
SOME CHEMICAL REACTIONS IN SILICA GELS: III.
FORMATION OF POTASSIUM ACID TARTARATE CRYSTALS¹

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ABSTRACT

This work was concerned with investigating methods for growing potassium acid tartrate (KHT) crystals by chemical reaction in acidic gels prepared with tartaric acid (H_2T) and sodium silicate and reacted with K^+ . H_2T ranging from 1N to 18N was used, and remarkable changes in size and perfection of shape of KHT crystals formed were noted as the concentration of H_2T was increased. Gels made with H_2T to 6N in strength permitted growth of mostly imperfect rhombohedra, some quite elongated and practically all veiled. Gels made with 8N, 10N, 15N, and 18N H_2T favored formation of clear, nonveiled, essentially perfectly shaped rhombohedra. KCl , KBr , KNO_3 , and K_2SO_4 appear equally useful as external reactants. KI permits growth of excellent crystals also, but forms HI , which reduces tartrate progressively to malate and succinate, releases I_2 , and produces an increasingly intense background color. K_2CrO_4 consumes tartrate in redox and prevents KHT formation. Potassium acetate causes gel cleavage and produces multitudes of clusters of tiny needles.

The purpose of this work was to study the growth of potassium acid tartrate by chemical reaction in silica gels and to establish reaction conditions which would

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favor the formation of the largest, clearest, and most perfectly shaped rhombohedral single crystals.

The formation of crystals of potassium acid tartrate in silica gels was described by Holmes (1917). He reported that when a gel, made from equal volumes of 1.16 sp gr sodium silicate and 3N tartaric acid, was covered with a dilute solution of a potassium salt, blocks 5 mm wide formed and ". . . in several hours crystals of notable size could be counted on. Changing the concentrations somewhat, wide-branching fern growths were obtained". Holmes' experiment was repeated, using four different 1.16 sp gr sodium silicates. In each instance, volunteer sodium acid tartrate crystals, $\text{NaHC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, formed in the gel before any external reactant was placed on the gel. All four gels contained axialities of $\text{NaHT} \cdot \text{H}_2\text{O}$. One gel contained free H_2T and no Na_2T ; the volunteer growths in it were unsymmetrical axialities. The three other gels contained no free H_2T and only small amounts of Na_2T ; in these, $\text{NaHT} \cdot \text{H}_2\text{O}$ crystals volunteered as symmetrical axialities. This acid salt formed also in other 3N tartaric acid 1.10 to 1.20 sp gr sodium silicate gels, but not in gels made with 1.08 or lower sp gr silicate solutions. Therefore, it is concluded that Holmes' figure of 1.16 for the specific gravity of his sodium silicate is a typographical error. This is understandable, because most of the gels he used were made with 1.06 sp gr silicate solutions. The shape, size, relative number, and distribution of the crystals of $\text{NaHT} \cdot \text{H}_2\text{O}$ which volunteer in gels made with 3N H_2T and six different N sodium silicate solutions ranging from 1.099 to 1.197 sp gr are shown in Figure 1.

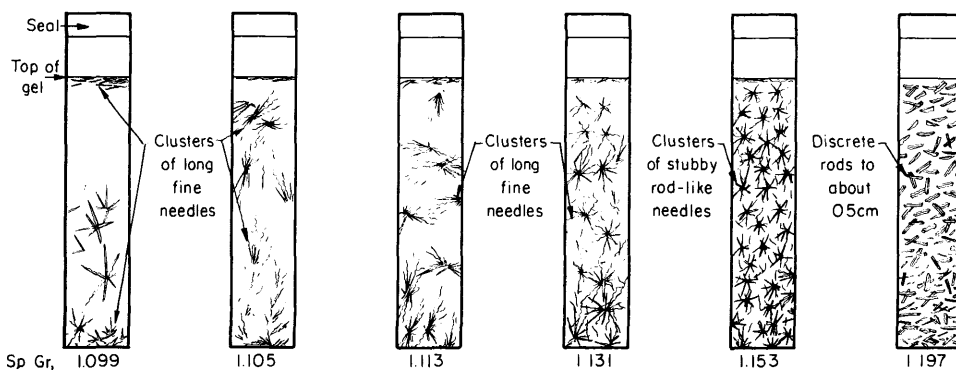


FIGURE 1. Location, Appearance, and Extent of Growth of $\text{NaHT} \cdot \text{H}_2\text{O}$ Crystal Volunteers in Silica Gels Prepared With 3N H_2T and N Sodium Silicate Solutions.

