the decrease of the residual iron(II) at the end of the reaction suggest that the iron(II) is disappearing by some additional method. This disappearance may be related to the emulsifier itself or some accompanying impurity.

Experimental

The source and purity of the ferrous sulfate 2,2′-bipyridine, acrylonitrile, water, acetate buffer and nitrogen have been described previously.[7,13] The potassium persulfate was Baker and Adamson reagent grade used without further purification and the potassium chloride and calcium sulfate Baker Analyzed reagents. The emulsifiers were the commercial products: General Aniline Agent 140 BK, Dewey and Almy Daxad 11, National Aniline Nacconol NRSF, Merrell cetylpyridinium chloride, Fine Organic cetyltrimethylammonium bromide, and Swift potassium fatty acid soap flakes.

The same apparatus procedure as described in a previous publication[7] was used with the exception that the bipyridine was added to the flask before the contents were deoxygenated. Calculations based on the value of the rate constant of the reaction

$$\mathrm{Fe^{++} + 3bip \longrightarrow Fe(bip)_3^{++}}$$

determined by Baxendale and George[14] indicated that the establishment of equilibrium under the actual experimental conditions is practically instantaneous. All reactions took place in tenth molar solutions of acrylonitrile in water under an atmosphere of oxygen-free nitrogen. Samples were removed at various intervals, centrifuged to remove any polyacrylonitrile and analyzed for residual iron(II) by a colorimetric bipyridine procedure.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The System Methyl Ethyl Ketone–Water below 0°[1]

BY MERLE RANDALL AND F. E. MCKENNA[2]

The freezing curves for the system, methyl ethyl ketone–water, have been determined in both the water-rich and the ketone-rich one-phase solutions. Mutual solubilities of the two liquid phases have been measured between -2 and $-19°$

The temperature–composition relations for solutions of methyl ethyl ketone and water were studied below 0° because of the non-ideality of the system. Rothmund,[3] Marshall[4] and the Shell Chemical Company[5] have reported solubility measurements in this system, and Marshall has also measured vapor pressures of the system. No determinations of the freezing curve have been reported.

Freezing Points of Aqueous Solutions of Methyl Ethyl Ketone. Apparatus.—In Fig. 1 the cryostat for binary solutions is shown at A; B is a dewar for an ice–water mixture for the reference junction of the thermo-element. These are suspended from a Bakelite panel, CC, by brass rods, DD, a circular brass disc, EE, and wing nuts, F. The copper thermo-element tube, G, terminates in the distributor head, H, with clear amber Bakelite cap, I, and six copper terminals, J; the distributor is supported by a Bakelite strip, KK. The stirrers, LL, are driven at 90 r.p.m. by a 0.03 H.P., 60-cycle continuous-duty motor, M, with a 20:1 gear ratio, mounted on a panel, NN. Brass rods, CN, connect CC with NN. Gears, OO, on the stirrers are connected by the chain, P, which also passes over an idler, Q. The stirrer shaft bearings, v, are packed with mica-impregnated asbestos twine; triangular plates, RR, prevent sidewise motion of the stirrers. Samples are removed through the tube, S. Heat losses along the stirrer are minimized by the rubber coupling disc, T.

Dry, CO_2-free air from an air liquefier system entered the system at 20 p.s.i. through brass tubing, U, W and X. Refrigeration was obtained by cooling the air stream in the copper coil, y, which was immersed in liquid air in the dewar, Y. Tubing, XX, was insulated with cotton bound with linen tape. The air flow was controlled by the solenoid valve, V5, operated by a switch at the potentiometer, so that the cryostat temperature could be held constant to 0.0001°. To warm the cryostat, valve V4 was closed, and V2 was opened to allow room temperature air to enter the system.

Samples were removed through S by application of air pressure to the cryostat through V1 and UU. Excess air pressure could be released through V6.

