also 76 systems with two separate binodal curves, 82 systems with a binodal band so highly concave on its borders as to indicate that it can be considered as a result of a merger of two binodal curves; and 29 systems with three liquid phases. The only type of ternary all-liquid system observed elsewhere but not among the carbon dioxide systems is that of island curves (ternary miscibility gaps not connected with binary ones).

The property of liquid carbon dioxide which makes these uncommon diagrams possible may be

(1) Presented before the Division of Physical and Inorganic Chemistry of the 126th Meeting of the American Chemical Society, New York, September 15, 1954.

(2) A. W. Francis, U. S. Patents 2,463,482 (1949); 2,631,966; 2,632,030; 2,646,387 (1953); three other U. S. Patents applied for; Ind. Eng. Chem., in press, 1955.

(3) A. W. Francis, J. Am. Chem. Soc., 76, 393 (1954).

(4) C. R. Bailey, J. Chem. Soc., 123, 2579 (1923); and several textbooks.

the proximity of its critical temperature, 31°, to the temperature of the observations. Carbon dioxide exhibits dual solubility effects which are apparently antagonistic to each other. At moderate concentrations, up to about 40% by weight, it acts as a dissolved gas and exerts a strong mixing action. Most pairs of partially miscible liquids become homogeneous on dissolving sufficient carbon dioxide in them. At higher concentrations, especially 60 to 90%, liquid carbon dioxide is a relatively poor solvent for many of these same liquids. It exerts a demixing or precipitating effect more intense than that of propane in deasphalting operations.

Hydrogen chloride and bromide are known[3,5] to behave somewhat similarly, being effective in homogenizing water with ether and higher alcohols although the hydrogen halides have limited solubility in water. Probably other condensed gases would have analogous effects. An investigation of nitrous oxide parallel to the present one was considered because of the similarity in physical properties to those of carbon dioxide. It was rejected because of possible explosibility of mixtures of organic compounds with liquid nitrous oxide.

Another respect in which the solubility relations of liquid carbon dioxide are abnormal is its negative selectivity. It is incompletely miscible with dicyclic hydrocarbons both naphthenic and aromatic (even if the rings are separate) but mixes with aliphatic and monocyclic hydrocarbons in the same boiling range as the dicyclics. This relation is the reverse of that with most solvents, in which the more highly cyclic hydrocarbons are more soluble. Fluorocarbons have similar negative selectivity.[6-8]

Liquid carbon dioxide is only weakly acidic, showing no noticeable affinity for moderately basic organic compounds like aniline and pyridine. It does form salts with stronger bases such as ammonia and aliphatic amines. p-Phenetidine is a borderline case, permitting observations of metastable liquid-liquid solubilities before solid salt appears. Systems of components forming salts are omitted from the graphs.

The literature abounds with observations on solubility of gaseous carbon dioxide in aqueous and organic liquids at various temperatures and pressures. But quantitative data are meager for the mutual solubilities of liquid carbon dioxide and other liquids. Büchner[9] made qualitative observations of solubility of several substances in liquid carbon dioxide. He stated that no hydrocarbon was known which gives two liquid phases with carbon dioxide. This is no longer true.[10]

Apparatus and Materials.—All of the observations on carbon dioxide miscibility were made in a visual autoclave.[11]

(5) A. W. Francis in "Solubilities of Inorganic and Organic Compounds," A. Seidell and W. F. Linke, eds., Suppl. to 3rd ed., D. Van Nostrand Co., New York, N. Y., 1952, pp. 991, 994, 997, 1002, 1018.

(6) J. H. Hildebrand, B. B. Fisher and H. A. Benesi, J. Am. Chem. Soc., 72, 4348 (1950).

(7) C. J. Egan, U. S. Patent 2,582,197 (1952).

(8) A. W. Francis and G. C. Johnson, U. S. Patent, 2,663,670 (1953).

(9) E. H. Büchner, Z. physik. Chem., 54, 665 (1906).

(10) E. B. Auerbach, Brit. Patents 277,946 (1926); 285,064 (1927); Can. Patent, 285,782 (1928); U. S. Patent, 1,805,751 (1931).

(11) W. F. Caldwell, Ind. Eng. Chem., 38, 572 (1946).

This is a Jerguson gage of 116-ml. capacity with narrow Pyrex glass windows about 17 mm. thick, front and back. It has been tested to 400 atmospheres. Incandescent lamps are mounted behind the vertical position. Agitation results from rotation end-over-end within a heat insulated case.

The reagents used were mostly from Eastman Kodak Company, first grade, but not further purified except to dehydrate those suspected of containing water. The inaccuracies due to the amounts of other impurities likely to be present are believed to be less than other experimental errors. The hydrocarbon mixtures mentioned had the following properties

Hydrocarbon mixture	d^{20}_4	$n^{20}D$	Aniline C.S.T., °C.
Gasoline (straight run)	0.723	1.397	58.7
Kerosene (refined)	.796	1.438	61.2
Fuel oil	.853	1.479	62
Transformer oil	.867	1.490	80
Lubricating oil (naphthenic)	.910	1.5076	72
Bright stock (residual, refined)	.948	1.532	73.2
Crystal oil (Nujol)	.891	1.4797	123

Binary Systems.—A "system" in this investigation includes only condensed phases, even though the weight of the vapor phase is appreciable, because, with a few exceptions, it is substantially pure carbon dioxide. The autoclave was charged with liquid reagents from pipets through a small glass funnel inserted through a 4.5 mm. hole in the autoclave. Their weights were calculated from their densities. Liquefied gas reagents were then added in the order of increasing vapor pressure (butane, sulfur dioxide, propane, propylene, hydrogen sulfide, ethane, carbon dioxide) from steel lecture bottles attached through cone joints and a valve. The lecture bottle was detached before agitation.

The weight of carbon dioxide (and those of other condensed gases) added to a system was estimated from the increase in liquid volumes, as indicated by the positions of the meniscuses, and from the apparent density of dissolved carbon dioxide as a function of the concentration. The apparent density was ascertained from the new actual density observed in typical cases by a special technique, and an average value (0.7 to 1.36 depending on concentration) was then used for the various systems. Apparent density is here defined as the ratio of total increase in weight to the total increase in volume.

Liquid Densities of Carbon Dioxide Mixtures.— Several sealed floats were made of thin glass tubing, about 3 × 60 mm., each containing a small quantity of mercury to make it float in a vertical position. The density of each float was found by adjusting a mixture of acetic acid or methanol and water or one of acetone and heptane so that the float would remain stationary while completely submerged in the mixture. The density of the liquid was then determined with a pycnometer. They were used as in the following example.

The visual autoclave was charged with 5.0 ml. or 4.39 g. of pure benzene and three floats of densities 0.8486, 0.8203 and 0.7916, respectively. Carbon dioxide was added. All three floated with a small volume and sank with a large volume. They barely floated at volumes (corrected for volumes of floats) of 30.1, 44.3 and 64.6 ml. corresponding to 25.5, 36.4 and 51.1 g., respectively (using the densities of the floats, which equalled those of the liquid mixtures). These indicated percentages of 82.8, 88 and 91.4% carbon dioxide, respectively. In a single binary system two compositions with the same density were often observed.

Although the floats were necessarily thin walled (less than 0.2 mm.) in order to float, they were sufficiently rugged to stand tumbling in agitating the system. They also had to support an external pressure of 65 atmospheres without crushing. The elastic contraction of the floats due to pressure, which would make density observations too low, must be very slight since a float which just sank (even in water)

was floated by an increase in pressure, showing that the liquid was more compressible than the float. In fact, it was found that a float was compressed less than one part in 10⁵ per atmosphere.

Results of density observations for mixtures of carbon dioxide with each of four solvents are shown in Table I and Fig. 1. In each case the dissolved carbon dioxide has an apparent density of about 1.0 g. per ml. at low concentrations, as indicated by the dashed lines tangent to the curves. Straight lines drawn through the zero point and a point of any other selected percentage on each of the four curves converge approximately to the same apparent density for dissolved carbon dioxide. In view of the diversity in structure of the four solvents this measure of carbon dioxide concentration was applied to all solvents tested. In water or glycerol (of low solvent power for carbon dioxide) the initial apparent density is about 1.36. This was calculated from the density of a saturated solution (6%) of liquid carbon dioxide in water at 26° and 65.1 atm., 1.016, in comparison with that of pure water, 0.9999, at the same temperature and pressure.

TABLE I

DENSITIES OF CARBON DIOXIDE MIXTURES AT 26°

Liquid	Wt. % CO₂	d^{26}_4
Acetic acid	0	1.0454
	49.5	0.9914
	65	.9429
	70.5	.9227
	76	.8912
	85.5	.8749
	100	.69
Benzene	0	0.8730
	20	.8952
	35	.8980
	48	.8952
	73	.8749
	82.8	.8486
	88	.8203
	91.4	.7916
Methanol	0	0.7888
	16	.8203
	40	8480
	65	.8480
	73.5	.8413
	76.5	.8250
n-Heptane	0	0.6785
	48	.7605
	88	.7605

The dotted curve on the right of Fig. 1 indicates compositions and corresponding densities calculated for solutions containing the same weight of carbon dioxide per milliliter as that present in pure liquid carbon dioxide, 0.69 g. per ml. On this curve the apparent density of the solvent is infinite. Density observations above this curve show a concentration of carbon dioxide higher than that of pure liquid carbon dioxide.