After the encounter with $\text{NaHT} \cdot \text{H}_2\text{O}$ volunteer crystals, the work was extended to include gels made with equal volumes of 1.039 to 1.083 sp gr sodium silicate solutions and 1 to 18N tartaric acid. The objective was to establish conditions which would limit nucleation and which would favor the growth of sizable, clear, essentially perfectly shaped crystals of potassium acid tartrate (KHT) in silica gels. After the gels had set, they were reacted with an excess of a potassium salt. The reaction with KCl as the external reactant is:



Only one of the gels in this series contained so little acid that tartrate (T^{2-}), as well as HT^- , was present; this was one made with 1N H_2T and 1.066 sp gr silicate. All reactions were carried out at 22 to 25°C.

Gels Made With 1N H_2T

In these, KHT forms almost exclusively as small, veiled rhombohedra when

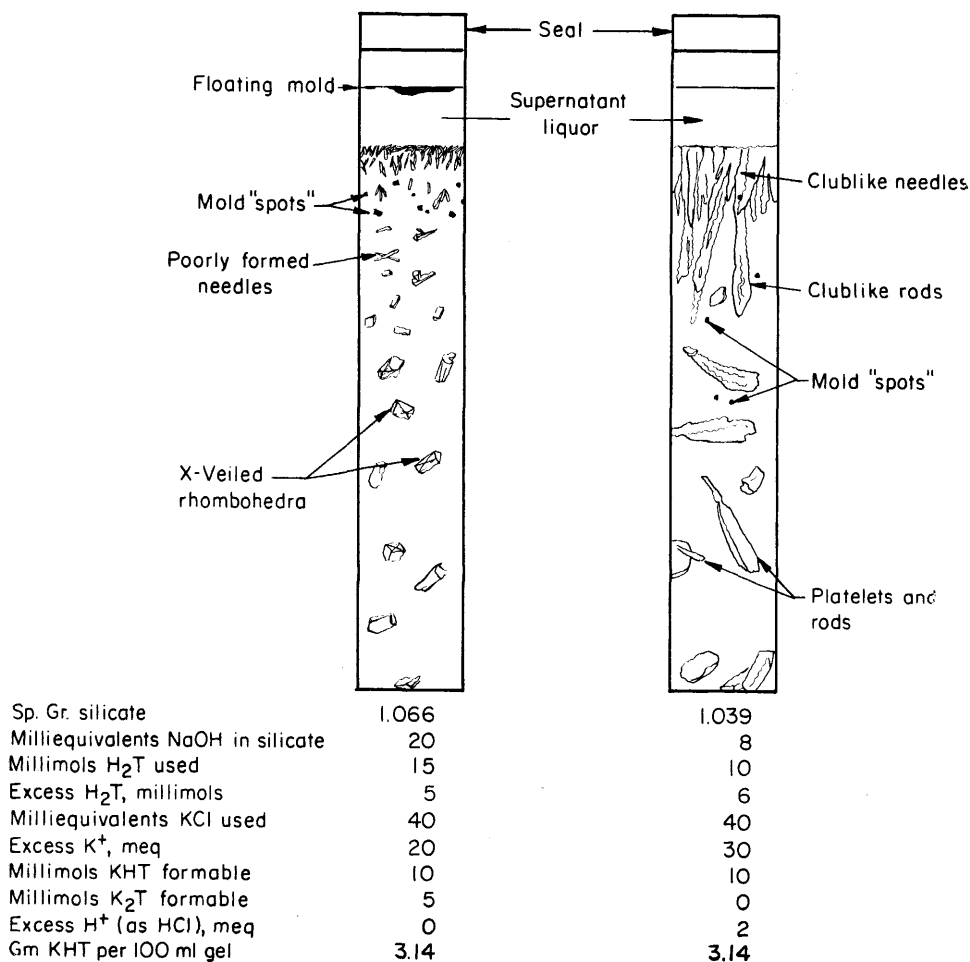


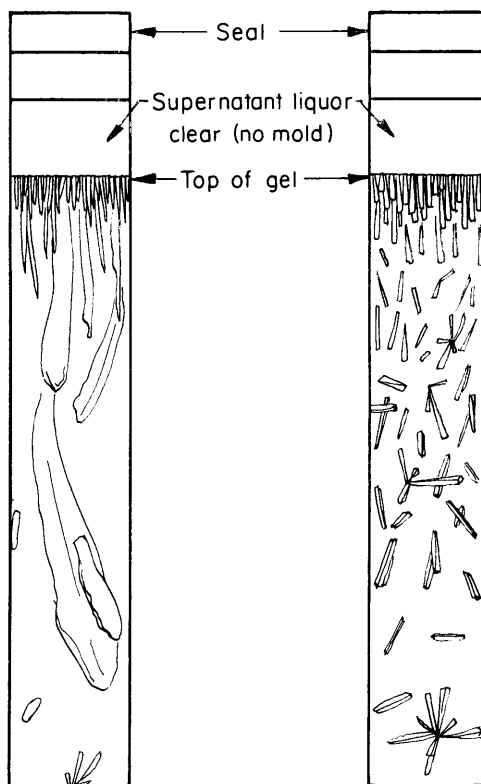
FIGURE 2. Comparison of Crystal Growths of KHT in Gels Made With N Silicate and 1N H₂T. Both Reacted With Excess KCl.

K₂T is present, but when K₂T is absent, KHT grows in long, flat imperfect rhombohedra. Figure 2 shows these formations.

Gels Made With 1.5N H₂T

Two gels were made with 1.5N H₂T and 1.066 sp gr N sodium silicate. One was reacted with KCl, the other with KI. Sufficient H⁺ is present in both systems to preclude the formation of K₂T. The gel reacted with KI and the supernatant liquor over it assumed a golden color. This results from oxidation of HI by tartrate (which is reduced progressively to malate, then to succinate) to form I₂, which is soluble since excess KI is present. The nature and distribution of the various crystal shapes and forms of KHT in these gels are similar to the growths depicted in Figure 2-2. In the top half of the gel, where the reaction to form KHT is relatively rapid, these growths take the forms of club-like needles, feathery in appearance and up to several cm in length. In the lower half of the gel, the KHT crystals are relatively flat, generally twinned, more or less veiled, imperfect

