

species studied most thoroughly, only cowpeas are likely to have sufficiently high levels of tannin to be of concern in nutrition. However, all had less than half as much tannin as was found in two representative high-tannin sorghum hybrids. Of the other species studied, only the adzuki bean and black gram have potentially harmful levels of tannin. None of the four winged bean varieties contained tannin. The failure to detect tannin in a few varieties of some species in this survey must not lead to the assumption that all varieties are similarly tannin-free.

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The System $K_2O-P_2O_5-SO_3-H_2O$ at 25 °C

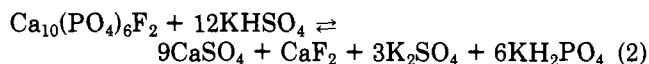
A. William Frazier

Measurements of solubility in the system $K_2O-P_2O_5-SO_3-H_2O$ at 25 °C showed that two major solubility zones are described by the double salts $K_4H_5(SO_4)_3PO_4$ and $K_2H_3SO_4PO_4$. These data indicate the most practical conditions for operation of a fertilizer process based on the acidulation of phosphate rock by potassium bisulfate.

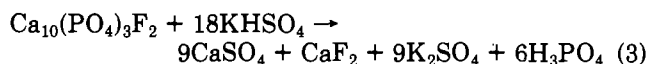
The fertilizer industry is continuing the search for the economical production of chlorine-free fertilizer materials containing all three primary plant nutrients. Combining some of the fertilizer processes now being used and some of the solvent purification processes being studied may permit the production of such fertilizers. The salt $KHSO_4$ can be produced at almost zero cost (Pennzoll, 1973) due to the value of anhydrous HCl recovered by the reaction



and presents numerous possibilities for the production of chloride-free fertilizers. The acidic nature of aqueous solutions of $KHSO_4$ can be used for the dissolution of phosphate rock according to the reaction



This reaction, however, will not go to completion due to the low level of acidity. A more favorable quantity of acid sulfate is indicated by the reaction



where the excess acid environment is sufficient to dissolve all the phosphate rock. Actually, a value between 12 and 18 mol of $KHSO_4$ appears at first to be indicated; however, the reaction is not this simple. It has been shown (d'Yvoire et al., 1963) that mixtures of K_2SO_4 and H_3PO_4 are not stable but react to form the solid phase $K_2H_3SO_4PO_4$ —similar to the ammonium analogue reported in another study (Frazier et al., 1971).

The evaluation of these reactions for the acidulation of phosphate rock has been hampered by inadequate knowledge of the acidic region in the phase system $K_2O-P_2O_5-SO_3-H_2O$ and the composition of the solid phases that control the maximum solution concentration. These solution compositions and solid phase characterizations have now been determined and are described below.

EXPERIMENTAL METHODS

The equilibrating mixtures for this study were prepared from reagent-grade orthophosphoric acid (60% P_2O_5) or superphosphoric acid (80% P_2O_5), sulfuric acid, potassium sulfate, potassium phosphate, and water. The solution compositions were adjusted so that three solid phases were present for the invariant point compositions, two solids for the tie-line compositions, and one solid phase at the system boundaries where the corresponding three-component systems are encountered. Optical microscopy was used to verify that the desired solid phases were present

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Table I. Solid Phases in the System $K_2O-P_2O_5-SO_3-H_2O$ at 25 °C

| compound | composition, wt % | | | | moles/mole of SO_3 | | |
|---|-------------------|--------|----------|---------------|----------------------|----------|--------|
| | K_2O | SO_3 | P_2O_5 | H_2O (diff) | K_2O | P_2O_5 | H_2O |
| $K_4H_5(SO_4)_3PO_4$ | | | | | | | |
| A | 34.3 | 43.1 | 14.1 | 8.4 | 0.677 | 0.184 | 0.866 |
| B | 34.9 | 45.4 | 12.2 | 7.5 | 0.654 | 0.151 | 0.734 |
| theoretical | 34.61 | 44.09 | 13.04 | 8.27 | 0.667 | 0.167 | 0.833 |
| $K_2H_3SO_4PO_4$ | | | | | | | |
| A | 34.4 | 29.4 | 26.1 | 10.1 | 0.996 | 0.500 | 1.580 |
| theoretical | 34.61 | 29.39 | 26.08 | 9.92 | 1.000 | 0.500 | 1.500 |
| $K_3H(SO_4)_2$ | | | | | | | |
| A | 45.3 | 51.3 | | 3.4 | 0.751 | | 0.294 |
| theoretical | 45.58 | 51.61 | | 2.90 | 0.750 | | 0.250 |
| $KHSO_4$ | | | | | | | |
| A | 34.4 | 58.3 | | 7.3 | 0.503 | | 0.556 |
| theoretical | 34.61 | 58.78 | | 6.61 | 0.500 | | 0.500 |
| $K_5H_3(SO_4)_7$ or $K_5H_3(SO_4)_4$ | | | | | | | |
| A | 37.7 | 55.4 | | 6.9 | 0.581 | | 0.553 |
| B | 37.8 | 55.7 | | 6.5 | 0.577 | | 0.518 |
| C | 37.1 | 55.6 | | 7.3 | 0.568 | | 0.406 |
| D | 37.2 | 55.4 | | 7.4 | 0.573 | | 0.587 |
| E | 36.7 | 55.4 | | 7.9 | 0.564 | | 0.437 |
| $K_5H_6(SO_4)_7$ theoretical | 38.03 | 56.52 | | 5.45 | 0.571 | | 0.429 |
| $K_5H_3(SO_4)_4$ theoretical | 40.43 | 54.94 | | 4.64 | 0.625 | | 0.375 |

