In the case of zinc and chromium trioxide, it is to be expected that oxides of these elements (or copper chromite) were present during the reaction. These materials may have interfered with regular crystal growth, since they would not fit into the copper lattice, and thus induced the formation of powder.

The control of the rearrangement pattern by foreign atoms on the surface suggests that one role of a promotor is to control the orientation of the facets produced on the catalytic surface. Many chemical reactions, including catalysis, have been shown to vary markedly with crystal face,[6,2] and materials which alter the crystal faces exposed should change the catalytic properties of the metal even if the added material itself has no effect on the reaction.

It should be pointed out that, with exception of evaporated silver, the foreign metal and metallic oxides which were added in these experiments were not evenly distributed over the surface of the crystal. The patterns obtained, therefore, reflect in part this distribution. The experiments with silver added both uniformly and non-uniformly indicate, however, that the change in pattern is not due just to the distribution of the added material on the surface. Because of the dependence of rate of surface processes on crystal face, difficulty will always be encountered in crystal growth processes in getting an evenly distributed layer of foreign atoms on all faces.

Measurements are now being made of the rates of reaction of hydrogen and oxygen on different faces of a copper single crystal to which foreign metal atoms have been added. These results, together with a more detailed description of the rearranged surfaces, will be presented in a later paper.

CHARLOTTESVILLE, VA.

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(6) See A. T. Gwathmey, H. Leidheiser, Jr., and G. P. Smith, NACA Tech. Note No. 1460, June, 1948, for a discussion of the influence of crystal face on chemical activities of single crystals of metals.

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL CO., INC.) RESEARCH AND DEVELOPMENT DEPARTMENT]

Ternary Systems with Two Separate Binodal Curves[1]

BY ALFRED W. FRANCIS

RECEIVED JUNE 8, 1953

Several ternary systems with two separate binodal curves have been found. The components are an aliphatic solvent, an aromatic solvent, and a non-aromatic hydrocarbon with critical solution temperatures not very different with the two solvents. One system, methanol–nitrobenzene–2,2,4-trimethylpentane, has been studied at several temperatures. The two curves meet at both plait points at 14.1°, the "col" temperature. The isotherm at this temperature resembles lines intersecting at a finite angle, not curves with a common tangent.

Only one ternary system with two separate binodal curves, that of water–ethanol–succinonitrile,[2] is described in the chemical literature. In that system two of the components freeze before the curves merge. The manner of coalescence of two separate binodal curves has not been observed previously.

Conditions for existence of these systems are indicated in a solid diagram of a ternary system of A, B and C in the shape of a triangular prism with the vertical axis denoting temperature. Suppose A and B are miscible at all temperatures considered, but C has a limited miscibility with either A or B up to the respective binary critical solution temperatures. These are the tops of the parabolic curves showing binary miscibilities against temperature for systems of C with A and B (Fig. 1). The binodal surface in the solid diagram is a ridge across the prism connecting these two curves. If A and B are similar chemicals, *e.g.*, both aromatic solvents, the ridge is practically straight, though in general sloping. If A and B are dissimilar, the ridge is usually concave upward; and if the two critical solution temperatures are fairly close together, within 20 to 40°, there may be a saddle point which is lower than either end. By analogy with a mountain pass it will be convenient to call this point a "col" (low point of the ridge). Under these conditions and in the temperature range between this col and the lower of the two critical solution temperatures, the isothermal diagram shows two separate binodal curves.

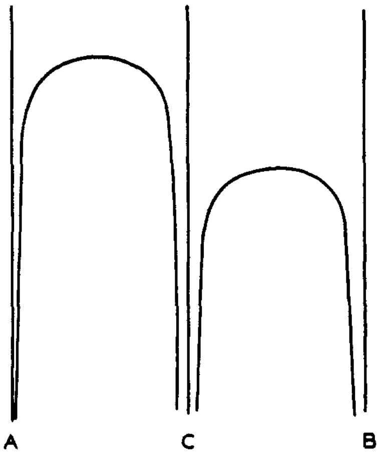

Fig. 1.

Examples are listed in Table I. "C.S.T." are critical solution temperatures between the two substances in adjacent columns. Several other

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 7, 1953.

[2] F. A. H. Schreinemakers, *Z. physik. Chem.*, **27**, 95 (1898). A related system water–phenol–salicylic acid with one curve almost submerged by a solid phase equilibrium was reported by C. R. Bailey, *J. Chem. Soc.*, 1951 (1925).

