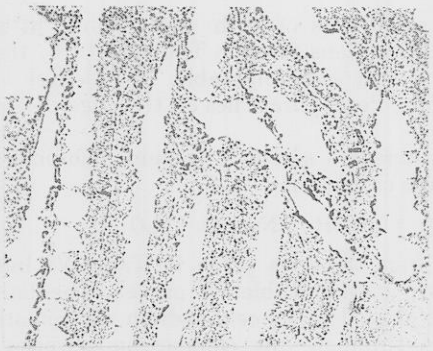

Figure 2. Microstructure of alloy containing 90% InBi–10% Sn, air cooled. Primary InBi (white) and eutectic. Etching solution: Vilella–Hydal (X100)

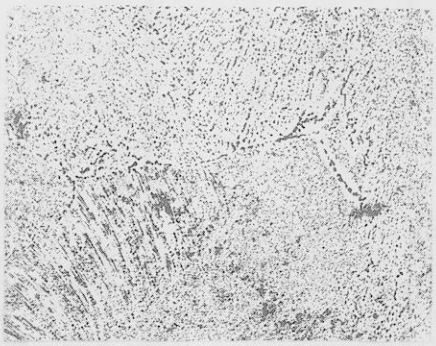

Figure 3. Microstructure of eutectic alloy: 83.7% InBi-16.3% Sn, air cooled. Etching solution: Vilella–Hydal (X 100)

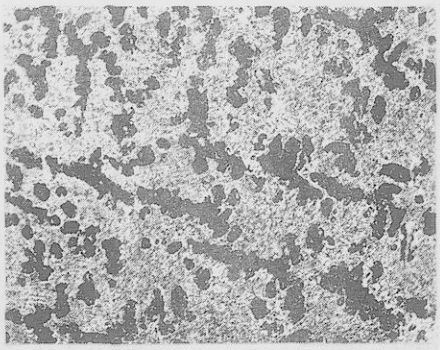

Figure 4. Photomicrograph of alloy containing 75% InBi–25% Sn, air cooled. Primary alpha (black) and eutectic. Etching solution: Vilella–Hydal (X150)

amined for the disappearance of the primary phase, approaching from both sides. Figures 2, 3, and 4 illustrate the different etching characteristics of the InBi and alpha phases. Figure 2 is a photomicrograph of an alloy which contains primary InBi and eutectic; Figure 3 is of the eutectic composition; and Figure 4 shows primary alpha and eutectic.

The solid solubility of Sn in InBi is so small that it could not be detected, but the solubility of InB is large—42% InBi at the eutectic temperature and 20% at 71° C.

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Phase Diagrams for the Na_2SO_4–$Na_2Cr_2O_7$–H_2O System

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Solubility data have been obtained for the Na_2SO_4–$Na_2Cr_2O_7$–H_2O system. Triangular phase diagrams have been plotted for a temperature range of 22.0 to 90° C. and a pH range of 2.0 to 10.0.

SOLUBILITY DATA have been obtained for sodium sulfate and sodium dichromate in water. This system was studied at temperatures from 22.0 to 90.0° C. and at pH's from 2.0 to 10.0. When the pH is increased above 7, sodium dichromate is converted to sodium chromate and the system is then one of chromate-sulfate and water.

EXPERIMENTAL PROCEDURES

Apparatus. Samples were allowed to reach equilibrium in a shaking, constant temperature bath. The bath was a Model 2156–1 temperature-controlled water bath shaker, manufactured by Research Specialties Co., Richmond, Calif.

Reagents. Mallinckrodt Analytical reagent grade sodium sulfate and sodium dichromate were used.

Sample Preparation and Sampling. Saturated solutions containing the salt used for the solid phase were placed in rubber-stoppered Erlenmeyer flasks and weighed quantities of the other salt and an excess of the solid phase salt were added. The flasks were placed in the bath. Mineral oil was used as the bath liquid, and the temperature was maintained at ±0.5° C.

After 3 days, aliquots were analyzed. Subsequently, aliquots were analyzed every two days until equilibrium was attained.