In all of the observations reported here involving carbon dioxide the pressure was autogenous, that corresponding to vapor–liquid equilibrium. When not otherwise indicated, the temperature was 21 to 26° and the pressure approached 65 atmospheres.
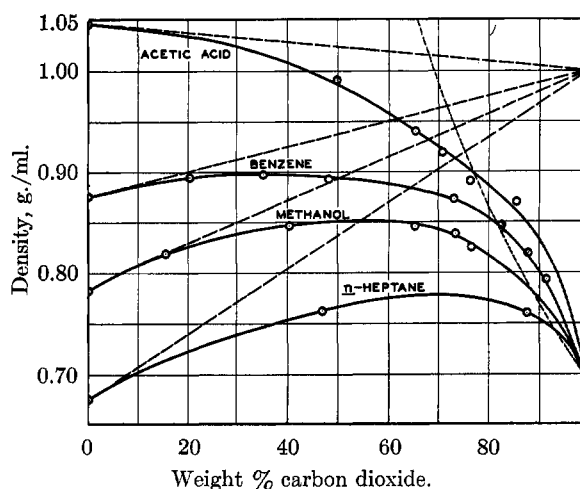

Fig. 1.—Densities of carbon dioxide mixtures at 26°.

Since moderate changes in temperature were found to have little effect on the liquid–liquid miscibility relations, precise temperature control was unnecessary. This was due to compensating factors. The normal increase in solubility with rising temperature is largely balanced by a decrease due to the more gas-like quality of liquid carbon dioxide.

No upper critical solution temperature with carbon dioxide was observed. Lower critical solution temperatures occur only in systems with a narrow miscibility gap. Those observed were α-chloropropionic acid 12°, p-nitrotoluene 15°, and ethyl phthalate 25°.

Mutual solubilities of carbon dioxide and another liquid were estimated as in the following example.

The visual autoclave was charged with 20 ml. or 17.9 g. of decahydronaphthalene (decalin) and carbon dioxide until a trace of upper layer remained after agitation. The initial interface was at 34 ml. The 14-ml. increase corresponded to 13 g. or 42% in the lower layer since the converging lines through the zero and 42% points of the curves of Fig. 1 indicate an average apparent density of 0.93. More carbon dioxide was then added until the levels after agitation were 18 and 62 ml. The additional carbon dioxide in the system was 28 ml. or 23.6 g. (apparent density 0.84) a total of 36.6 g. of which 6.9 g. ($^{18}/_{34} \times 13$) was in the lower layer and 29.7 g. in the upper. The latter contained 8.4 g. ($^{16}/_{34} \times 17.9$) or 22% of decalin.

Mutual solubilities of liquid carbon dioxide with each of 261 other substances are presented in Table II. The first column gives an arbitrary code abbreviation for designation of the components on the graphs and in column 2 of Table III. Solids (m.p. given) melt at room temperature in contact with liquid carbon dioxide in those cases in which M or a numerical value is listed under "x" (column 4).

Since ternary systems usually involving hydrocarbons were to be studied, the miscibilities of the liquids with various hydrocarbons are indicated qualitatively in column 3 as explained in the footnotes. The last column lists the graphs showing systems studied involving these components, and with column 2 serves as an alphabetical index for the graphs. A few metal salts were tested because other relations between them and certain hydrocarbons had been noted previously. Of these only stannic chloride was appreciably soluble in liquid carbon dioxide.

TABLE II

MUTUAL SOLUBILITIES WITH LIQUID CARBON DIOXIDE

Each code letter or pair of letters refers only to the substance opposite it. Substances without codes are listed by name in Table III (except those forming solid salts, which are not illustrated in the graphs).

Hydrocarbon miscibilities are at 25° as liquid. A solid is considered miscible with a hydrocarbon or carbon dioxide if it is highly soluble in it without the formation of two liquid layers in equilibrium, and it is probable that the subcooled liquid would mix with the solvent at 25°.

If a substance is miscible with one group of hydrocarbons, as indicated by a footnote letter, it is also miscible with all of the hydrocarbons indicated by letters following this one in the series, a to f. Thus "b" means "b, c, d, e, f"; "c" means "c, d, e, f"; "d" means "d, e, f"; and "e" means "e, f."

Code (legend in graphs)	Substance	Hydrocarbon miscibility (see footnotes)	Carbon dioxide solubility (M = Miscible)t x	y	Graphs
AA	Acetal	a	M	...	A64
AB	Acetaldehyde	b	M	...	C25
AC	Acetamide (m.p. 82°)	g	..	1	B10
AD	Acetic acid	c	M	...	A7, 42, 64, B9, 10, C21
...	Acetic anhydride	e	M	...	C8, 21
AE	Acetone	b	M	...	A26, 49, 50, 52, B51, C11, 22
AF	Acetonitrile	f	M	...	A8, C12, 20
AG	Acetophenone	b	M	...	B1
AH	Acetyl chloride	a	M	...	A64
AJ	Acrolein	d	M	...	A65
...	Acrylonitrile	d	M	...	C8
AK	Aldol	d	31	11	B33, D8, 43, 56
Al	Aluminum chloride (m.p. 190°)	g	..	0	A47
...	2-(2-Aminoethylamino)-ethanol	g	..	...	Forms salt
...	2-Amino-2-methyl-1-propanol	f	..	...	Forms salt
AM	t-Amyl alcohol	a	M	...	A44
A	Aniline	^	20	3	A64, B17, 27, 35, D9, 38, 44, 53, 54
AN	o-Anisidine	e	20	1	B13, D38
AS	Anisole	a	M	...	A64
PE	Benzalacetone (m.p. 42°) (4-Phenyl-3-butene-2-one)	d	40	5	C67, D5
BD	Benzaldehyde	b	M	...	B1, 49
B	Benzene	a	M	...	A16, 32, 36, 37, 43, 45, 51, 64, B1, 4, 19, 34
...	Benzoic anhydride (m.p. 42°)	e	20	3	B40, D39
BE	Benzonitrile	b	M	...	A60, B62
BF	Benzophenone (m.p. 48°)	c	25	4	A31, C65
BH	Benzoyl chloride	a	M	...	B6
BI	Benzyl alcohol	d	27	8	B18, C34, 41, 46, D11, 37
BJ	Benzyl benzoate	c	40	10	A19, C62
BK	Bibenzyl (m.p. 52.5°)	a	..	1	A16, C66
...	Biphenyl (m.p. 71°)	a	..	2	C66
BL	Bright stock	a	15	0.5	B4, 62
...	Bromine	a	8	2	A17
BM	Bromoform	a	40	30	A13, C26
BN	n-Butane	a	M	...	A64, B1, 4
BO	sec-Butyl alcohol	b	M	...	B54
BP	t-Butyl alcohol	b	M	...	A64
BS	2-Butanone (methyl ethyl ketone)	a	M	...	B1, 55
BT	n-Butyl ether	a	M	...	B1
BU	Butyl oxalate	a	M	...	A64
BV	Butyl phthalate	b	55	8	C47
BX	Butyl stearate	a	55	3	A18
BY	n-Butyraldehyde	a	M	...	A65, 66
Ca	Calcium nitrate (m.p. 561°)	g	..	0	A50
CA	Camphor (m.p. 176°)	a	M	...	A38, 61
CB	Caproic acid	a	M	...	B1
CC	Caprylic acid	a	M	...	A34, B1
DH	Carbitol (see below)	c	M	...	A35, B62
CD	Carbon disulfide	a	M	...	B6
CE	Carbon tetrachloride	a	M	...	A17, B1

Table II (*Continued*)