The outer brass jacket, aa, of the cryostat is fastened to the panel, CC, by rubber washers and knurled nuts, bb. The dewar, ee, is held in place by a balsa wood block, c, a spring bronze support, dd, and a balsa wood ring, ff. Within the dewar is a copper tube, h, of 5-cm. diameter, to which is soldered the cooling coil XX, with exit at Z. The copper thermocouple tube, gg, which is coiled inside the tube h, has a junction at i to German silver tubing to lessen the heat-leak. The German silver sample tube, S, terminates in a fan-shaped stainless steel gauze, k (200-mesh). The stainless steel stirrer tube, m, has three sets of blades, n. The outer jacket is sealed to the Bakelite panel by a cork ring, oo. Glands, p and q, were packed with beeswax-impregnated cotton string. A liquid drain, r, is provided in the bottom of the outer jacket.

Construction and Calibration of the Multiple Thermo-element.—The No. 30 double silk-covered constantan wire which was used by Randall and Vanselow[6] and No. 36 double silk-covered copper wire were arc-welded (1 amp., 110 v., d.c.) to form a 6-junction thermo-element. The constantan wire was tested for homogeneity by the method of White,[7] while the copper wire was assumed to be of sufficient uniformity. The entire thermo-element was doubly coated with Bakelite varnish and wrapped with silk lingerie binding tape, which was also coated with the varnish. The annealed copper tubes were filled with molten naphthalene before insertion of the couple. The thermo-element leads were soldered to copper binding posts in the Bakelite cap before the tubing was coiled and mounted in the apparatus. The resistance of the thermo-element was checked at each stage of its construction. Joints between the copper tubes and the compression T-fitting, t, were moisture-proofed with "Vinyl-Seal."

The thermo-element was calibrated against melting ice, subliming carbon dioxide, and boiling oxygen as suggested by Wiebe and Brevoort.[8] The solid CO_2 which was ob-

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(1) Presented at Pittsburgh, Pennsylvania, Meeting of the American Chemical Society, September 6, 1943, by the late Dr. Randall.

(2) Air Reduction Co., Inc., Research Laboratories, Murray Hill, New Jersey.

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(8) R. Wiebe and M. J. Brevoort, "U. S. Dept. Commerce, Bur. Mines Rept. Investigations," No. 3077 (1931).

