TABLE II

EFFECT OF VARYING HCl

K' ignored, $T = 25°$

$(Sn^{++})_0$, moles/l.	$(ClO_4^-)_0$, moles/l.	(W^{VI}), moles/l.	(HCl), moles/l.	K, l./mole/hr.	K''[b] moles/l./sec.
0.1	0.227	10^{-2}	10.00	20.0	36,000
.1	2.27	10^{-3}	7.77	31.8	53,000
.1	4.54	4×10^{-4}	5.56	51.4	65,300
.1	6.81	2×10^{-4}	3.33	110.0	59,300
.06[a]	7.94	2×10^{-5}	2.25	257.0	65,000

[a] As $SnSO_4$. [b] K'' calculated from $-d(Sn^{++})/dt = K''(W^{VI})a_{HClO_4}/a^2_{HCl}$.

There is indication that two chlorides are involved. There is also a suggestion that the polarographic reduction and stannous chloride reduction proceed by the same mechanism.

The variation of K with temperature does not follow well the usual proportionality between log K and reciprocal T. However, the energy of activation seems to lie between 12000 and 17000 cal. comparing very well with the activation energy found by Laitinen and Ziegler for the polarographic reduction.

The author wishes to express thanks for the interest and helpful suggestions received from Professors W. J. Argersinger and A. W. Davidson. This work was sponsored by the Office of Ordnance Research, U. S. Army.

LAWRENCE, KANSAS

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, PLASTICS DIVISION RESEARCH DEPARTMENT]

Solid–Liquid Equilibria of the System $NaCN-NaOH-H_2O$[1]

BY GEORGE D. OLIVER AND S. E. J. JOHNSEN

RECEIVED APRIL 26, 1954

Ternary phase diagrams, expressed in weight %, were determined for three isotherms, 25, 35 and 55°, on the system $NaCN-NaOH-H_2O$. There were two isothermally invariant points, hydrates and anhydrous salts found on each isotherm. A new double compound, $NaCN \cdot NaOH$, of equimolar composition found at 35 and 55°, did not exist at 25°. A NaOH concentration greater than 10% prevented the formation of $NaCN \cdot 2H_2O$ at 25°. Density values were determined on some samples at each temperature.

Introduction

In the course of fundamental research on cyanide solutions, interest developed in the behavior of NaCN and NaOH in a ternary system with water. The small amount of data in the literature were not sufficient to establish the desired phase relationships; therefore, the ternary phase diagrams were determined at 25, 35 and 55°. These isotherms were chosen for the following reasons. At 25° both solid components are precipitated as hydrates from binary solutions. At 35° anhydrous NaCN is precipitated, but at 34.7° the dihydrate is the stable form. The solubility of each salt in water is approximately 50 weight % at 55°.

Experimental

Materials.—Both compounds were J. T. Baker reagent grade material. Assays showed a purity of 97.2% for NaCN and 97.7% for the NaOH. No attempt was made to purify either compound; however the carbonate formed in the strong NaOH solutions was removed by filtration.

Procedure.—A series of 100-g. samples were prepared by weighing, to the nearest 0.1 g., the required amount of NaCN, NaOH and H_2O into a flask. After heating to promote solution, the samples were filtered to remove the carbonate and transferred to 200-ml. glass tubes.

Equilibrium was attained in the samples by agitating for 4 to 5 hours in a thermostated bath (±0.05°) by means of a rocking mechanism. An analysis of duplicate samples that had been agitated for 2 and 24 hr. proved that a short agitation time was sufficient for equilibrium. Usually, the samples were allowed to stand in the bath overnight so that the solid phase could settle out. After sampling the liquid with a pipet, it was either decanted from the tube or removed by suction through a glass filter stick so that the solid phase could be sampled. The filter stick was necessary in most cases on the samples of high NaOH content since the solid phase did not settle compactly.