Code (legend in graphs)	Substance	Hydrocarbon miscibility (see footnotes)	Carbon dioxide solubility (M = Miscible)i		Graphs
			x	y	
CF	Castor oil	d	15	1	B21, D22
...	Cellosolve (β-ethoxyethanol)	b	M	...	B63
...	Chloral hydrate (m.p. 48°)	e	..	2	A16
DC	Chlorex (see below)	c	M	...	B61, 63, 66
CG	Chloroacetic acid (m.p. 61°)	f	..	10	A10, 56, D47, 57
...	Chloroacetone	e	M	...	C13
CH	o-Chloroaniline	c	25	5	D6, 33
CI	m-Chloroaniline	e	23	1	B35, D38, 49
CJ	Chlorobenzene	a	M	...	A65
CK	β-Chloroethanol	f	40	10	B31, 32, C30 43, D15, 57
...	β-Chloroethyl acetate	c	M	...	C13
CL	Chloroform	a	M	...	A65, B50
CM	Chloromaleic anhydride (m.p. 33°)	f	M	...	A62
...	α-Chloronaphthalene	a	15	1	A29, C49
CO	o-Chlorophenol	c	M	...	A54, 55, B2, C1
CP	p-Chlorophenol (m.p. 43°)	d	25	8	B39, D7, 23
CR	2-Chloro-6-phenylphenol	d	20	1	B14
CS	α-Chloropropionic acid	f	52	26	D2, D55
CT	Cinnamaldehyde	e	20	4	B25, D27
CU	Cinnamyl alcohol (m.p. 30°)	e	20	5	B40, D59
CV	o-Cresol (m.p. 30°)	b	30	2	D18
C	m-Cresol	b	20	4	A28, 30, 33, C42, 45, C49, 61, D16, 33
...	p-Cresol (m.p. 36°)	b	30	2	D18
CW	Crotonaldehyde	b	M	...	A64
CX	Crystal oil	a	20	1	C1, 7, D26
CY	Cyclohexane	a	M	...	B13, 17, 44, 53
...	Cyclohexanol	a	20	4	A28
CZ	Cyclohexanone	a	M	...	A60
D	Decahydronaphthalene (decalin)	a	42	22	32 Systems
...	1-Decene	a	M	...	B17
DA	1-Decyl alcohol	a	30	1	D28
HY	Diacetone alcohol (see below)	c	M	...	C6
DB	Di-sec-butylbenzene	a	M	...	A27, B37, 53
...	p-Dichlorobenzene (m.p. 53°)	a	M	...	B7
DC	β,β'-Dichloroethyl ether (Chlorex)	c	M	...	B61, 63, 66
DD	β,β'-Dichloroisopropyl ether	a	M	...	A60
DE	2,4-Dichlorophenol (m.p. 45°)	a	30	14	A23, C29, 63
DF	α,α-Dichlorotoluene	a	M	...	B6
...	Di-(β-cyanoethyl)-amine	f	..	...	Forms salt
DG	N,N-Diethylacetamide	c	M	...	A1
...	N,N-Diethylaniline	a	45	17	C36, 62
...	Diethylene glycol	g	10	1	B23, 47, D50
DH	Diethylene glycol monoethyl ether (Carbitol)	c	M	...	A35, B62
...	N,N-Diethylformamide	e	M	...	A4
DI	p-Dimethoxybenzene (m.p. 53°)	a	M	...	B7
DJ	N,N-Dimethylacetamide	e	M	...	A4
DK	N,N-Dimethylaniline	a	M	...	B6
...	N,N-Dimethylformamide	f	M	...	C3, 8, 9, 19
DL	Dimethylnaphthalenes (mixed)	a	40	2	A21
DM	2,2-Dimethylpentane	a	M	...	A30, B32, 35, 39
...	2,5-Dimethylpyrrole	a	32	5	C28, 33, 48
DN	2,4-Dinitrochlorobenzene (m.p. 62°)	f	15	1	A32, D66
DO	p-Dioxane	b	M	...	B1
...	Diphenylamine (m.p. 53°)	c	..	1	A51, C66
DP	N,N'-Diphenylethylenediamine (m.p. 62°)	e	..	1	A36
DT	Diphenylmethane (m.p. 27°)	a	30	4	A63
DV	Dipropylene glycol	e	15	2	B26, D12, 60

TABLE II (*Continued*)

Code (legend in graphs)	Substance	Hydrocarbon miscibility (see footnotes)	Carbon dioxide solubility (M = Miscible) t		Graphs
			x	y	
DX	*n*-Dodecane	*a*	M	...	A5, 6, 8, 12, 14, 20, 51, B8
...	Ethane	*h*	M	...	C25
...	β-Ethoxyethanol (Cellosolve)	*b*	M	...	B63
EA	Ethyl acetate	*a*	M	...	B1, 51
EB	Ethyl acetoacetate	*d*	M	...	A3, B67
EC	Ethyl alcohol	*b*	M	...	A41, C12
ED	N-Ethylaniline	*a*	35	13	A14, C31
...	Ethyl anthranilate	*b*	40	6	C62
EE	Ethyl benzoate	*a*	M	...	A64
EF	N-Ethyl-N-benzylaniline	*a*	33	4	C58
EG	Ethyl carbonate	*a*	M	...	B1
EH	Ethyl chloroacetate	*b*	M	...	B59
EI	Ethyl chloroformate	*a*	M	...	A64
EJ	Ethylene bromide	*a*	M	...	A64, B48
..	Ethylene diformate	*f*	M	...	A5, C20, 21
E	Ethylene glycol	*g*	7	0.2	A35, B49, 50, 51, D28, 48, 51
EK	Ethylene glycol monobutyl ether (Butyl Cellosolve)	*a*	M	...	A65
EL	Ethyl ether	*a*	M	...	A47, 65
EM	Ethyl formate	*b*	M	...	A64
EN	2-Ethylhexanol	*a*	53	17	C28, 59
EO	Ethyl lactate	*c*	M	...	C6, 14
...	Ethyl maleate	*d*	M	...	C13
...	Ethyl oxalate	*c*	M	...	A2, B67
EP	*p*-Ethylphenol (m.p. 46°)	*b*	8	1	C53, 54
EQ	Ethyl phenylacetate	*a*	M	...	A60, B23
ER	Ethyl phthalate	*d*	60	10	B12, D46
ES	Ethyl salicylate	*a*	M	...	A65
...	Ethyl succinate	*d*	M	...	B67
...	Ethyl sulfate	*e*	M	...	C9, 13
EU	Eugenol	*b*	38	10	C48, D1
FA	Formamide	*g*	10	0.5	B47, D50
FB	Formanilide (m.p. 47.5°)	*f*	10	0.5	A43, B53
FC	Formic acid	*g*	M	..∗	A11, 12, C10, 16, 24
FO	Fuel oil	*a*	42	18	C9, 23
F	Furfural	*e*	M	...	A5, 63, B56, C3, 8, 17
FU	Furfuryl alcohol	*f*	30	4	B16, 34, C41, 44, D12, 58
...	Gasoline	*a*	M	...	B47
G	Glycerol	*g*	7	0.05	A44, B51, 52, C55, 56, 61, D52
HA	1-Heptaldehyde	*a*	M	...	A65
H	*n*-Heptane	*a*	M	...	62 Systems on A & B
HB	Heptyl alcohol	*a*	38	6.2	C33, 43
HD	*n*-Hexadecane (Cetane)	*a*	38	8	44 Systems (after A53)
...	2,5-Hexanedione	*e*	M	...	C21
HE	Hexyl alcohol	*a*	M	...	B6
HN	Hydrocinnamaldehyde	*c*	55	17	D3, 4, 19
H₂S	Hydrogen sulfide	*a*	M	...	A67
HV	*o*-Hydroxybiphenyl (m.p. 56°)	*d*	..	1	D30
HX	β-Hydroxyethyl acetate	*f*	50	17	D25, 34, 41, 42, 55
HY	4-Hydroxy-4-methyl-2-pentanone (diacetone alcohol)	*c*	M	...	C6
HZ	β-Hydroxypropionitrile	*g*	30	1	B22, 34
IN	Indene	*a*	M	...	B15
I₂	Iodine (m.p. 113.7°)	?	..	0.2	A53
IA	Isocaproic acid	*a*	M	...	B52
IP	Isopropyl alcohol	*b*	M	...	A39, B60
IS	Isopropyl ether	*a*	M	...	A64
K	Kerosene	*a*	M	...	A2, 5, 7, 9, 11, 33, B6, 27

TABLE II (*Continued*)