Table II. Optical Properties of Solids from $K_2O-P_2O_5-SO_3-H_2O$ System at 25 °C^a

| interfacial | crystal system, class, and habit | refractive index | optical properties ^b |
|--------------------------------------|--|---|--|
| $K_4H_5(SO_4)_3PO_4$ | triclinic, 1, elongated tablets showing interfacial angles of 92°, 126°, and 144° with $N_f \Delta$ length = 29° | $\alpha = 1.446$ $\beta = 1.471$ $\gamma = 1.498$ | Bix (+), 2V = 89°, $d = 2.40$ |
| $K_2H_3SO_4PO_4$ | monoclinic, 2/m, (010) tablets modified by {011}, {111}, and {101} and elongated along a | $\alpha = 1.466$ $\beta = 1.475$ $\gamma = 1.512$ | Bix (+), 2V = 60° (53°), $Z = b$, OAP \perp (010), $Y \Delta a = 5^\circ$ in acute β , $\beta = 108^\circ$, $d = 2.41$ |
| $K_5H_3(SO_4)_4$ or $K_5H_6(SO_4)_7$ | monoclinic, 2/m, (001) rods elongated along a modified by {011}, {101}, and small {111} | $\alpha = 1.457$ $\beta = 1.459$ $\gamma = 1.478$ | Bix (+), 2V = 40° (36°), $X = b$, OAP \perp (010), $Y \Delta a = 20^\circ$ in obtuse β , $\beta = 102^\circ$, $d = 2.45$ |
| $K_3H(SO_4)_2$ | monoclinic, 2/m, plates tabular on (001) and modified by (101) and (101), (111), (111), (111), and (111); massive twinning on {110} and {310} resulting in hexagonal-shaped tablets comprising six twinned units | $\alpha = 1.482$ $\beta = 1.500$ $\gamma = 1.507$ | Bix (-), 2V = 70° (63°), $Z = b$, OAP \perp (010), $d = 2.65$ |

^a Optical data for the other compounds (not listed) agree with data reported by Winchell and Winchell (1964) and Frazier et al. (1972). ^b Values for 2V in parentheses are calculated. Densities are calculated by Gladstone-Dale equation (Larsen and Berman, 1934).

in each equilibrium cell before being rotated in a 25 ± 0.1 °C bath for 8–10 weeks.

The sulfate salts encountered were isolated and purified for chemical analysis, and the results are shown in Table I. The crystallographic and optical data were determined for those salts which have not been previously reported and are given in Table II.

After equilibration, the solid phases in each cell were again examined microscopically to confirm that the crystals of each phase were well-developed, fully faceted, and not in the process of dissolving. Also, the invariant points were replicated, and agreement was obtained before the chemical analysis of the liquid phases shown in Table III were accepted. These results are plotted in Figure 1 with respect to the $P_2O_5-SO_3-H_2O$ face of the four-component system; K_2O concentrations (in projection) are identified in Table III for the plotted composition points. Earlier results (Frazier et al., 1971) had shown that above 60% ($P_2O_5 + SO_3$) there is a rapid increase in condensed phosphate species with increasing anionic concentrations; thus, no attempt was made to define the limits for the $KHSO_4$ or $K_4H_5(SO_4)_3PO_4$ fields at higher P_2O_5 values. In

this region the data do not apply to a simple four-component phase system.

DISCUSSION OF RESULTS

The chemical analyses of well-crystallized, homogeneous, synthetic preparations of the sulfate compounds, when compared with the theoretical values for the idealized empirical formula, consistently showed K_2O values that were slightly lower by about 0.2–0.3%. The precision of these analytical results are presented here in relation to the discrepancy between our composition for the acid salt formed by $KHSO_4$ and $K_3H(SO_4)_2$ and that reported by Silber and Avinens (1963). The weight percent water was determined by subtracting the sum of the other oxides from 100 and cannot be used for comparison since this figure includes all errors and impurities. However, the other chemical data agree much better for the formula $K_5H_6(SO_4)_7$ than for $K_5H_3(SO_4)_4$. X-ray powder diffraction patterns show that the salt is the same as Silber's compound and he presents a good argument for the formula $K_5H_3(SO_4)_4$ which will be used for this report. Single crystal x-ray unit-cell data, when available, will prescribe