TABLE I

TERNARY SYSTEMS WITH TWO SEPARATE BINODAL CURVES

Aliphatic solvent	C.S.T., °C.	Hydrocarbon	C.S.T., °C.	Aromatic solvent	Col, °C.
Methanol	14.75	*n*-Pentane	24	Nitrobenzene	2
Methanol	51	*n*-Heptane	18	Nitrobenzene	12
Methanol	42.6	Isoöctane[a]	29.65	Nitrobenzene	14.1
Methanol	46	Methylcyclohexane	40.3	Aniline	36.7
Methanol	46	Methylcyclohexane	34	*o*-Nitrobiphenyl	25
Acetic acid	10.5	*n*-Heptane	18	Nitrobenzene	4.5
Chlorex[b]	23	Isoöctane	29.65	Nitrobenzene	22
Chlorex	16	*n*-Heptane	18	Nitrobenzene	15.5

[a] 2,2,4-Trimethylpentane. [b] β,β-Dichloroethyl ether.

systems including an aliphatic solvent (preferably miscible with water), a hydrocarbon and an aromatic solvent could be found to show the phenomenon. In systems with Chlorex, which is not miscible with water, the concavity is so slight that the two critical solution temperatures must be very close together.

The system methanol–isoöctane–nitrobenzene was selected for detailed study because room temperature is included in the range for two separate curves, and because each component could be obtained in very pure form. The isoöctane was reagent grade for antiknock determination. Methanol was J. T. Baker anhydrous C.P. grade. The critical solution temperature of these two was 42.6°, agreeing closely with the literature value,[3] 42.5°. This observation is very sensitive to moisture content. Water is the only probable impurity which in traces would seriously affect the results. The nitrobenzene used was Eastman Kodak Co. first grade, further purified by crystallization from a melt until its freezing point range was 5.6 to 5.5°.

The observations were made in narrow graduated glass stoppered tubes immersed in a water-bath in a large silvered Dewar flask. This was preferred to a thermostat because near the col a slightly variable temperature was desired. It was found impractical to use open tubes because the mixtures are slightly hygroscopic and the miscibility temperatures are extremely sensitive to moisture. Compositions were made up by volume from graduated pipets until cloudiness just disappeared or reappeared. The end-point compositions by weight were calculated from the densities at 25°, 0.6877 for isoöctane, 0.7873 for methanol and 1.1987 for nitrobenzene. The temperature was observed with a 0 to 65° calibrated thermometer graduated in 0.2°. The bath temperature was adjusted by addition of small quantities of cooler or warmer water and stirred several minutes before each final reading. Data are presented in Table II and illustrated in Fig. 2.

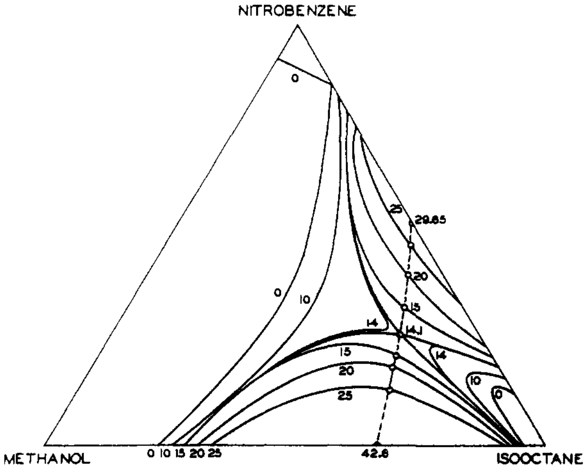

Fig. 2.

The manner in which the curves merge as temperature is lowered is of interest in view of conflicting speculation in the literature. It seems evident that the first contact of the curves occurs at both plait points since these are points along the top of the ridge in the solid diagram. This ridge is indicated by a smooth curve (dashed line), which is practically straight.

The col is the common plait point of the two binodal curves when they meet. At the col temperature the isotherm has the appearance of lines intersecting at a finite angle rather than curves with a common tangent, as sometimes postulated. These lines are in effect the common asymptotes of the two pairs of hyperbola-like curves, namely, the two binodal curves at higher temperatures and the two arms of the binodal band at lower temperatures.

A few aqueous systems with two separate binodal curves were noted,[4] but in each case only one of the two curves has been studied and published. These systems involve hydrogen chloride, which is soluble in water only up to 63.7% (at 25°).[5] The third component is ether, dioxane, *n*-butyl, isobutyl, or isoamyl alcohol (the last two with hydrogen bromide also). The positions of the curves on the water–hydrogen halide side, except for their extremities, are speculative and were shown by dashed lines. The same conditions hold for two other more recently published aqueous systems, hydrogen bromide–dioxane[6] and hydrogen chloride isopropyl ether.[7]

Another group of ternary systems with two

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(3) R. E. Cornish, R. C. Archibald, E. A. Murphy and H. M. Evans, *Ind. Eng. Chem.*, **26**, 399 (1934).

(4) 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.

(5) F. F. Rupert, THIS JOURNAL, **31**, 860 (1909).

(6) W. T. Grubb and R. C. Osthoff, *ibid.*, **74**, 2108 (1952); *cf.* R. A. Robinson, *ibid.*, **74**, 6125 (1952).