Code (legend in graphs)	Substance	Hydrocarbon miscibility (see foot-notes)	Carbon dioxide solubility (M = Miscible)t		Graphs
			x	y	
. . .	Lactic acid	g	8	0.5	B23
LA	Lauric acid (m.p. 48°)	a	40	1	A22, C64
. . .	Limonene	a	M	. . .	A5, 67
Li	Lithium chloride (m.p. 600°)	g	. .	0	A48
L	Lubricating oil	a	20	0.7	151 Systems
MA	Maleic anhydride (m.p. 57°)	f	55	7.5	B57, D65
MC	Mercuric chloride (m.p. 282°)	g	. .	0	A52
MD	Mesityl oxide	a	M	. . .	A64
ME	Methanol	f	M	. . .	A6, 9, 35, 40, 46, 48, B11, C8, 9, 12, 16, 23
. . .	2-Methoxybiphenyl (m.p. 29°)	a	20	5	A28
MF	β-Methoxyethanol	e	M	. . .	B64, C4, 5, 19
MG	α-Methoxynaphthalene	a	15	1	A29, C37
. . .	Methyl acetate	b	M	. . .	A67
MH	Methylal	a	M	. . .	B1
MI	N-Methylaniline	b	40	20	A14, C36, 40, 50, 62, D26, 48
MJ	Methyl benzoate	a	M	. . .	A65
MK	Methylcyclohexane	a	M	. . .	B28, 45
ML	p-Methylcyclohexanol	a	20	4	A25
MM	Methylene iodide	e	30	30	B44, 45, 46
BS	Methyl ethyl ketone (2-butanone)	a	M	. . .	B1, 55
. . .	Methyl formate	c	M	. . .	C11
M	α-Methylnaphthalene	a	30	6	A27, 55, 56, 58, 62, B5, C16, 43, 44, 45, 46, 52, C54, 59, D34, 35, 50
MN	β-Methylnaphthalene (m.p. 35°)	a	29	9	A59
MP	Methyl phthalate	e	43	6	B30, D17, 40
. . .	Methyl salicylate	a	M	. . .	B2, 23
. . .	Methyl sulfate	f	M	. . .	C18, 21
MT	Monoacetin	g	10	1	A26
. . .	Morpholine	c	. .	. . .	Forms salt
. . .	Naphthalene (m.p. 80°)	a	. .	2	A51, C57, 66
NA	α-Naphthylamine (m.p. 52°)	e	20	1	B43
. . .	o-Nitroanisole	e	35	2	B34, D58
N	Nitrobenzene	c	M	. . .	A53, 54, 57, B5, 6, 61, 62, 63, C7
NB	o-Nitrobiphenyl (m.p. 37°)	e	15	2	B41, D39
NC	o-Nitrochlorobenzene (m.p. 32°)	d	42	21	C32, 52, D14, 20
. . .	Nitroethane	d	M	. . .	B64, C13
NM	Nitromethane	f	M	. . .	A5, 54, 58, 59, C9, 18, 21
NN	α-Nitronaphthalene (m.p. 58°)	e	. .	1	D32
NP	o-Nitrophenol (m.p. 45°)	d	M	. . .	C2
. . .	1-Nitropropane	b	M	. . .	B60
NS	o-Nitrotoluene	b	M	. . .	B6
NT	p-Nitrotoluene (m.p. 51°)	b	56	20	C27
O	n-Octadecane (m.p. 28°)	a	30	3	C9, 15, 18, 20, 50
. . .	1-Octadecene	a	26	10	D8
ON	2-Octanone	a	M	. . .	A60
. . .	Oleic acid	a	22	2	A33
. . .	Oleum (20%)	f	6	0.1	A42
. . .	Olive oil	a	20	4	A28
OX	p-Oxathiane (thioxane)	a	M	. . .	A60
PA	Paraffin wax (m.p. 52°)	a	. .	1	B8
PB	Paraldehyde	b	M	. . .	A64
. . .	p-Phenetidine	e	12	1	Forms salt
P	Phenol (m.p. 41°)	d	. .	3	A38, B29, C56, D29, 31, 67
PC	Phenylacetic acid (m.p. 77°)	c	. .	0	A34
PD	Phenylacetonitrile	e	52	13	B24, D36
PE	4-Phenyl-3-butene-2-one (benzalacetone) (m.p. 42°)	d	40	5	C67, D5
PF	Phenylcyclohexane	a	35	8	C30

TABLE II (*Continued*)

Code (legend in graphs)	Substance	Hydrocarbon miscibility (see footnotes)	Carbon dioxide solubility (M = Miscible) [i]		Graphs
			x	y	
PG	Phenylethanol	d	15	3	B36, D22
...	Phenylethanolamine	f	15	1	A45, D60
PH	Phenyl ether (m.p. 28°)	a	35	8	C51
...	Phenylhydrazine	f	..	...	Forms salt
PI	Phenyl isocyanide	a	M	...	B1
...	Phenyl phthalate (m.p. 70°)	e	..	1	A37
PJ	Phenyl salicylate (m.p. 43°)	b	38	9	A23
PK	Phosphorus trichloride	a	M	...	B1
PL	Phthalyl chloride	d	33	4	B20, D21
PM	2-Picoline	a	M	...	A60
PN	Pinacol (m.p. 38°)	c	23	2	A24, D23
PO	Pinene	a	M	...	B16
PP	Piperonal (m.p. 37°)	f	45	10	B28, 42
PR	Propane	h	M	...	B3, 4
PT	Propionaldehyde	a	M	...	A64
PV	Propylene	a	M	...	B58
PX	Propylene glycol	g	10	0.5	A35, B23, 38, 48, D61
PY	Pyridine	b	M	..	A60
R	Resorcinol (m.p. 109°)	g	..	0.1	A40
..	Salicylaldehyde	d	M	...	B67
...	Saligenin (m.p. 86°)	f	..	0.1	A40
SN	Silver nitrate (m.p. 212°)	g	..	0	B58
...	Stannic chloride	a	M	...	A1
SU	Succinonitrile (m.p. 54.5°)	g	20	2	B19, D64
S	Sulfur dioxide	c	M	...	A2, 55, C5, 13, 15
...	Sulfuric acid (95%)	g	6	0.1	A41, 42
...	Sulfuryl chloride	a	M	...	A54
TB	Tetrabromoethane	c	10	1	D24
T	*n*-Tetradecane	a	50	16	C4, 10, 28, 35, 37, 58, 66, D3, 6, 7, 11, 16, 17, 24, 41, 51, 61
TD	Tetrahydrofurfuryl alcohol	e	20	3	B25, D10, 38
TE	Tetrahydronaphthalene (tetralin)	a	41	12	A14, 54, 57, C41, 42, C60, D25, 63
TF	Thiophene	a	M	...	A60, B22, 23, 38
OX	Thioxane (*p*-oxathiane)	a	M	...	A60
TH	Thymol (m.p. 51.5°)	a	41	9	A15
...	Toluene	a	M	...	B36
TK	*o*-Toluidine	c	37	7	D8, 45
TL	*m*-Toluidine	c	40	15	D8, 52
TM	*p*-Toluidine (m.p. 45°)	c	37	7	C55, D13
TN	Tolunitriles (mixed)	b	M	...	A60
TO	Transformer oil	a	14	2	A64, 66, B63, 66, C14, 17, 19, 22, D54
TP	Triacetin	f	M	...	B65, C8, 17, 18
...	Tri-*sec*-butylbenzene	a	M	...	B17
TQ	α,α,α-Trichlorotoluene (benzotrichloride)	a	20	2	A17, C38, 42
TR	Triethylene glycol	f	12	2	A45, B15, 36, 37, D35, 60, 61, 62, 63
TT	2,2,3-Trimethylbutane (triptane)	a	M	...	A5, 28, 33, B31, 34, 35, 39
U	Urea (m.p. 132.7°)	g	..	0	B9, 11
V	Valeraldehyde	a	M	...	A64
W	Water	g	6	0.104	A39, 41, 42, 46, 49, B54, 55, 56, D64, 67
X	3,5-Xylenol (m.p. 68°)	a	..	1	A37, 51, C35, 57
XY	3,4-Xylidine	b	33	9	C39

[a] Miscible with all liquid hydrocarbons. [b] Miscible with *n*-dodecane and lower liquid paraffins. [c] Miscible with *n*-heptane. [d] Miscible with methylcyclohexane and lower naphthenes. [e] Miscible with di-*sec*-butylbenzene and lower aromatics. [f] Miscible with benzene. [g] Not miscible with any hydrocarbon. [h] Propane is miscible with liquid hydrocarbons except those with three or more condensed aromatic rings. Ethane is miscible with liquid paraffins including *n*-octadecane, but not with the four heaviest oils mentioned. [i] M, complete miscibility; x, solubility of liquid carbon dioxide in substance in weight per cent. of the solution; y, solubility of the substance in liquid carbon dioxide in weight per cent. of the solution.

TABLE III

ADDITIONAL TERNARY SYSTEMS DESCRIBED BY THE GRAPHS
(Indicated there by plus signs)