A satisfactory method of analyzing a solution for both cyanide and base was not found in the literature. Therefore, the analytical procedure for determining the composition of the solubility samples was established by carefully preparing four samples that varied from 5 to 45% of each compound. These samples were titrated first with 0.1 N $AgNO_3$ (Liebig's method) to determine the cyanide content; then the same aliquot was titrated with 0.1 N H_2SO_4, to determine the NaOH content. Phenol red was the indicator employed. It was found necessary to remove the cyanide ion from solution before analyzing for the base since HCN is formed and liberated in acid solution. The accuracy of the analytical procedure was very satisfactory, although in highly concentrated NaOH samples more dilution was required to give a satisfactory end-point for the cyanide analysis.

In the analysis of the solubility samples two to three-gram aliquots were taken from the liquid and from the wet solid. After diluting to 250-ml. volume, an aliquot of 25 or 50 ml., depending on the basicity, was used for the titration. Accordingly, the results were expressed in weight percentage. Schreinemaker's "Method of Wet Residues"[2] was used to determine the composition of the "dry salt." This method enables one to analyze the solid phase wet with the mother liquor.

Density values were determined on the mother liquor of several samples at each temperature. At 25 and 35°, they were determined with a simple Westphal balance to four significant figures. At 55°, a 10-ml. pipet was heated to 55° and filled with the supernatant liquid; then the tube was cooled to room temperature where the sample either solidified or became too viscous to flow from the pipet. The difference in the weights of the full and empty pipet, divided by ten, was the density in g./ml. Density values were not determined on samples of high NaOH content because of their viscosity.

Results and Discussion

A summary of the solubility data and density values are given for 25, 35 and 55° in Table I. These isotherms are plotted on trilinear diagrams,

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(1) Presented at the American Chemical Society Meeting, Chicago, Illinois, September, 1953.

(2) J. E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 323.

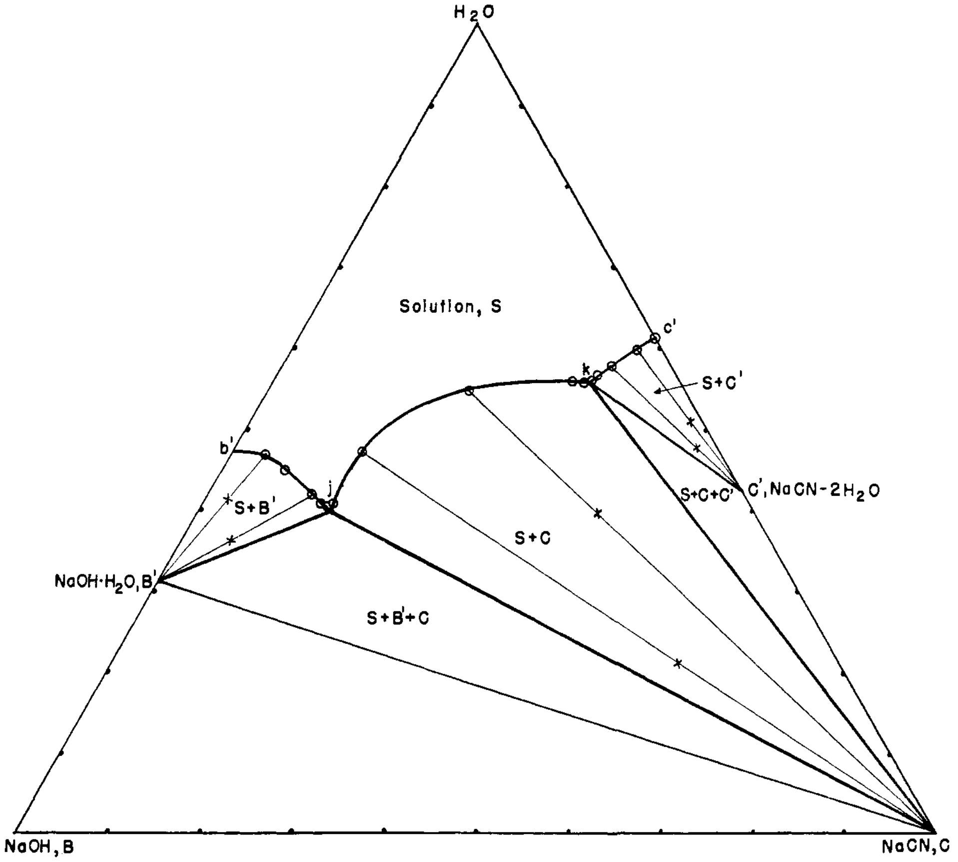

Fig. 1.—Isotherm for system NaCN–NaOH–H_2O at 25°; composition in wt. %.