rhombohedra, some 2 to 3 cm long. Mold forms in the supernatant liquor and in small needle-cluster spots in the gel reacted with KCl, but not in the gel reacted with KI. Presumably I_2 , liberated by oxidation of HI, inhibits mold growth in the latter system.



K^+ salt used	KCl	K_2T
Sp. Gr. silicate	1.066	1.066
Milliequivalents NaOH in silicate	13.4	16
Millimols H_2T used	20	24
Excess H_2T , millimols	13.3	16
Milliequivalents K^+ salt used	50	50
Excess K^+ salt, meq	30	18
Millimols KHT formable	20	32
Excess H^+ , meq	6.6	0
Gm KHT per 100 ml gel	9.4	12.5
Gm K_2T per 100 ml gel	0	—

FIGURE 3. Crystal Formations of KHT in Gels Made with 2N H_2T and 1.066 sp gr N Silicate and Reacted With Excess KCl or K_2T .

Gels Made With 2N H_2T

Three gels were made with 2N H_2T and 1.066 sp gr N sodium silicate solution. One of these gels was reacted with KCl and contained in a 300-mm by 38-mm test tube which permitted the formation of long (to 15 cm), thin, club-like, rhombo-

hedral plates (fig. 4-1). The two other gels, each 48 ml in volume, were reacted, one with KCl and the other with K_2T . Figure 3 compares the growths of KHT in the initially identical gels. KHT crystals, shown in sketch 3-1, are essentially identical (except for length, which does not exceed 10 cm) to those grown in the 300-mm tube. When K_2T is the external reactant, the growths of KHT crystals are in parallel-sided rods, some clustered, as shown in sketch 3-2. It is believed that growth of KHT in rods and rod clusters occurs in the presence of Na_2T and K_2T . It was shown in an earlier section describing volunteer growths of $NaHT \cdot H_2O$ that the absence of H^+ and the presence of Na_2T enhance rod-like growths of the sodium analog of KHT (fig. 1-6).