(7) D. E. Campbell, A. H. Laurene and H. M. Clark, *ibid.*, **74**, 6193 (1952).

separate binodal curves has been observed in the author's laboratory.[8] These involve liquid carbon dioxide and will be presented in a later paper. They include also several examples of ternary systems with three separate binodal curves on the three sides of the triangular diagrams, a novel phenomenon. Practical uses for some of these systems are shown.

TABLE II

SYSTEM METHANOL–NITROBENZENE–ISOÖCTANE (WEIGHT PERCENTAGES)

Methanol	Nitrobenzene	Temp., °C.	Methanol	Nitrobenzene
77.0	0	0	8.0	92.0
55.7	17.0		0	85.9
40.3	29.0		(Equil. with solid nitrobenzene)	
27.3	45.5			
25.5	48.2		4.5	0
16.1	60.6		4.7	7.0
5.2	78.1		4.5	8.4
0	86.1		3.8	14.3
			0	12.2
74.2	0	10		
62.1	9.5		5.0	0
40.3	24.5		6.5	3.9
32.1	32.2		7.5	9.7
21.1	42.4		8.7	14.8
16.8	51.0		3.7	17.4
11.8	60.8		0	16.0
4.9	74.0			
0	83.0			
23.5	27.1	14	9.5	8.5
18.0	27.2		12.0	18.2
18.0	32.3		11.3	22.8
14.2	47.0		10.3	24.8
			0	19.5
22.0	27.0	14.1	13.0	20.0
			15.0	25.0
16.0	27.0	Col	16.0	27.0
			12.0	25.0
16.0	30.0		4.0	21.0
72.0	0	15	0	79.7
59.8	9		4.7	70.9
50.9	15.3		12.8	48.3
37.2	22.5		11.8	32.9p.p.[a]
30.8	24.8		10.1	27.7
19.2	21.8p.p.		0	20.2
14.9	20.3			
8.0	6.0			
7.0	0			
69.6	0	20	0	76.2
53.8	9.7		3.7	68.7
46.1	13.9		7.4	57.5
32.0	19.3		7.5	45.5
28.8	20.9		7.0	41.4p.p.
21.9	18.6p.p.		6.4	38.4
9.8	5.8		3.2	28.5
7.5	0		0	23.8
66.6	0	25	0	73.5
52.3	7.9		3.5	60.0
37.7	12.8		3.3	47.9p.p.
24.5	13.4p.p.		0	34.2
14.8	8.9			
11.4	4.9			
8.0	0			
		29.65	0	53.0p.p.
			(also C.S.T.)	
33.6	0p.p.	42.6		
(also C.S.T.)				

[a] Plait points, P.p.

PAULSBORO, N. J.

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[8] A. W. Francis, U. S. Patents 2,631,966 and 2,646,387 (1953).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Diradicals in Solution: Role in Polymerization

BY K. E. RUSSELL AND A. V. TOBOLSKY

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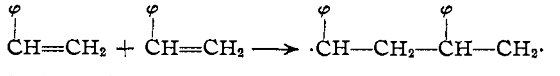
Diradicals have been produced by the photolysis of 1,4,5-oxadithiacycloheptane. A minimum value for their rate of formation in benzene solution is given by the rate of disappearance of 2,2-diphenylpicrylhydrazyl. In methyl methacrylate the great majority of the diradicals either undergo primary recombination, or form small rings after the addition of one or two monomer units. Few, if any, of the diradicals grow to form long polymer chains. The photolysis of butyl disulfide has been investigated so that comparisons can be made with a disulfide source of monoradicals. The photodecomposition of the *trans*-annular peroxide ascaridole has been shown to lead to monoradicals.

Introduction

For many years it has been considered that the thermal and photopolymerization of styrene proceed by way of diradical intermediates. Flory[1] suggested that initiation of thermal polymerization involves the reaction



$$\overset{\varphi}{\mathrm{CH}}{=}\mathrm{CH_2} + \overset{\varphi}{\mathrm{CH}}{=}\mathrm{CH_2} \longrightarrow \cdot\overset{\varphi}{\mathrm{CH}}{-}\mathrm{CH_2}{-}\overset{\varphi}{\mathrm{CH}}{-}\mathrm{CH_2}\cdot$$

and that photopolymerization is initiated by the opening up of the carbon–carbon double bond of a single monomer molecule to give a diradical.

Recently the role of diradicals in these types of polymerization has been questioned.[2,3] It has been shown that if diradicals are formed in the initiation reaction, they are unlikely to grow to long polymer chains but have a high probability of undergoing self-termination to form small rings.[3] In photopolymerization the relationship between the molecular weight of the polymer isolated and the rate of polymerization leads to the conclusion that long chain photopolymer is formed from growing monoradicals[2]; no evidence was found that thermal polymer is formed from growing diradicals.[2]

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[1] P. J. Flory, THIS JOURNAL, **59**, 241 (1937).

[2] D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952).

[3] B. H. Zimm and J. K. Bragg, *J. Polymer Sci.*, **9**, 476 (1952).