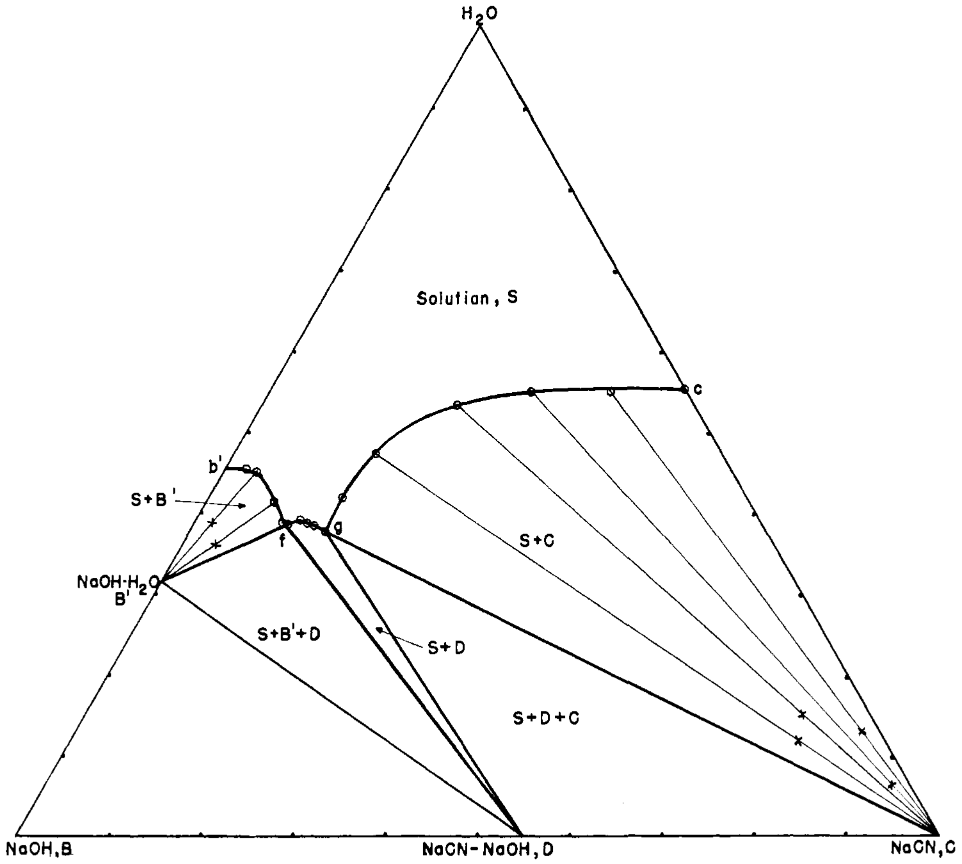

Fig. 2.—Isotherm for system NaCN–NaOH–H_2O at 35°; composition in wt. %.