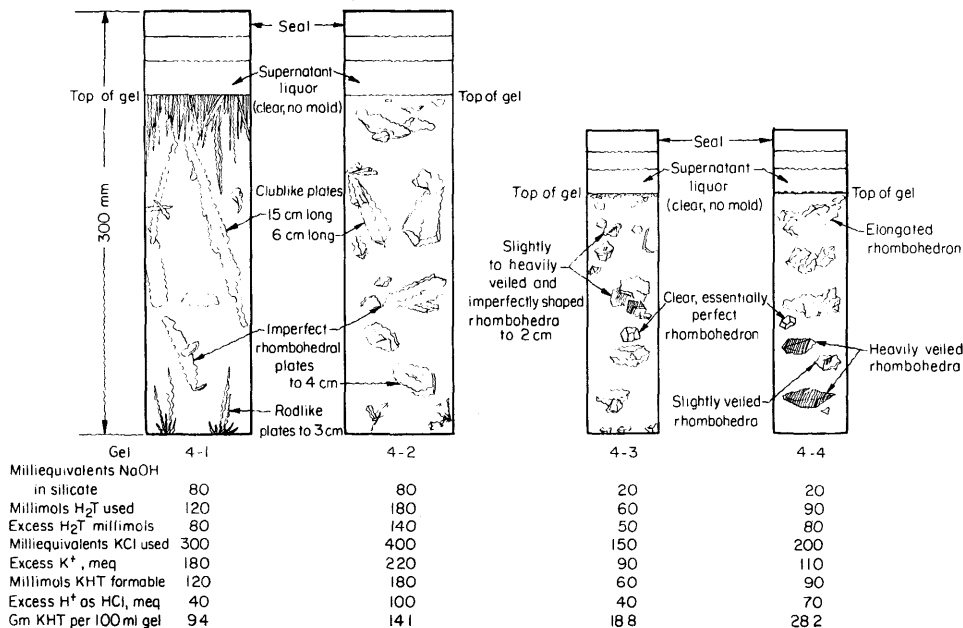


FIGURE 4. Crystal Formations of KHT in Gels Made With 2N, 3N, 4N, and 6N H_2T and 1.066 sp gr N Silicate and Reacted With Excess KCl.

Gels Made With 3N H_2T

Several gels were made with 3N tartaric acid and 1.039, 1.049, 1.066, or 1.083 sp gr N sodium silicate solutions for subsequent reaction with KCl to form KHT crystals. Typical of these was one of the gels made with 1.066 sp gr silicate and contained in a 300-mm test tube. In this gel, as shown in Figure 4-2, growths of KHT are thick club-like rods to 6 cm in length and imperfect rhombohedra some 4 and 5 cm in length. Increasing the strength of the H_2T influences crystal growth in two noteworthy ways, by substantially shortening the rhombohedral growths, and by increasing the thickness to approximately the width of the rhombohedra. In gels made with 2N, or weaker, H_2T , the long dimension of the crystals was many times the width, and the width was several times the thickness, except when K_2T , or K_2T and Na_2T , were present. Then the width and thickness of the crystals were approximately equal, but still much smaller than the length.

Another of the gels made with 3N H_2T and 1.066 sp gr was contained in a slant-necked, 1-liter jar. The jar was filled to the brim with gel-forming mixture. After the gel had set, the jar was inverted and supported so that its mouth was

below the surface of a saturated solution of KCl containing solid KCl. All of the crystals of KHT which grew in this gel were rod-like imperfect rhombohedra up to about 5 cm in length, diamond shaped in cross section, of about equal width and thickness, and substantially greater in length than in width. Distribution and orientation were random, though some of the crystals were clustered as radii from a common nucleus with the growth of the cluster in the same plane, thus differing from axialities where the growth was multiplanar.

Gels Made With 4N H₂T

The crystal formations of KHT which grew in a gel system prepared with 4N H₂T and 1.066 sp gr N silicate and reacted with excess KCl are shown in Figure 4-3. The crystals are all rhombohedral; most are more or less veiled and quite imperfect. One small (about 0.5 cm) rhombohedron which grew in the lower fourth of the gel appears to be entirely clear and essentially perfect in shape. Some of the rhombohedra in this system still have one pronouncedly long dimension; however, none of the crystals are club-like.