Chemical Analyses. The sodium sulfate was determined gravimetrically by precipitation as barium sulfate (*1*). Chromium (VI), which interferes with this method by precipitating out as barium chromate, was removed by reduction to chromium (III) with hydroxylamine hydrochloride in dilute hydrochloric acid. Chromium (III) is solube under the conditions used in precipitate barium sulfate.

The sodium dichromate was determined gravimetrically by precipitation as the chromium (III) oxide (*2*). The chromium (VI) was reduced to chromium (III) in acid solution with hydroxylamine hydrochloride. The hydrated oxide was precipitated on the addition of ammonium hydroxide and converted to the oxide by ignition at 850° C.

The degree of hydration of the solid phases was determined from the loss of weight incurred when the sample was heated to 110° C. for 2 hours. The samples were vacuum filtered and approximately 1 gram was spread on filter paper and blotted to remove adsorbed water. Sodium sulfate loses its water of hydration above 33° C. and sodium

dichromate loses its water of hydration above 85° C.

Adjustment of pH. The pH of a solution of sodium dichromate is about 3.4. Sulfuric acid was added to lower the pH and sodium hydroxide was added to increase the pH.

RESULTS

Table I to VII give the solubility data for the conditions of pH and temperature investigated. At temperatures above 32.4° C., the anhydrous salt is the only solid phase of sodium sulfate formed (3). The solid phase formed below 32.4° C. is the decahydrate. The phase diagram shown in Figure 1 and Table I is the only one that was obtained at a temperature less than 32.4° C. The calculated water of hydration for the decahydrate is 55.90%, and the average hydration found for the solid phase was 55.34%. The solid phase for the sample containing 6.70% sodium sulfate in solution was a mixture of the decahydrate and the anhydrous salt containing 5.35% water. The maximum amount of water found for the anhydrous solid phases given in Table I was 0.4% which probably results from incomplete removal of the adsorbed water. The solid phase for sodium dichromate is the dihydrate; calculated 12.08%, average found 11.87%.

The phase diagram shown in Figure 2 was plotted from the data in Table II, but it is representative of the data in Tables II to V, covering a pH range from 2.0 to 6.0 and a temperature range from 45.5° to 90° C. At temperatures above 32.4° C. and a pH lower than 7, the anhydrous sodium sulfate and the sodium dichromate dihydrate are the only salts formed. The solubilities of both salts change little with the changes in conditions given in Tables II to V; the phase diagrams are almost superimposable. The tie line to the sodium dichromate decahydrate lies on the edge of the diagram.

When the pH is increased above 7, sodium dichromate is converted to sodium chromate:

$$Na_2Cr_2O_7 + 2NaOH = 2Na_2CrO_4 + H_2O$$

Figure 3 is plotted from the data given in Table VI but is representative of the data in Table VII as well. The data were calculated and plotted as per cent sodium dichromate rather than sodium chromate for comparison purposes.

Table I. Solubility Data, pH 3.4, 22.0° C.

Wt., %		
Na_2SO_4	$Na_2Cr_2O_7$	Solid Phase
18.82	...	$Na_2SO_4 \cdot 10H_2O$
17.56	0.86	$Na_2SO_4 \cdot 10H_2O$
17.09	0.45	$Na_2SO_4 \cdot 10H_2O$
12.88	3.03	$Na_2SO_4 \cdot 10H_2O$
12.05	5.26	$Na_2SO_4 \cdot 10H_2O$
10.38	11.24	$Na_2SO_4 \cdot 10H_2O$
8.44	21.03	$Na_2SO_4 \cdot 10H_2O$
8.46	25.93	$Na_2SO_4 \cdot 10H_2O$
6.70	29.43	Mixture
7.51	32.37	Na_2SO_4
2.69	51.09	Na_2SO_4
2.50	53.29	Na_2SO_4
1.08	59.96	Na_2SO_4
0.67	63.09	$Na_2Cr_2O_7 \cdot 2H_2O$
0.65	64.34	$Na_2Cr_2O_7 \cdot 2H_2O$
...	65.23	$Na_2Cr_2O_7 \cdot 2H_2O$

Table II. Solubility Data, pH 3.4, 45.5° C.