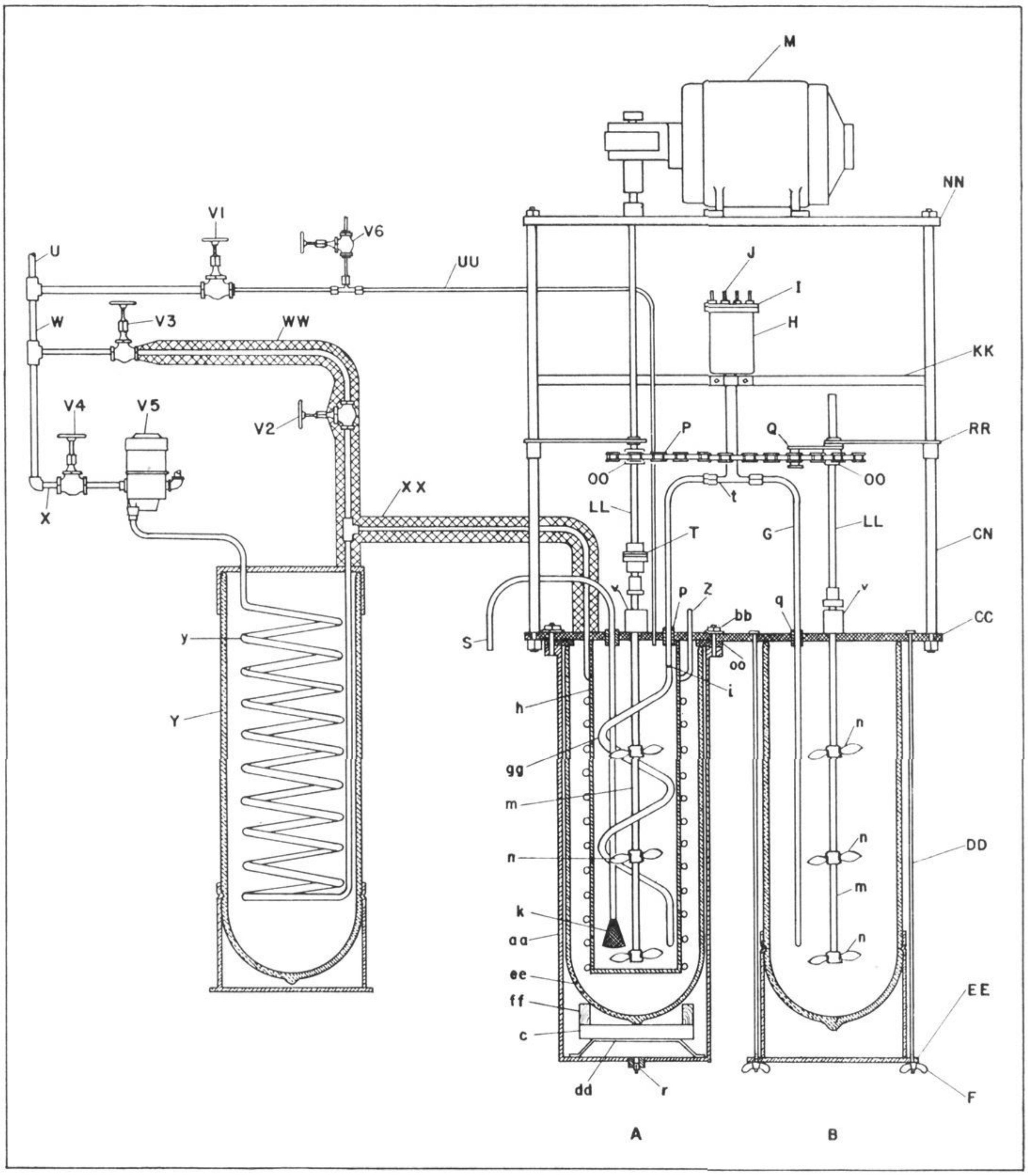

Fig. 1.—Cryostat.

tained from the Pure Carbonic Co., Berkeley, Calif., was powdered before it was placed in the cryostat. The liquid oxygen was prepared by passing electrolytic oxygen through $CaCl_2$ before it was condensed in a glass bulb which was submerged in liquid air. A small quantity of liquid oxygen was introduced into the cryostat, so that the boiling oxygen would displace the air before the cryostat was filled with the liquid oxygen. A plot of e.m.f. *versus* volume of oxygen in the cryostat indicated that a very small amount of nitrogen was present; the e.m.f. was extrapolated to pure oxygen.

Clear portions of commercial artificial ice were crushed in well-washed linen bags with a mallet; the resultant pieces were used when they passed through a 1.0-cm. sieve but not through a 0.6-cm. sieve. The ice was washed with ice-cold twice-distilled water before it was placed in the dewar with another portion of the distilled water.

From the e.m.f. values for the three calibration temperatures the constants in the Eastman–Rodebush equation,[9] $E = E° + aT^n$, were evaluated: $E° = 12568.2$ μv., $a = -0.836204$ and $n = -1.71437$. A White double potentiometer, Leeds and Northrup Co., Type 7623, of 100,000 μv. range was used.

Purification of Methyl Ethyl Ketone.—Fractionation of the ketone in a packed tower (*ca.* 22 plates) produced a fraction which distilled 79.57–79.58° (760 mm.) (f.p. −83.36 ± 0.01°; d^{25}_4 0.79948). The boiling point of methyl ethyl ketone as reported by various investigators ranges from 796.15 to 79.9° with the best values from 79.56 to 79.60°.[4,10-16] The freezing points reported range from −86.6 to −85.9° with the best value at −86.35°.[10,11,16]

Analytical Methods.—Methyl ethyl ketone was determined by the modified hydroxylamine method of Marasco[17] as recommended by the Shell Chemical Company.[5] This product gave consistent values of 98.3% for the pure ketone; this factor was applied in all determination. The precision of the method has been reported as *ca.* ±0.2%.

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A check on the ketone analysis was obtained by determination of the water in the sample by a modification[18] of the acetylpyridinium chloride method of Bryant and Smith.[19] The precision of this method as reported by the original investigators is about ±1.0% of the water content with a systematic error of 2.8% which is taken into account in the calculations.

Agreement between the ketone and water analyses was *ca.* 0.2%.