Graph[a]	Left hand components[b]	Right hand components
A1	Stannic chloride	n-Heptane
A2	Ethyl oxalate	n-Heptane
A4	Diethylformamide	n-Heptane
A5	Ethylene diformate	n-Heptane, limonene, or triptane
A5	Nitromethane	n-Dodecane, n-heptane, or triptane
A12	Formic acid	n-Dodecane
A14	Ethylaniline or methylaniline	n-Heptane
A16	Chloral hydrate	Benzene
A17	Bromine	Carbon tetrachloride
A23	2,4-Dichlorophenol	n-Heptane
A28	m-Cresol, cyclohexanol, 2-methoxybiphenyl or olive oil	n-Heptane
A29	α-Chloronaphthalene	n-Heptane
A33	Oleic acid	n-Heptane or triptane
A35	Propylene glycol	Methanol
A37	Phenyl phthalate	Benzene
A40	Saligenin	Methanol
A41	Sulfuric acid	Ethyl alcohol
A42	Oleum or sulfuric acid	Acetic acid
A45	Phenylethanolamine	Benzene
A51	Diphenylamine	n-Heptane
A51	Naphthalene	Benzene or n-dodecane
A54	o-Chlorophenol or nitrobenzene	Decalin
A54	Sulfuryl chloride	n-Hexadecane
A55	o-Chlorophenol	n-Hexadecane
A60	BE, CZ, DD, EQ, ON, OX, PM, TF, or TN	Lubricating oil
A64	AA, AH, AS, BP, BU, CW, EE, EI, EJ, EM, IS, MD, PB, PT, or V	Lubricating oil
A64	Benzene or n-butane	Transformer oil
A65	AJ, BY, CJ, EK, EL, ES, HA, or MJ	Lubricating oil
A67	Limonene or methyl acetate	Lubricating oil
B1	AG[c], BD[c], BN, BS, BT, CB, CC, CE[c], DO, EA, EG, MH, PI, or PK[c]	Lubricating oil
B2	Methyl salicylate	Lubricating oil
B4	n-Butane or propane	Bright stock
B6	BH, CD, DF, DK, HE, K, or NS	Lubricating oil
B7	p-Dichlorobenzene	Lubricating oil
B17	Aniline	1-Decene or tri-sec-butylbenzene
B23	Diethylene glycol	Methyl salicylate
B23	Lactic acid	Thiophene
B25	Cinnamaldehyde	n-Heptane
B32	β-Chloroethanol	2,2-Dimethylpentane
B34	Furfuryl alcohol	n-Heptane or triptane
B34	o-Nitroanisole	n-Heptane
B35	Aniline	n-Heptane, triptane, or 2,2-dimethylpentane
B36	Triethylene glycol	Toluene
B39	p-Chlorophenol	n-Heptane or triptane
B40	Benzoic anhydride	n-Heptane
B47	Diethylene glycol	Gasoline or n-heptane
B51	Ethylene glycol	Ethyl acetate
B53	Formanilide	Cyclohexane
B60	1-Nitropropane	Lubricating oil
B61	Chlorex	n-Hexadecane
B62	Benzonitrile or nitrobenzene	Bright stock
B63	Chlorex or β-ethoxyethanol	Lubricating oil
B64	Nitroethane	Decalin
B67[c]	Ethyl oxalate, ethyl succinate, or salicylaldehyde	Lubricating oil
C3	Dimethylformamide	Decalin
C5	β-Methoxyethanol	n-Hexadecane
C6	Ethyl lactate	Lubricating oil
C8	Acetic anhydride	Decalin
C8	Acrylonitrile, dimethylformamide, furfural or triacetin	n-Hexadecane
C9	Methanol	Fuel oil
C9	Ethyl sulfate	n-Hexadecane
C9	Dimethylformamide	n-Octadecane
C11[c]	Methyl formate	Lubricating oil
C12	Acetonitrile or ethyl alcohol	Lubricating oil
C13[c]	Chloroacetone, β-chloroethyl acetate, ethyl maleate, ethyl sulfate, or nitroethane	Lubricating oil
C16[c]	Methanol	n-Hexadecane
C17[c]	Furfural or triacetin	Lubricating oil
C18[c]	Methyl sulfate or nitroethane	n-Hexadecane
C19[c]	Dimethylformamide	Lubricating oil or transformer oil
C20[c]	Acetonitrile or ethylene diformate	n-Hexadecane
C21[c]	Acetic acid, acetic anhydride, ethylene diformate, 2,5-hexanedione, or methyl sulfate	Lubricating oil
C23[c]	Methanol	50% n-Hexadecane 50% Fuel oil
C25	Ethane at 15°	Lubricating oil
C28	2,5-Dimethylpyrrole	n-Tetradecane
C33	2,5-Dimethylpyrrole	Decalin
C36	Diethylaniline	Decalin
C41	Benzyl alcohol	Tetralin
C42	α,α,α-Trichlorotoluene	n-Hexadecane
C43	Heptyl alcohol	α-Methylnaphthalene
C48	2,5-Dimethylpyrrole	Lubricating oil
C49	α-Chloronaphthalene	Lubricating oil
C54	p-Ethylphenol	n-Hexadecane
C57	Naphthalene	n-Hexadecane

TABLE III (Continued)

Graph[a]	Left hand components	Right hand components
C58	Ethylbenzylaniline	Decalin
C62	Benzyl benzoate, diethyl-aniline, or ethyl anthra-nilate	Lubricating oil
C66	Biphenyl, diphenylamine, or naphthalene	n-Tetradecane
D8	o-Toluidine	n-Hexadecane
D8	m-Toluidine	1-Octadecene
D12	Dipropylene glycol	Decalin
D18	p-Cresol	n-Hexadecane
D22	Castor oil	Lubricating oil
D23	Pinacol	Lubricating oil
D33	o-Chloroaniline	n-Hexadecane
D38	o-Anisidine, m-chloro-aniline, or tetrahydro-furfuryl alcohol	Lubricating oil
D39	Benzoic anhydride	Lubricating oil
D41	β-Hydroxyethyl acetate	Decalin
D50	Diethylene glycol	α-Methyl-naphthalene
D53	Aniline at 0°	Lubricating oil
D55	Chloropropionic acid	Lubricating oil
D57	Chloroacetic acid	Lubricating oil
D58	o-Nitroanisole	Lubricating oil
D60	Dipropylene glycol or phenylethanolamine	Lubricating oil
D61	Propylene glycol	n-Tetradecane

[a] The temperature observed for all graphs was 21 to 26° except those noted, as follows: C25, below 17.6° the minimum critical temperature of ethane and carbon dioxide mixtures; D53, at 0° to permit merging of band and bite. D57, at 37° to melt chloroacetic acid in contact with carbon dioxide. [b] Capital letters refer to first column of Table II. [c] These systems have isopycnics or twin density lines (17).

Nearly half (127) of the 261 substances tested were miscible with liquid carbon dioxide (M in column 4). In nine other cases of incomplete miscibility the carbon dioxide *poorer* phase contained over 50% of carbon dioxide. It will be noted from Table II that the solubility of carbon dioxide in another liquid is (with one exception) much greater than that of the other liquid in carbon dioxide, and that the ratio of these two solubilities is greatest for those liquids of low miscibility with carbon dioxide. The solubilities in and for water were taken from the work of Wiebe and Gaddy[12] and that of Stone,[13] respectively; and those for lubricating oil, naphthalene, iodine and glycerol in carbon dioxide from the work of Quinn and Jones.[14]

From Table II the miscibilities of many other solvents with carbon dioxide may be predicted. Homologs differ only slightly in miscibility. With increasing molecular weight, solubilities may increase at first and then steadily decrease (*e.g.*, aniline–toluidines–xylidine). Halogen atoms and carbonyl and ether groups also have slight effects (carbon tetrachloride, 2-octanone and n-butyl ether are all miscible with carbon dioxide); but hydroxyl,

(12) R. Wiebe, *Chem. Revs.*, **29**, 475 (1941); R. Wiebe and V. L. Gaddy, *J. Am. Chem. Soc.*, **61**, 315 (1939); **62**, 815 (1940); **63**, 475 (1941).

(13) H. W. Stone, *Ind. Eng. Chem.*, **35**, 1285 (1943).

(14) E. L. Quinn, *ibid.*, **20**, 735 (1928); *J. Am. Chem. Soc.*, **50**, 677 (1928); E. L. Quinn and C. L. Jones, "Carbon Dioxide," Reinhold Publ. Corp., New York, N. Y., 1936, pp. 109–10.

amino and nitro groups diminish solubility, especially if two or more are present. Complete mixing is prevented also by a bicyclic structure in derivatives (*e.g.*, methoxynaphthalene) as well as in hydrocarbons. These effects are similar to but not quite parallel with those involved in hydrocarbon miscibilities.[15]

Ternary Systems.—Mutual binary solubilities of two normally liquid components, usually a hydrocarbon and a non-hydrocarbon, were observed in graduated test-tubes if not already known. They are indicated approximately in the graphs by miscibility gaps on the base line. Then various charges of the two liquids were placed in the autoclave and carbon dioxide was added as before. With increasing amounts the composition of the system follows a straight line (isologous line or line with a constant binary ratio) toward the apex (carbon dioxide corner) of the triangular diagram from a point on the base line corresponding to the relative weights of liquid reagents charged. Whenever a new interface appeared (after agitation), or one disappeared, the weight of carbon dioxide added, when plotted as percentage on the isologous line gave a point on a binodal curve of the diagram.

Sometimes with increasing amounts of carbon dioxide two liquid phases became miscible; and with further additions of carbon dioxide another two layers appeared which did not mix on agitation. It is even possible for the second pair of layers to mix at compositions higher up on the same isologous line. The diagrams (*e.g.*, graph D38) clarify the reasons for this peculiar behavior.

After proceeding up the isologous line as far as was practicable (when the autoclave was full), the carbon dioxide was released, sometimes gradually so as to check the previous observations. If the other two reagents were sufficiently non-volatile so that no loss was feared, more of one of them was added and a new isologous line was studied. Otherwise, the whole system was discharged, and a new proportion of reagents was charged. Sometimes one or two isologous lines were sufficient to define the system adequately, provided they were chosen judiciously with respect to the expected diagram. In other cases a dozen of them might be required, depending on the complexity of the diagram.

Graphs.—The 464 systems studied are presented in 268 graphs numbered 1 to 67 on each of pages A to D. Carbon dioxide is assigned the top corner in each graph. The other components are indicated by code letters under the appropriate corners, referring to the first column of Table II. The left hand component or "solvent" is the more polar one, usually the non-hydrocarbon.