Table III. The System K₂O-P₂O₅-SO₃-H₂O at 25 °C

| chemical analysis, wt % | | | petrographic analysis, solids ^a |
|-------------------------|-----------------|-------------------------------|--|
| K ₂ O | SO ₃ | P ₂ O ₅ | |
| 11.7 | 3.1 | 24.1 | K ₂ S + KH ₂ P + K ₂ SP |
| 9.7 | 2.6 | 9.2 | K ₂ S + KH ₂ P |
| 7.5 | 3.4 | 5.1 | K ₂ S |
| 6.2 | 5.3 | | K ₂ S |
| 11.9 | 20.8 | | K ₂ S + K ₃ HS ₂ |
| 8.5 | 7.4 | 10.7 | K ₂ S + K ₂ SP |
| 11.5 | 18.4 | 5.1 | K ₂ S + K ₂ SP |
| 11.4 | 20.6 | 5.2 | K ₂ HS ₂ + K ₂ SP + K ₄ S ₃ P |
| 9.6 | 25.4 | 2.7 | K ₃ HS ₂ + K ₃ S ₄ + K ₄ S ₃ P |
| 11.9 | 26.3 | | K ₃ HS ₂ + K ₃ S ₄ |
| 6.7 | 25.9 | 4.5 | K ₅ S ₄ + KHS + K ₄ S ₃ P |
| 9.5 | 26.1 | 2.5 | K ₅ S ₄ + KHS |
| 9.7 | 26.8 | | K ₅ S ₄ + KHS |
| 3.0 | 10.2 | 42.7 | KHS + K ₂ S ₃ P |
| 2.8 | 11.6 | 41.5 | KHS + K ₄ S ₃ P |
| 2.2 | 16.6 | 31.3 | KHS + K ₄ S ₃ P |
| 2.3 | 5.8 | 52.7 | KHS + K ₄ S ₃ P |
| 12.8 | 0.6 | 46.5 | KH ₂ P + K ₄ SP + KH ₅ P ₂ |
| 9.1 | 1.2 | 10.3 | KH ₂ P |
| 6.9 | | 10.2 | KH ₂ P |
| 12.8 | | 47.2 | KH ₂ P + KH ₅ P ₂ |
| 11.6 | 0.5 | 41.3 | KH ₂ P + K ₂ SP |
| 7.4 | 1.5 | 52.8 | KH ₂ P ₂ + K ₂ SP |
| 9.0 | 4.4 | 57.3 | KH ₂ P ₂ + K ₂ SP + K ₄ S ₃ P |
| 3.8 | 7.7 | 39.3 | K ₂ SP + K ₄ S ₃ P |
| 7.6 | 16.9 | 10.6 | K ₂ SP + K ₄ S ₃ P |
| 4.4 | 11.9 | 22.7 | K ₂ SP + K ₄ S ₃ P |

^a K₂S = K₂SO₄; KH₂P = KH₂PO₄; K₂SP = K₂H₃SO₄PO₄; K₃HS₂ = K₃H(SO₄)₂; K₄S₃P = K₄H₃(SO₄)₃PO₄; K₅S₄ = K₅H₃(SO₄)₄; KHS = KHSO₄; KH₅P₂ = KH₅(PO₄)₂.

the correct composition.

The potassium system is much more complex than the ammonium system (Frazier et al., 1971). For example, two sulfate-phosphate double salts exist instead of one, the volume of the phase system controlled by these double salts is much larger, an extra potassium acid sulfate salt is involved, and the overall level of sulfate is much lower. However, similarities do exist with respect to the dissolution of 1 mol of phosphate rock by 16 mol of the acidic bisulfate to form the mixed sulfate-phosphate double salts which can be decomposed in methyl or ethyl alcohol to give solid K₂SO₄ and an alcoholic solution of H₃PO₄. These are

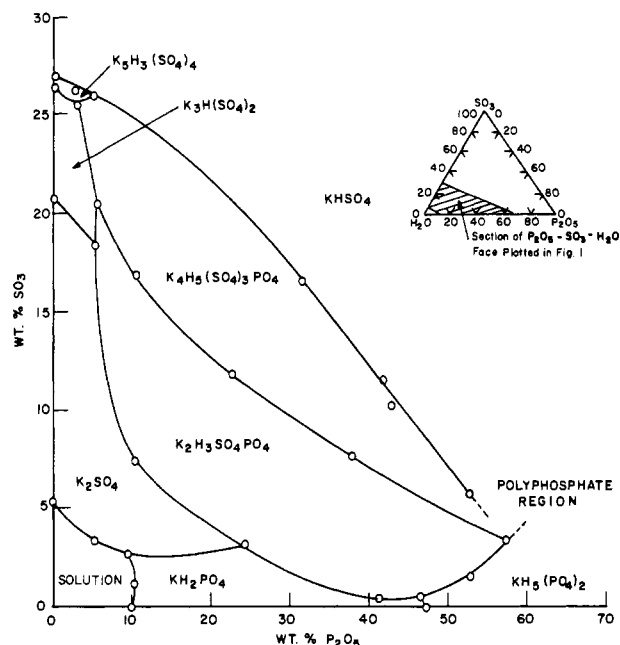


Figure 1. The system K₂O-P₂O₅-SO₃-H₂O at 25 °C projected on the (K₂O + H₂O)-P₂O₅-SO₃ face.

easily separated for application in numerous fertilizer processes as previously discussed.

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