literature. No evidence is found for the oxidation by O_3 of Br^- by a free radical process.

Paths II and III are chain paths initiated by reaction of ozone with peroxide and bromine, respectively, to produce free radicals. The chain continuing steps are the same for both paths;

the nature of the chain breaking step depends on the ratio $(O_3)/(H_2O_2)$. An explanation of the variation of the rate by Path II with (H^+) is afforded by the assumption that HO_2 is a fairly strong acid with $K_{diss.}$ $ca.$ 10^{-2}.

The System Sodium Nitrate–Dioxane–Water at 25°

BY B. SELIKSON AND J. E. RICCI

In connection with studies on the solubilities of salts in dioxane–water mixtures the formation of a two liquid system was observed in high dioxane solutions saturated with sodium nitrate. The experimental study of the phase relationships of such ternary systems involving a solid and two liquid components is in general rendered difficult by the problem of analysis for one of the liquid components in addition to the usually simple determination of the solid component. For solids forming no solid solvates with the liquid components the solubility curve is easily determined as a binary problem by using mixed solvents of known composition. Under favorable circumstances a binodal curve in such a system may be established by the synthetic method of titration with one of the liquid components, as in the system potassium carbonate–dioxane–water studied by Kobe and Stong.[1] Otherwise the analytical problem has usually been solved through the measurement of some physical property of the solution, or of the distillate from some ternary solution or phase, for the determination of the ratio of the two liquid components; examples of such properties are the refractive index (used for the study of the system lithium chloride–dioxane–water, by Lynch[2]), the density, or even the solubility of some reference salt in the unknown mixture of the two liquids. For more precise work it is desirable to attempt some direct determination of one of the liquid components. In the system silver nitrate–dioxane–water,[3] in which a solid dioxanate of silver nitrate appears at 25°, water was determined directly gravimetrically, with fairly accurate results, by volatilization of the solvents and absorption of water in barium monoxide. In the present system, a more rapid and possibly more exact method was attempted, by the application of the Karl Fischer reagent for the direct volumetric determination of water.[4]

Materials and Analysis.—The sodium nitrate was a c. p. sample used without further purification, after grinding and drying at 110°. The dioxane was treated and dried as described in previous similar investigations.[5] The Karl Fischer reagent (active ingredients: iodine, sulfur dioxide and pyridine, in methanol as solvent) prepared according to the directions of Smith, Bryant and Mitchell,[6] was used with synthetic "anhydrous" methanol as back-titrating solution, and was standardized against a standard solution containing a known weight of pure water in the same methanol. The water content of the methanol and the effective titer of the reagent itself were calculated from a set of titrations using 1, 2 and 5 ml. (all at least in duplicate) of the standard solution of water (1 ml. containing 0.01793 g. of H_2O by preparation). The titer of the Karl Fischer reagent was found to fall with time, as expected (from 0.002582 to 0.001986 g. of water per ml. in fifty-eight days); in the actual use of the reagent, however, standardization titrations against the standard water solution were always run just before and just after any set of analyses, all being done within a few hours at most, so that the error from such changing strength could be kept low. It was found, moreover, that the water content of the back-titrating methanol also changed (increased) with time, so that a curve of this effect was used to estimate the water content of the methanol for some of the standardizations for which there had not been a satisfactory simultaneous determination of the water equivalent of the methanol. These corrections were, of course, small, inasmuch as relatively only small volumes of the methanol were used in back-titration, and the change in its water titer was only from 0.00033 to 0.00056 g. of water per ml., in the same period of fifty-eight days.

Solubility Determinations.—The methods for the preparation of complexes, temperature control, attainment of equilibrium, sampling of liquids for analysis and approximate density determination, were as used in previous investigations.[3] The equilibrium solutions were analyzed

(1) Kobe and Stong, J. Phys. Chem., **44**, 629 (1940).

(2) Lynch, ibid., **46**, 366 (1942).

(3) Skarulis and Ricci, THIS JOURNAL, **63**, 3429 (1941).

(4) Fischer, Angew. Chem., **48**, 394 (1935).

(5) Davis and Ricci with Sauter, THIS JOURNAL, **61**, 3274 (1939).

(6) Smith, Bryant and Mitchell, ibid., **62**, 3504 (1940).