A considerable saving in number of graphs results from the close similarity in many of the simpler systems. Additional ternary systems illustrated by a single graph are listed in Table III. Indication that there is an alternate component for either position is by means of a plus sign after the code letters. Thus, graph A64 illustrates 18 systems with a binodal curve on the right side. One of these is acetic acid–aniline as indicated by the codes AD and A on the graph. Plus signs after

(15) A. W. Francis, *Ind. Eng. Chem.*, **36**, 764, 1096 (1944).

these codes refer to Table III which lists the other 17 systems, namely, 15 solvents designated by code letters, each with lubricating oil, and also benzene or n-butane, each with transformer oil. The curve has an altitude of about 30% solvent, and the tie lines are nearly parallel to the side line, as indicated by the position of the plait point near the apex of the curve. This multiple representation by graphs results in compromises and minor inaccuracies in drawing. Binary solubilities with carbon dioxide should be taken from Table II in preference to scaling the graphs.

The tie lines shown as shading on the binodal areas were not observed; but their orientations were estimated from observed plait points and phase boundaries. They serve to clarify the differences in those areas.

The graphs are arranged in order of number, positions and altitudes of binodal curves. In graph A1 all components are miscible. It would represent an unlimited number of systems not tested because of no interest. However, a few ternary systems with three pairs of consolute components were tested in an unsuccessful search for a system with an island curve. In graphs A2 to A12 carbon dioxide is miscible with each of the other two components, which are not mutually miscible. They are miscible in the systems of graphs A13 to B11, but carbon dioxide is incompletely miscible with the solvent in graphs A13 to A53 and with the hydrocarbon (or other right hand component) in the others. In graphs B12 to B58 only the carbon dioxide and right hand component, and in graphs B59 to C25 only the carbon dioxide and solvent are miscible. In C26 to C66 the liquid components are miscible with each other, but neither with carbon dioxide. In the systems of graphs C67 to D67 no pair of components is miscible. In the first 18 of this group of graphs (21 systems) the three binodal curves are separate, and there are three plait points.

Solids are considered "miscible" for this purpose if it is probable that subcooling of melted solid would not give two-liquid phases in metastable equilibrium. However, solid phase equilibria are shown in the graphs. Some are isolated from the binodal curves (58 systems in which solid–liquid tie lines radiate from a base corner of the diagram, e.g., A15, 56); some submerge probable binodal curves (no plait point, graphs A51, 52, 53, B11); and some intersect the curves or bands (39 systems, e.g., A10). The last occurrence gives a triangular three phase area (a solid and two liquids) one corner of which is at a base corner of the graph. These are shown in black with white crosshatching. Graph B58 is a special case of this type in which some of the phase boundaries coincide with the side lines. It is virtually identical with that published[16] for silver nitrate–propane–propylene. In graphs D30, 32 two S–L₁-L₂ triangles appear, one across each binodal area.

Systems with three liquid phases (29 systems, graphs C10, 24, D48 to D67) are shown as usual with an internal triangle not quite touching any border line, though often close to some of them.

These triangles are crosshatched. The last three graphs contain triangular areas of both types. Graph C10 is almost unique in having three plait points although one pair of components is miscible.

In 45 systems (especially those of graphs C13 to C23) a change in the amount of carbon dioxide present caused a reversal in the relative densities of the phases, so that the layers inverted. These isopycnics or twin density lines[17] are marked on the graphs with straight dashed lines though in some systems they should be slightly curved. An inversion is interesting to watch but has no theoretical significance. Quinn[14] considered it pertinent that the greatest solubility of a lubricating oil in carbon dioxide occurred at the temperature, 10°, at which the densities of the two liquid phases were equal (binary twin density line). This was probably coincidental. In two graphs (C22, 23) two twin density lines are shown.

The "dual solubility effects" of liquid carbon dioxide at different concentrations mentioned above are shown in 99 graphs with a binodal curve on the bottom side and other binodal curves on the left or right side or both, and also in 23 graphs (D18 to D40) with a binodal curve on the bottom side and a band across the other two sides. Thus in graph D39, o-nitrobiphenyl, a solid, and lubricating oil (of only moderate mutual miscibility) are mixed by adding about 30% carbon dioxide to the system. Yet carbon dioxide dissolves only about 2% of o-nitrobiphenyl and less than 1% of the oil. Neither is it very soluble in either of them nor much more so in their mixture.

The homogenizing action of carbon dioxide, evident in almost every graph, is common to many solvents. The precipitating action is recognized in at least seven patents.[18] In the fourth of these, for example, Lantz states "an increase in the quantity of the carbon dioxide actually reduces the amount of oil dissolved. .."

Merging of Curves.—The existence of 97 systems with separate binodal curves and 118 systems with concave bands apparently resulting from coalescence of such curves affords an opportunity for testing the validity of conflicting speculations[19-21] as to the manner of merging.

Examples were sought but not found of two separate convex binodal curves approaching each other externally at points other than both plait points, or of a three phase area resulting from such a merger.[20,21] In the only graph suggestive of this postulate, that for formic acid–n-hexadecane (C24), the triangular area was shown to be present as in graph C10 before the band was formed by direct plait point merger of two small binodal curves.

(16) A. W. Francis, J. Am. Chem. Soc., **73**, 3710 (1951).

(17) A. W. Francis, Ind. Eng. Chem., **45**, 2789 (1953).

(18) U. S. Patents, 2,130,147; 2,166,503; 2,188,013; 2,188,051; 2,246,227; 2,315,131· 2,346,639.

(19) Reference 5, pp. 829–31; A. W. Francis in "Physical Chemistry of Hydrocarbons," A. Farkas, ed., Academic Press, Inc., New York, N. Y., 1950, pp. 251–4.

(20) J. E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., New York, N. Y., 1951, pp. 215, 244.

(21) A. E. Hill in "Treatise on Physical Chemistry," H. S. Taylor, ed., D. Van Nostrand Co., New York, N. Y., 1931, pp. 574–575; R. E. Treybal, "Liquid Extraction," McGraw-Hill Book Co., Inc, New York, N. Y., 1951, p. 17; and several other textbooks.
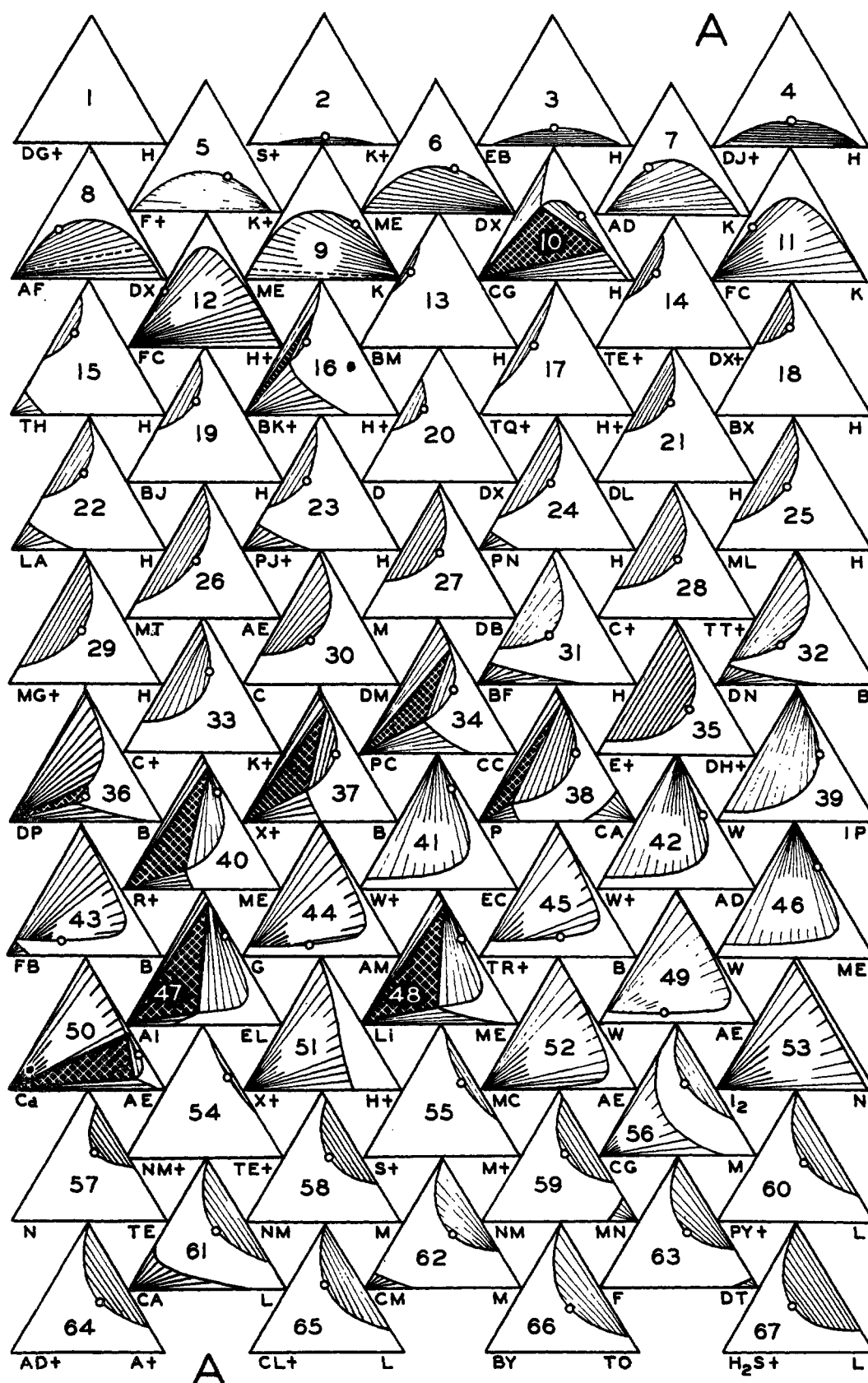
Components: Carbon dioxide is assigned the top corner in each graph. The other components are indicated by letters referring to the first column of Table II. Additional systems are indicated by plus signs after one or both sets of the code letters. These are listed in Table III.