Freezing Point Measurements.—The cryostat was filled with a methyl ethyl ketone and water solution whose approximate concentration was known. The stirrers were set in motion and refrigeration was started. After the solution had frozen, the mass was allowed to melt to obtain the primary freezing point from the change in slope of the time–temperature curve. After the freezing point was well-defined as a result of repetitions of this process, the solution was maintained at the freezing point for *ca.* 45 min. so that equilibrium could be definitely established between solid and liquid phases before duplicate liquid samples were withdrawn for analysis. The refrigeration was increased slightly during removal of the samples to avoid a temperature increase in the cryostat.

The freezing point–composition data are given in Table I and are plotted in Fig. 2. A few unstable melting points, which were observed in the composition range between A and B, apparently fall on extensions of the stable freezing curves, F_w and F_k; the temperatures of these unstable points were not reproducible.

The eutectic point of the system, *E*, is so near the freezing point of pure methyl ethyl ketone that no measurements could be made on the ketone-rich side of the eutectic. The thaw–melt method[20] was used to find the eutectic temperature in solutions which contained less than 0.5% methyl ethyl ketone; the average of five observations is −88.88 ± 0.01°. The composition of the eutectic point was determined by extrapolating the freezing curve to −88.88°, and was found to be 99.91 weight per cent.

Solubility Measurements.—The mutual solubility curves, S_w and S_k, were determined after introduction of a second sample tube into the cryostat. The end of this tube terminated five inches below the mouth of the dewar. This arrangement of the two tubes permitted the simultaneous removal of samples from the upper and the lower liquid layers. After the two phase mixture had been maintained at a predetermined temperature for 45 minutes, while the stirrers were in operation, duplicate samples of each layer were withdrawn for analysis. The data for these solubility measurements are given in Table II.

TABLE I

FREEZING POINTS IN THE METHYL ETHYL KETONE–WATER SYSTEM

Weight fraction, MEK	F.p., °C.	Weight fraction, MEK	F.p., °C.
0.015	−0.361	0.910	− 6.033
.043	−0.879	.935	− 8.807
.080	−1.476	.973	−16.53
.102	−1.751	.989	−26.09
.146	−2.370	.994	−40.10
.234	−3.892	.998	−58.75
.357	−5.213	.998	−61.28
.389	−5.587	.998	−65.53
.869	−5.587	.999	−86.64
.907	−5.693		

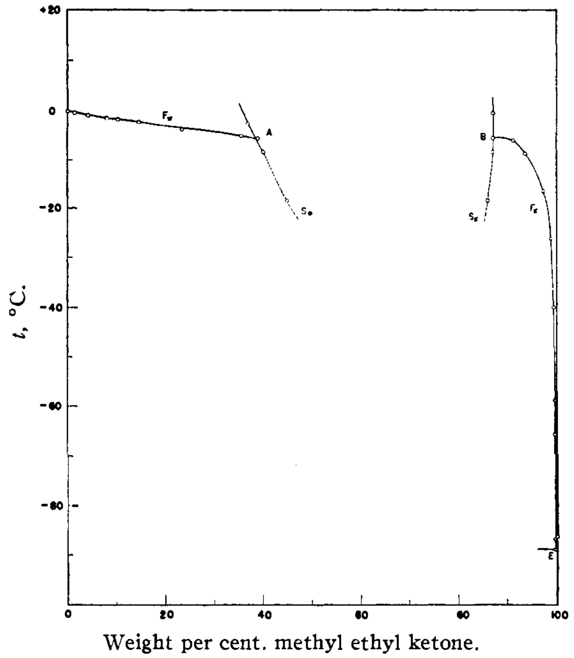

Fig. 2.—Freezing point curves and solubility curves. Stable equilibria are represented by the solid lines and metastable conditions are indicated by the dotted lines.

TABLE II

MUTUAL SOLUBILITY OF LIQUID PHASES IN THE METHYL ETHYL KETONE–WATER SYSTEM

Weight fraction in water-rich phase	Weight fraction in ketone-rich phase	*t*, °C.
0.3695	0.8693	− 2.53
.3974	.8689	− 8.60
.4501	.8590	−18.51

Supersaturation could not be caused below −20°, because a spontaneous separation of ice from the solutions occurred below this temperature. The slopes of the two arms of the solubility curve are so pronounced that there can be no doubt that an unstable lower critical mixing point should exist about −50° under a pressure of one atmosphere.

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