Wt., %		
Na_2SO_4	$Na_2Cr_2O_7$	Solid Phase
31.58	...	Na_2SO_4
28.61	4.43	Na_2SO_4
23.61	9.73	Na_2SO_4
16.57	18.86	Na_2SO_4
6.05	34.74	Na_2SO_4
3.11	42.62	Na_2SO_4
2.04	48.32	Na_2SO_4
1.22	52.53	Na_2SO_4
0.36	57.97	Na_2SO_4
0.38	61.10	Na_2SO_4
0.62	63.92	Na_2SO_4
0.30	65.13	Na_2SO_4
0.50	69.53	Mixture
0.16	69.66	Mixture
...	69.70	$Na_2Cr_2O_7 \cdot 2H_2O$

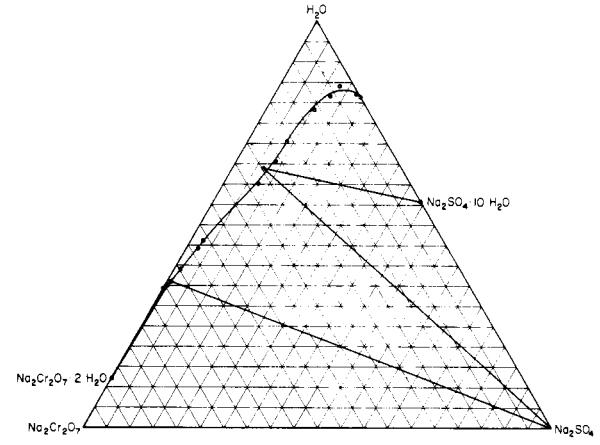

Figure 1. Phase diagram for the Na_2SO_4–$Na_2Cr_2O_7$–H_2O system at pH 3.4, 22.0° C.

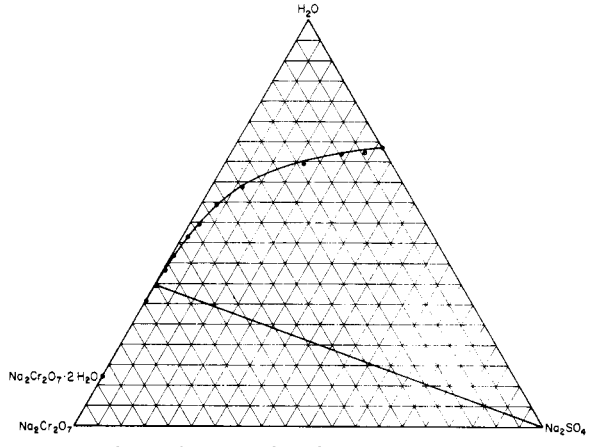

Figure 2. Phase diagram for the Na_2SO_4–$Na_2Cr_2O_7$–H_2O system at pH 3.4, 45.5° C.

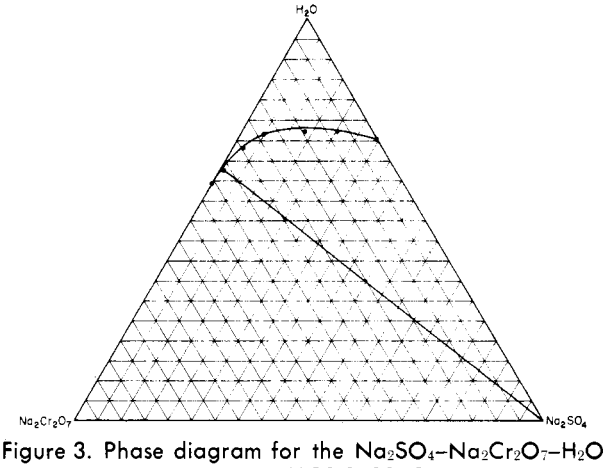

Figure 3. Phase diagram for the Na_2SO_4–$Na_2Cr_2O_7$–H_2O system at pH 10.0, 90° C.

Table III. Solubility Data, pH 2.0, 60.0° C.

Wt., %		
Na_2SO_4	$Na_2Cr_2O_7$	Solid Phase
31.64	...	Na_2SO_4
23.23	9.76	Na_2SO_4
17.74	18.29	Na_2SO_4
12.03	26.00	Na_2SO_4
10.94	27.49	Na_2SO_4
7.96	32.32	Na_2SO_4
6.68	33.70	Na_2SO_4
4.62	41.10	Na_2SO_4
3.12	45.37	Na_2SO_4
1.47	51.89	Na_2SO_4
...	72.41	$Na_2Cr_2O_7 \cdot 2H_2O$

Table IV. Solubility Data, pH 2.0, 90.0° C.