Shading: White areas indicate homogeneous compositions. Oriented shading indicates two phases. It is solid–
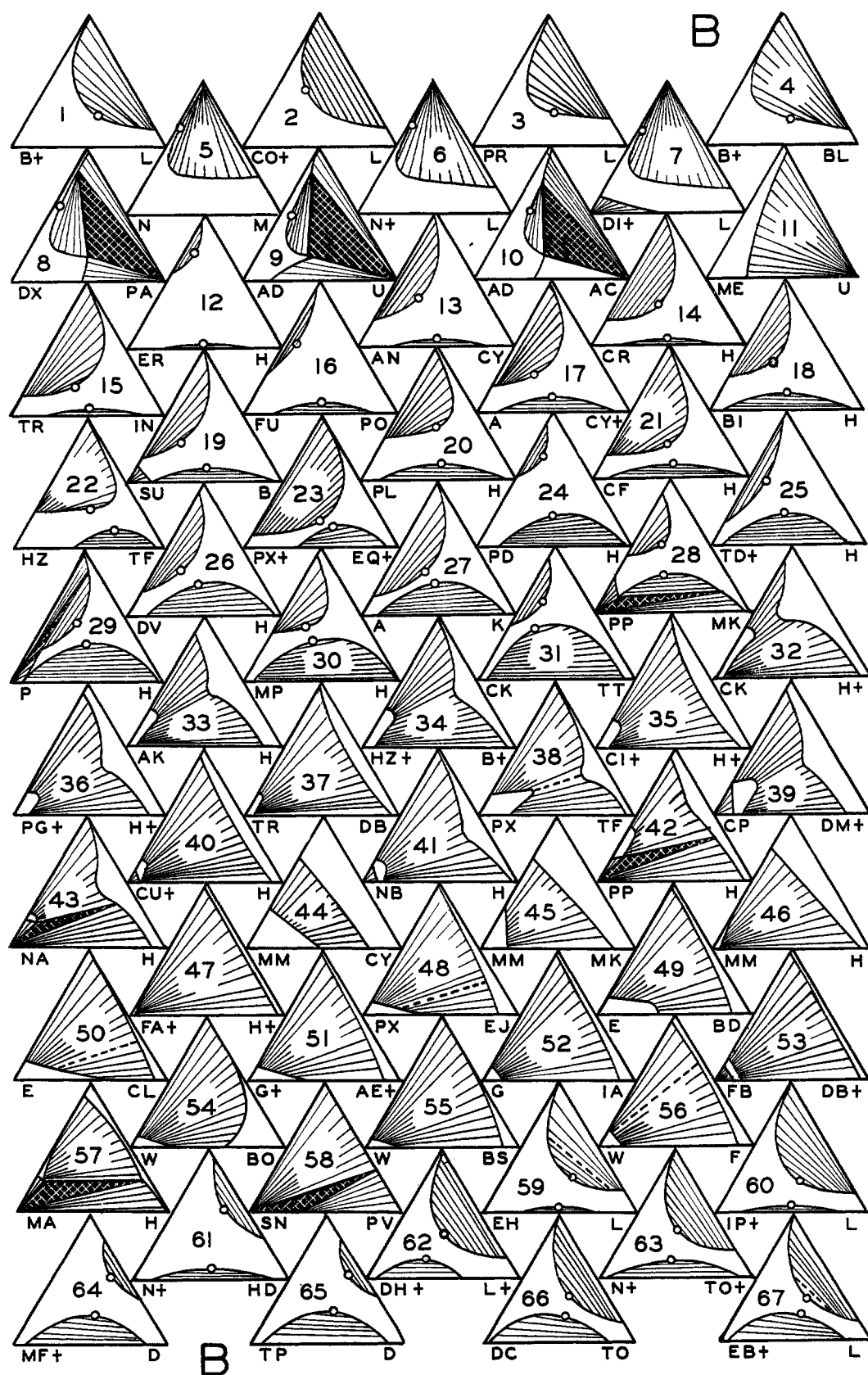
liquid if the lines radiate from a base corner of the graph. Otherwise it is a binodal or two liquid phase area. A cross-hatched triangle indicates three phases. Black on white shows three liquid phases. White on black (with a corner at a base corner of the graph) indicates a solid and two liquid phases. No solid phases other than the pure compound are shown on these graphs. A dashed line across a binodal area is an isopycnic or twin density line.
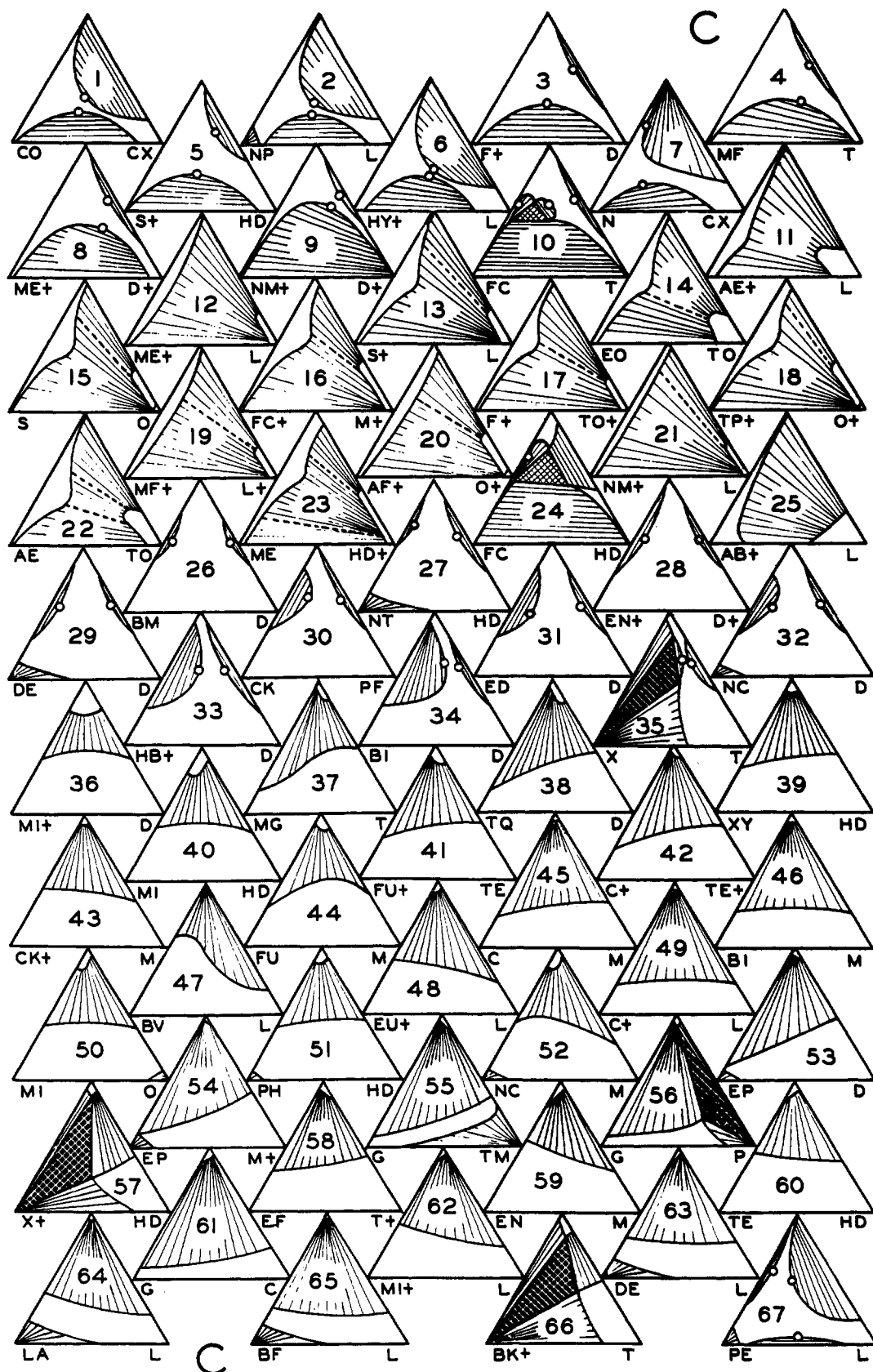
As in the systems reported previously,[3] *external contact of convex curves always occurs at both plait points.* Two separate curves do not necessarily meet at all. Thus in graph C7 the upper curve probably would contact the side line instead.