<div align="center">

TABLE I

System NaNO₃–Dioxane–Water at 25°
</div>

No.	Original complex %NaNO₃	%H₂O	Lower liquid %NaNO₃	%H₂O	Density	Upper liquid %NaNO₃	%H₂O	Density	Solid phase	Extrapolation error, %H₂O
1	..	..	47.87	(52.13)	1.384				NaNO₃	
2	55.44	36.37	40.91	48.22	1.321				NaNO₃	+0.03
3	51.03	33.70	34.94	44.85	1.266				NaNO₃	− .23
4	49.28	32.41	32.35	43.27	1.252				NaNO₃	− .19
5	43.89	27.30	24.69	36.60	1.191				NaNO₃	+ .12
6	37.92	24.81	20.02	31.88	1.157				NaNO₃	+0.29
7	Excess NaNO₃		17.74	30.09	1.144	0.43	6.14	1.032	NaNO₃	
8	Excess NaNO₃		17.84	30.07	1.147	.46	6.22	1.030	NaNO₃	
9	Excess NaNO₃		18.02	29.92	1.146	.45	6.13	1.035	NaNO₃	
	Average		17.84	30.03^a	1.146	.44	6.16^b	1.032	NaNO₃	
10	By synthesis		15.36	29.20					None	
11	6.96	16.81	14.71	28.70	1.129	.57	7.08	1.035	None	
12	7.36	19.34	12.17	27.99	1.108	.74	7.88	1.033	None	
13	By synthesis					2.34	14.47		None	
14	14.90	4.13				.24	4.63	1.029	NaNO₃	+1.23
15	16.71	3.28				.12	3.86	1.028	NaNO₃	+0.37
16	18.54	1.62				.05	2.00	1.029	NaNO₃	− .05
a						.072	3.74		NaNO₃	
b						.032	2.86		NaNO₃	
c						.009	1.90		NaNO₃	
d						.005	0.96		NaNO₃	
e						.003	.00		NaNO₃	

^{a} Point A of Fig. 1. ^{b} Point B of Fig. 1.

for sodium nitrate by evaporation to constant weight at 100–150°. For the determination of water weighed samples of the ternary solutions were diluted with dioxane in 25-ml. volumetric flasks, and suitable aliquots (usually 1 or 2 ml., requiring on the average about 15 ml. of titrating solution) were analyzed by means of the Karl Fischer reagent. Preliminary experiments had established that neither dioxane nor sodium nitrate interfered with the water determination. Addition of definite volumes of dioxane during standardizations showed the presence of only a very small amount of water in the dioxane, amounting to a practically negligible correction of only about 0.02 ml. of the reagent per ml. of dioxane.

Except for an occasional loss of sample, the solutions were all analyzed in duplicate for each of the two components determined. Five of the analyses (which were generally made after a day or two of rotation of the complexes) were repeated after a few more days or longer, to verify the attainment of equilibrium. The values listed in the table are the final average compositions thus determined for each point on the isotherm. The isothermally invariant solutions saturated with sodium nitrate were analyzed from three different complexes. The relative disagreement in the duplicate determinations of sodium nitrate were generally very small, as expected; for the water determination the disagreement of duplicates averaged 3–4 parts per 1000. The average absolute error in the water determination may be estimated from the algebraic extrapolations of the eight tie-lines for single liquids saturated with sodium nitrate as solid phase. These tie-lines extrapolate to 100% sodium nitrate with an average deviation of 0.31% calculated as water; conversely, assuming the solid phase to be pure sodium nitrate, as it evidently is, the average absolute error of the determination of the water content of these solutions is calculated to be 0.08%.

Results.—The results of the solubility determinations are listed in Table I and shown graphically in Fig. 1. The compositions are given in terms of weight per cent.
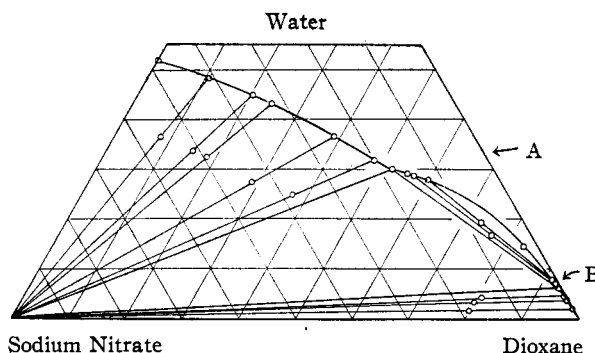

Fig. 1.—System sodium nitrate–dioxane–water at 25°.