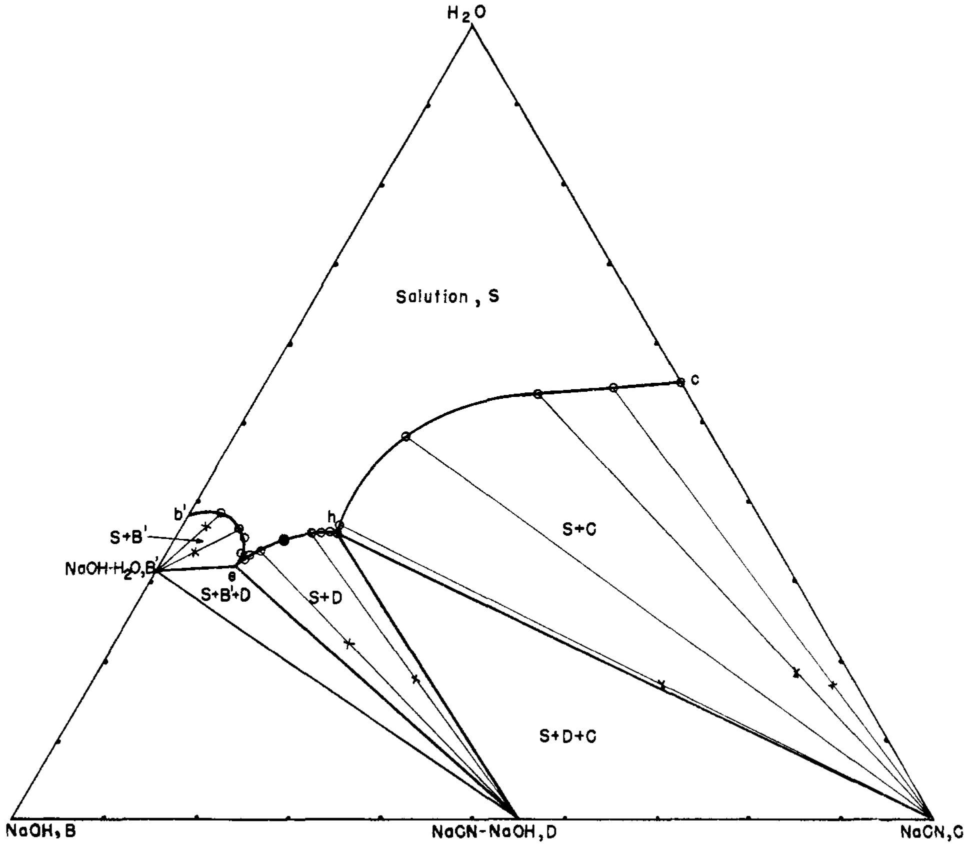

Fig. 3.—Isotherm for system NaCN–NaOH–H_2O at 55°; composition in wt. %.

Figs. 1, 2 and 3, to show effectively the lines of saturation, invariant points and solid phases formed.

TABLE I

TERNARY SYSTEM NaCN–NaOH–H_2O

Composition in wt. %					
Satd. liquid		Wet solid		Extrapolated dry solid	Density, g./ml.
NaCN	NaOH	NaCN	NaOH		
25° Isotherm					
38.8	0			$NaCN\cdot 2H_2O$	
37.8	2.5	48.2	1.2	$NaCN\cdot 2H_2O$	1.225
35.6	6.4	50.2	2.5	$NaCN\cdot 2H_2O$	1.255
34.5	8.9	46.2	4.4	$NaCN\cdot 2H_2O$	
35.5	9.5	45.5	5.2	$NaCN\cdot 2H_2O$	
33.7	10.2	79.0	3.6	NaCN	1.290
32.7	11.5	67.0	5.2	NaCN	
21.5	23.8	43.6	17.0	NaCN	1.370
14 1	38.7	61.3	17.0	NaCN	1.488
13.9	45.2	40.7	32.6	NaCN	1.548
13.2	46.2	9.9	52.0	$NaOH\cdot H_2O$	
12.8	46.5	11.7	48.6	$NaOH\cdot H_2O$	
11.0	46.8	4.8	58.8	$NaOH\cdot H_2O$	
6.7	48.2	5.3	52.7	$NaOH\cdot H_2O$	1.560
3.7	49.2	2.0	56.9	$NaOH\cdot H_2O$	
35° Isotherm					
45 0	0			NaCN	
37.2	8.2	85.3	1.7	NaCN	1.270
28.3	16.8	92.0	2.0	NaCN	1.312
21.5	25.6	77.8	7.8	NaCN	1.370
19.9	26.7	59.4	15.1	NaCN	1.379
15.5	37.5	79.0	9.0	NaCN	1.454
14.7	43.7	73.0	13.4	NaCN	1.508
14.9	47.3	49.9	28.4	NaCN	1 541
13.4	48.2	19	48	NaCN·NaOH	
12.5	49.0	26.0	48.4	NaCN·NaOH	
11.3	49.6	18.3	49	NaCN·NaOH	
10.6	51.6	3.6	62.8	$NaOH\cdot H_2O$	
10.3	51.8	4.4	62.5	$NaOH\cdot H_2O$	
7.6	51.5	3.4	60.5	$NaOH\cdot H_2O$	
6.5	52.5	3.7	60.2	$NaOH\cdot H_2O$	
3.7	51.6	1.7	59.3	$NaOH\cdot H_2O$	
2.4	52.3	1.3	63.5	$NaOH\cdot H_2O$	
0	55.0			$NaOH\cdot H_2O$	
55° Isotherm					
45.2	0				
38.1	7.6	81.4	2.4	NaCN	1.265
30.2	16.1	76.0	5.5	NaCN	
18.8	32.9			NaCN	1.433
17.1	45.9	62.0	20.8	NaCN	1.547
17.2	46.8	41.8	32.8	NaCN	
16.5	47.5	24.0	46.6	NaCN·NaOH	
15.8	48.5	34.0	46.5	NaCN·NaOH	
14.8	49.7	34.8	47.3	NaCN·NaOH	
12.6	52.6	32	48	NaCN·NaOH	
12.6	52.6	31.8	47.7	NaCN·NaOH	
10.3	56.0	25.7	52.3	NaCN·NaOH	1.623
9.4	57.4	25.9	52.0	NaCN·NaOH	
9.3	58.3	23.9	52.6	BaCN·NaOH	
9.0	58.5	16.1	56.5	NaCN·NaOH	
8.6	58.2	6.6	61.0	$NaOH\cdot H_2O$	
7.7	57.0			$NaOH\cdot H_2O$	
6.7	57.2	3.3	63.0	$NaOH\cdot H_2O$	
3.5	57.9	2.8	60.4	$NaOH\cdot H_2O$	
0	61.4			$NaOH\cdot H_2O$	