Wt., %		
Na_2SO_4	$Na_2Cr_2O_7$	Solid Phase
31.96	...	Na_2SO_4
20.52	12.21	Na_2SO_4
10.58	26.01	Na_2SO_4
7.25	36.79	Na_2SO_4
4.82	41.35	Na_2SO_4
2.79	49.94	Na_2SO_4
1.01	58.75	Na_2SO_4
0.66	60.06	Na_2SO_4
...	78.55	$Na_2Cr_2O_7 \cdot 2H_2O$

Table V. Solubility Data, pH 6.0, 90.0° C.

Wt., %		
Na_2SO_4	$Na_2Cr_2O_7$	Solid Phase
30.93	...	Na_2SO_4
11.12	26.15	Na_2SO_4
8.42	31.57	Na_2SO_4
0.85	58.92	Na_2SO_4
0.75	59.95	Na_2SO_4
0.68	70.41	Na_2SO_4
0.60	74.14	Na_2SO_4
...	81.17	$Na_2Cr_2O_7 \cdot 2H_2O$

The solid phases formed were the anhydrous sodium sulfate and the anhydrous sodium chromate.

CONCLUSIONS

Results of the investigation can be shown in three diagrams: temperature less than 32.4° C., pH less than 6.0; temperature between 32.4° and 90° C., pH less than 7.0; temperature above 32.4° C. and pH greater than 7.0.

When the temperature is between 32.4° C. and 90° C., and the pH is less than 6.0, the phase diagrams are almost identical. The changes in pH and temperature within this range have no effect. When the pH is raised to greater than 7.0, the sodium dichromate is converted to sodium chromate and again one phase diagram represents the conditions investigated. The change in pH from 6.0 to 8.0 changes the phase diagram. The solubility of the chromate and sulfate decreases with the increase in pH. Temperature changes above 32.4° C. within the two pH ranges, above and below pH 7.0 do not affect the solubilities. At temperatures above 32.4° C., the sodium sulfate solid phase is the anhydrous salt.

Table VI. Solubility Data, pH 10.0, 90.0° C.

Wt., %		
Na_2SO_4	$Na_2Cr_2O_7$	Solid Phase
29.95	...	Na_2SO_4
20.46	7.47	Na_2SO_4
13.40	14.29	Na_2SO_4
4.95	23.24	Na_2SO_4
2.04	29.80	Na_2SO_4
0.94	36.29	Na_2SO_4
...	40.72	Na_2CrO_4

Table VII. Solubility Data, pH 8.0, 90.0° C.

Wt., %		
Na_2SO_4	$Na_2Cr_2O_7$	Solid Phase
29.78	...	Na_2SO_4
21.85	7.72	Na_2SO_4
15.42	14.31	Na_2SO_4
9.34	18.72	Na_2SO_4
4.66	29.89	Na_2SO_4
2.38	34.92	Na_2SO_4
...	42.84	Na_2CrO_4

Only one set of conditions below 32.4° C. was investigated. Two sodium sulfate solid phases were observed, the anhydrous and the decahydrate. At low concentrations of dichromate, sulfate solubility was less than it was above 32.4° C. At higher concentrations of dichromate, the sulfate and dichromate sulubilities were about the same as those obtained above 32.4° C. when the pH was less than 7.

Temperature appears to control the $Na_2Cr_2O_7$–Na_2SO_4–H_2O system of 32.4° C. only. Solubilities change above and below this temperature. At temperatures above 32.4° C. the pH of the system controls the solubility changes taking place.

LITERATURE CITED

(1) Diehl, Harvey, Smith, G.F., "Quantitative Analysis," 1st. ed., pp. 106–110, John Wiley, New York, 1952.
(2) *Ibid.*, pp. 120–3.
(3) Glasstone, Samuel, "Textbook of Physical Chemistry," 2nd ed., pp. 773, 774, 804. D. van Nostrand, Inc., Princeton, N. J., 1946.

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