Discussion.—On the basis of the diagram and of the algebraic extrapolation of tie-lines, the only solid phase is seen to be unsolvated sodium nitrate. The solubility curve of this solid, however, is seen to be broken by a rather flat binodal region in which immiscible liquids are formed. The isothermally invariant conjugate liquids in equilibrium with excess of solid sodium nitrate have the following compositions

	% NaNO₃	% H₂O	Density
Lower layer	17.84	30.03	1.146
Upper layer	0.443	6.16	1.072

Two pairs of conjugate solutions in the binodal area, not saturated with solid sodium nitrate, were determined by direct and complete analysis of the equilibrium phases formed from known mixtures of the three components (complexes 11 and 12 of Table I). The two tie-lines so obtained are sufficient to indicate that the plait point of the binodal curve must lie considerably over toward the dioxane-rich side. Two other points on the binodal curve (numbers 10 and 13 of Table I) were determined synthetically by a kind of titration: addition of solid sodium nitrate, in successive small portions, with shaking, to known weights of suitable mixtures of water and dioxane. The appearance of a turbidity indicating the formation of a second liquid marked a point on the binodal curve. In experiment no. 13 the liquids so formed were almost immediately approximately equal in volume, indicating proximity to the plait point, which, however, was not further investigated.

The last five values (a-e) listed in Table I were obtained in some earlier more precise work on the effect of water on the solubility of sodium nitrate in dioxane, using more highly purified dioxane and sodium nitrate. These mixtures were rotated for at least two weeks, and were analyzed in duplicate, and only for sodium nitrate, the percentage of water in the equilibrium solutions being calculated from the exact composition of the mixed solvent, prepared by weight. An enlarged plot of these special points for this region of the system is shown in Fig. 2, in which the shape of the curve

is seen to be similar to the corresponding portion of the solubility curve of silver nitrate in dioxane containing small amounts of water.[3]
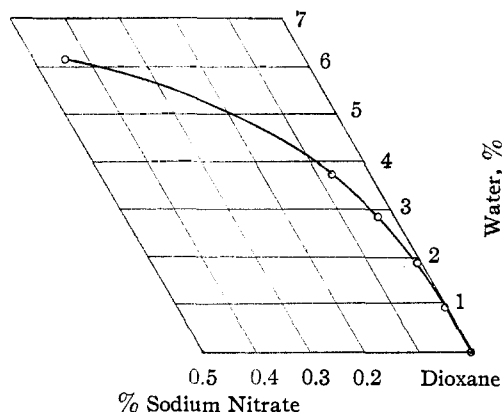

Fig. 2.—Effect of water on solubility of sodium nitrate in dioxane, at 25°.

Summary

The solubility relationships in the ternary system sodium nitrate–dioxane–water at 25° have been investigated, using a direct analytical determination of water in the equilibrium liquids by means of the Karl Fischer reagent. A small region of immiscible liquids appears, for solutions containing between 52.13 and 93.40% dioxane and between 17.84 and 0.44% sodium nitrate. Exact determinations are also given for the solubility of sodium nitrate in dioxane containing very small percentages of water.

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The Relative Surface Tension of Potassium Chloride Solutions by a Differential Bubble Pressure Method[1]

BY F. A. LONG AND G. C. NUTTING

The surface tensions of dilute aqueous solutions of electrolytes have been investigated recently by a capillary height[2] and by a ring method.[3] Both show a minimum in the surface tension at about 0.001 normal although the depth of the minimum is considerably larger for the ring method. To explain the discrepancy of these results from the theoretical Onsager–Samaras[4] prediction, two

different types of explanations have been advanced. Dole[5] and also Bikerman[6] have developed theories on the assumption that the results are true surface tensions. Langmuir[7] postulated that the true surface tension did not have a minimum and that the experimental results were due to the neglect of the zeta potential at the silica-solution interface. This theory has been discussed in more detail by Jones and Frizzell.[8]

(1) Presented at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) Jones and Ray, THIS JOURNAL, **59**, 187 (1937); **63**, 288, 3262 (1941).

(3) Dole and Swartout, *ibid.*, **62**, 3039 (1940).

(4) Onsager and Samaras, *J. Chem. Phys.*, **2**, 528 (1934).

(5) Dole, THIS JOURNAL, **60**, 904 (1938).

(6) Bikerman, *Trans. Faraday Soc.*, **34**, 1268 (1938).

(7) Langmuir, *Science*, **88**, 450 (1938).

(8) Jones and Frizzell. *J. Chem. Phys.*, **8**, 986 (1940).