Some of the tie lines between each liquid phase point on the line of saturation and its respective wet solid phase point, x, have been omitted for clarity. However, boundary tie lines are given to separate isothermally invariant three phase regions from the two phase regions.

A new double compound, having an equimolecular composition of NaCN and NaOH, was found at 35 and 55° (see D in Figs. 2 and 3). As a consequence, there are two isothermally invariant points on each isotherm, e (9.0% NaCN, 59.0% NaOH) and h (17.0% NaCN, 47.0% NaOH) at 55°, and f (10.5% NaCN, 51.5% NaOH) and g (15.0% NaCN, 47.5% NaOH) at 35°. The range of existence of the compound is much wider at 55° than at 35°, and it vanishes somewhere between 35 and 25°. The double compound, NaCN·NaOH, has a retrograde effect on the solubility of $NaOH \cdot H_2O$ at 55° but not at 35°. Since the compound is incongruently saturating, it will decompose with the deposition of a single salt when added to water, and can never give a saturated solution lying within areas S + D. Solubility curves fg and eh of Figs. 2 and 3 were more difficult to obtain than the others because of the high viscosity of the caustic solutions and the nature of the solid phase. The solid phase, NaCN·NaOH, deposited as fine crystals which made the separation from the mother liquor very difficult; consequently, a greater scattering of tie lines around D prevailed. The dihydrate,[3] $NaCN \cdot 2H_2O$, is the stable solid below 34.7°; however, the anhydrous salt appears as a solid phase at 25° in NaOH concentrations above 10%. Thus, a caustic concentration greater than 10% prevents the formation of the dihydrate at 25°. The invariant points for the 25° isotherm are j (14.0% NaCN, 56.0% NaOH) and k (34.2% NaCN, 9.8% NaOH).