On the other hand, meeting of a band with a bite
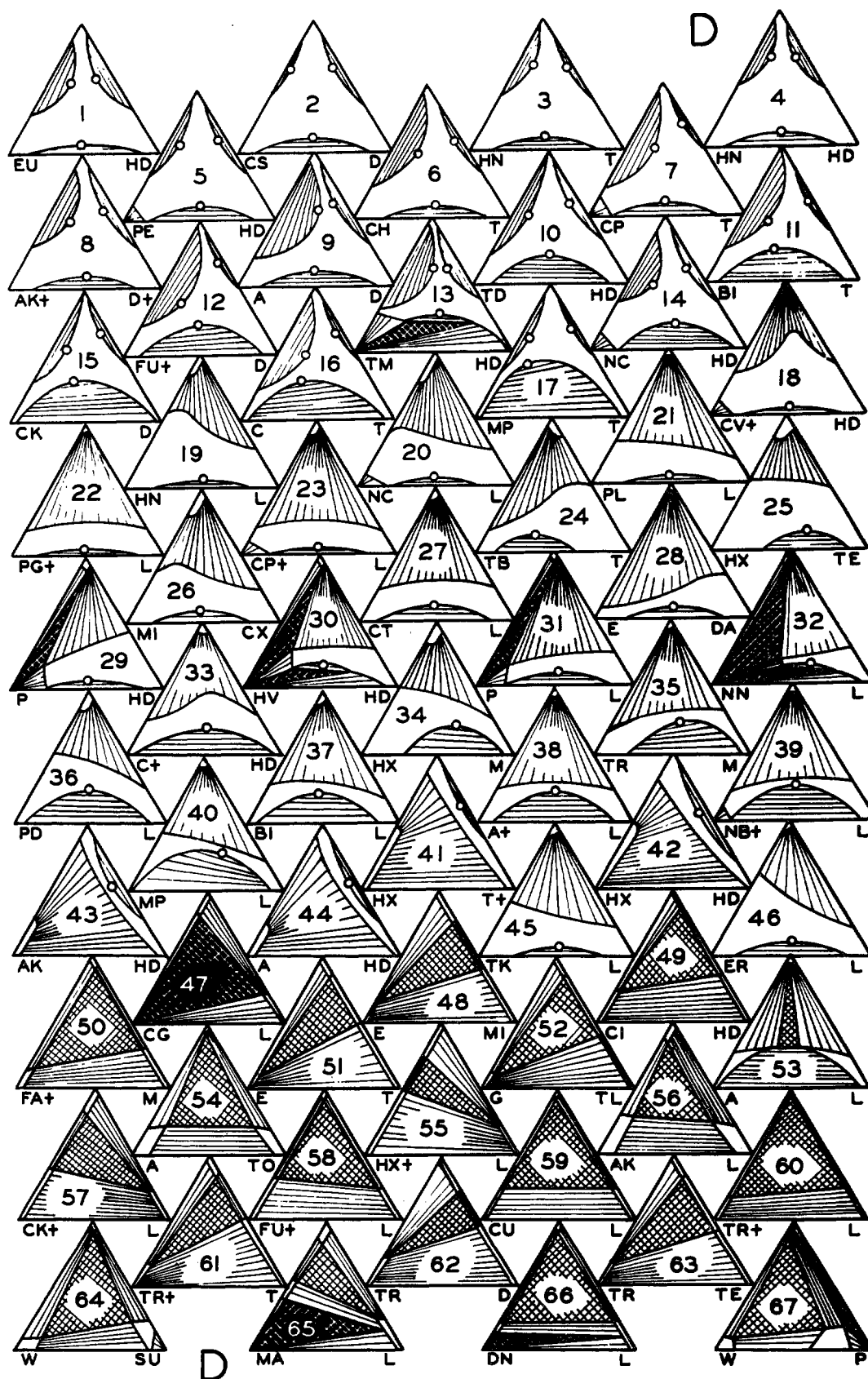
(free binodal curve) is possible although there is only one plait point. The system aniline–lubricating oil (graph D38) was cooled to about 0° (or diluted with a little hexadecane) to accomplish the merger as in graph D53. The result was a triangular three-liquid phase area, as predicted.

However, at the point of contact (which occurred at the plait point of the bite) the border of the band just before contact was distinctly concave. This is a theoretical requirement to satisfy Schreinemakers' rule[19,20] with respect to triangular areas representing three phases. That rule would prohibit the more usual illustration of merger of convex curves.[20,21]

The three-liquid phases in some of the carbon dioxide systems result from the above mechanism. Those of the others, including the formic acid systems mentioned above, and probably all of the published systems with three liquid phases[22] result from eruption of a second binodal curve from *within* another one at a point other than the latter's plait point. This is possible, and is the type cited by Hill[21] in support of his hypothetical diagram.

(22) Reference 5, pp. 847, 977, 1009, 1015, 1029-31, 1035-6, 1070.

A STUDY OF THE EQUATION OF STATE FOR EDNA[1]

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Thermohydrodynamic calculations were made by the "inverse" method (measured detonation velocity–density equation included in the solution) for EDNA using three fundamentally different equations of state leading to widely different internal pressures $((dE/dv)_T)$. Two sets of measured velocity data were used with each equation of state. The results show that all the calculated thermodynamic quantities except temperature are less sensitive to the form of the equation of state than to errors in the determination of detonation velocity. Hence, temperature alone provides an adequate criterion of an objective evaluation of the equations of state when one approaches the problem solely from detonation theory. However, so far reliable detonation temperature measurements have not been possible, and this criterion cannot therefore be applied. A corollary of this conclusion is that any reasonable equation of state provides, through detonation theory and measured velocities, as reliable thermodynamic data as any other. Objective detonation equation of state studies must evidently await more accurate velocity–density measurements and the development of methods for measuring some detonation property with sufficient accuracy to allow one to evaluate the various forms of the equations of state unambiguously.

Numerous equations of state of various forms have been used in thermohydrodynamic calculations. In spite of wide differences in form and character of these equations of state the thermodynamic quantities computed, either by direct use of experimental detonation velocity *vs.* density data or by adjustment of parameters to give best agreement with observed velocities, have been in surprisingly close agreement, except for computed detonation temperatures. Temperature alone turns out to be strongly dependent upon the nature of the equation of state. This situation led one of us[2] to conclude that the detonation temperature is the only factor where a comparison between computed and observed values could be used to evaluate the accuracy of the equation of state. Unfortunately, even such a comparison with detonation temperatures is inadequate in view of the great limitations of temperature measurements. It was therefore considered advisable to make a thorough theoretical study of the influence of the form of the equation of state on the various thermodynamic quantities computed from the thermohydrodynamic theory and also to study theoretically the influence of experimental errors in velocity.

The explosive EDNA (Haleite)[3] was selected for this study since it appeared to be well suited both from the viewpoint of reliability of computed products of detonation and from measured velocities. In fact, two sets of velocities have been obtained showing good agreement at high densities but differing considerably in the velocity at low density and in the slope of the velocity-density curve. These were as follows[4]

$$D = 5650 + 3860(\rho_1 - 1.0) \quad (1a)$$

$$D = 5960 + 3275(\rho_1 - 1.0) \quad (1b)$$

(See Appendix I for definitions of symbols)

The general equation of state

$$pv = nRT\varphi \quad (2)$$

was adopted for this study. Specific forms of φ were selected such as to exaggerate differences in the equation of state, using the specific definition

$$\varphi = e^x \quad (3)$$

where

$$x = K(v)\frac{T^c}{v}$$

Three cases were treated using the following values of c

$$c = -0.25 \quad (3a)$$

$$c = 0 \quad (3b)$$

$$c = +0.1 \quad (3c)$$

Definition 3a leads to an equation of state of much the same form as that of Kistiakowsky–Wilson–Brinkley,[5] although K is here allowed to vary with density (experimental velocities being used to determine K) whereas in the KWB equation it is a constant. Also here $\varphi = e^x$, but in the KWB case $\varphi = 1 + xe^x$. One will, however, note that these two forms are not radically different. Definition 3b is equivalent to the $\alpha(v)$ approximation used by Cook[2] and in different form by Caldirola[6a] and Paterson.[6b] Definition 3c is probably completely

(1) This project was supported by Office of Naval Research (Contract Number N7-onr-45107, Project Number 357 239).

(2) M. A. Cook, *J. Chem. Phys.*, **15**, 518 (1947).

(3) Ethylenedinitramine $O_2NHNCH_2CH_2NHNO_2$.

(4) Measured at Bruceton, Pennsylvania (NDRC, Division 8).

(5) OSRD No. 69, 905, 1231, 1510, 1707. NDRC Division 8 Staff.

(6) (a) P. Caldirola, *J. Chem. Phys.*, **14**, 738 (1946); (b) S. Paterson, *Research*, **1**, 221 (1948).