(3) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 1190.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

The Binary Systems $NaPO_3$–KPO_3 and $K_4P_2O_7$–KPO_3

BY GEORGE W. MOREY

RECEIVED APRIL 16, 1954

The phase equilibrium curves in the binary systems $NaPO_3$–KPO_3 and $K_4P_2O_7$–KPO_3 have been determined. In the system $NaPO_3$–KPO_3 a compound, $3NaPO_3 \cdot KPO_3$, is formed which melts incongruently at 552° to form crystalline $NaPO_3$ and a liquid containing 0.31 weight fraction KPO_3. $3NaPO_3 \cdot KPO_3$ is the stable crystalline phase from its incongruent melting point to its eutectic with KPO_3, at 547°, 0.505 weight fraction KPO_3. In the system $K_4P_2O_7$–KPO_3 a compound, $K_5P_3O_{10}$, is formed which melts incongruently at 641.5° to form crystalline $K_4P_2O_7$ and a liquid containing 0.54 weight fraction KPO_3. $K_5P_3O_{10}$ is the stable crystalline phase from its incongruent melting point to its eutectic with KPO_3, at 613°, 0.59 weight fraction KPO_3.

The two systems described in this paper are parts of a larger system, $Na_4P_2O_7$–$NaPO_3$–KPO_3–$K_4P_2O_7$, work on which has not yet been completed. The binary system $NaPO_3$–$Na_4P_2O_7$ was described by Partridge, Hicks and Smith[1] and by Morey and Ingerson,[2] and the binary system H_2O–$NaPO_3$ by Morey.[3]

These studies offered no difficulty. The components in the system $NaPO_3$–KPO_3 were easily made by heating recrystallized $NaH_2PO_4 \cdot H_2O$ or KH_2PO_4 until all the water was driven off. They were usually heated to above the melting point, then crystallized by heat treatment. Intermediate compositions were made by mixing weighed portions of the two end members, melting, powdering and remelting. The mixtures were all easily crystallized and all measurements in this system could be made by the quenching method,[4] often described from this Laboratory. All mixtures are easily quenched to glass, but pure KPO_3 requires rapid cooling. $K_4P_2O_7$ and mixtures rich in it cannot be quenched to a glass, and hence the heating curve method was used for it and for the mixture containing 0.18 weight fraction KPO_3 in the binary system $K_4P_2O_7$–KPO_3; the quenching method was used for the mixtures richer in KPO_3. Temperatures were measured by a platinum–platinum 10% rhodium thermocouple and a White potentiometer. The couples were standardized at the melting point of gold, 1092.6°; of NaCl, 800.4°[3]; of zinc, 419.4°; and were frequently checked at the incongruent melting point[2] of $Na_5P_3O_{10}$, 622°.

The phase equilibrium diagram for the binary system $NaPO_3$–KPO_3 shown in Fig. 1, is based on the quenching results of Table III. The optical properties of the compounds are given in Table I. Table II gives the X-ray spacings in ångström units as determined by my colleague J. L. England by the Debye–Scherrer powder method with a North American Philips high-angle Geiger counter goniometer, using copper Kα radiation and a nickel fil-

TABLE I

COMPOUNDS AND INVARIANT POINTS IN THE SYSTEM $NaPO_3$–KPO_3

$3NaPO_3 \cdot KPO_3 \rightleftarrows NaPO_3 + L$; $t = 552°$; $L = 0.31$ wt. fraction KPO_3. $3NaPO_3 \cdot KPO_3 + KPO_3 \rightleftarrows L$; $t = 547$; $L = 0.505$ wt. fraction KPO_3

Compound	Sign	2V	α	ω	β	ϵ	γ	M.p., °C.
$NaPO_3$	−	80°	1.474		1.478		1.480	627.6
$3NaPO_3 \cdot KPO_3$	−	40°	1.493		1.500		1.514	552.0
KPO_3	+			1.465		1.483		

(1) E. P. Partridge, V. Hicks and G. W. Smith, THIS JOURNAL, **63**, 454 (1941).

(2) G. W. Morey and E. Ingerson, *Am. J. Sci.*, **242**, 1 (1944).

(3) G. W. Morey, THIS JOURNAL, **75**, 5794 (1953).

(4) E. S. Shepherd and G. A. Rankin, *Am. J. Sci.*, **28**, 293 (1909); G. W. Morey, *J. Wash. Acad. Sci.*, **13**, 326 (1923); G. W. Morey and N. L. Bowen, *J. Phys. Chem.*, **28**, 1167 (1924).