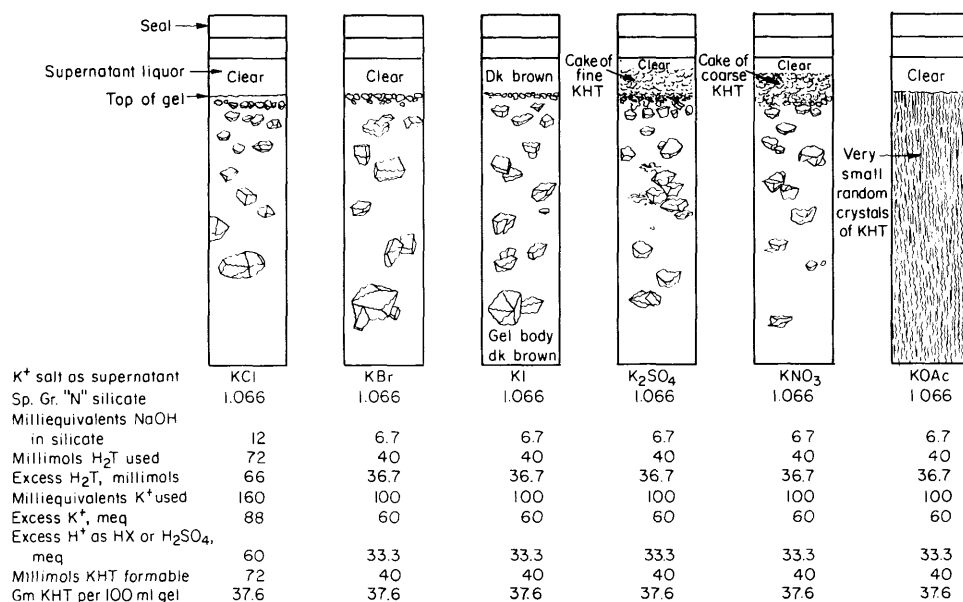


FIGURE 5. Crystal Formations of KHT in Gels Made With 8N H₂T and 1.066 sp gr N Silicate and Reacted With Six Different K⁺ Salts, Each in Excess.

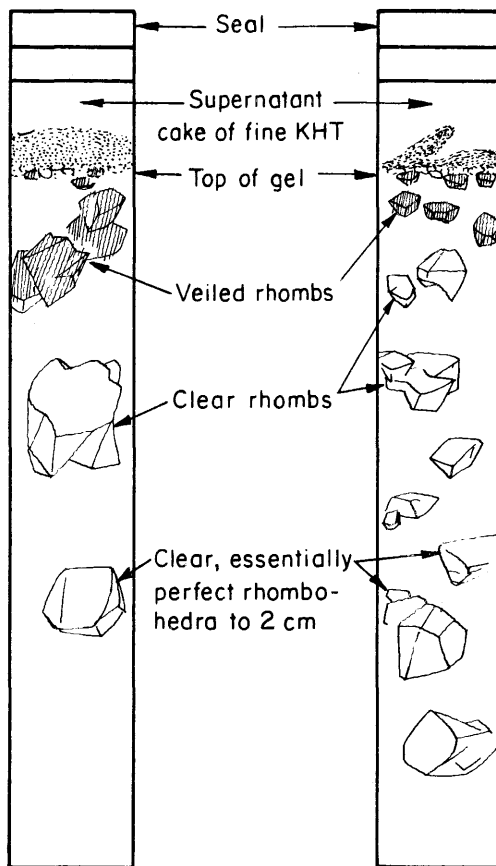
Gels Made With 6N H₂T

One gel made with equal volumes of 6N H₂T and 1.066 sp gr N sodium silicate was reacted with KCl. Figure 4-4 shows the resulting KHT crystals, which are all rhombohedral. One crystal is entirely clear and essentially perfectly shaped; several have only very small veil defects; a number are more or less heavily veiled. Only one of the imperfect rhombohedra is elongated; the rest generally have good rhombohedral shapes and their imperfections are veils or twinning.

Gels Made With 8N H₂T

Several gels were made with 8N H₂T: one each with 1.048 and 1.063 sp gr E silicate and the rest with 1.066 sp gr N silicate. All were reacted with excess K⁺, either as KCl, KBr, KI, K₂SO₄, KNO₃, KOAc (potassium acetate), or K₂CrO₄. Each salt was placed as a slurry in water over 20 ml of gel in a 150-mm test tube.

The resulting crystal formations are shown in Figure 5. Clear and veiled, essentially perfectly shaped rhombohedra of KHT ranging to 0.8 to 1.0 cm in size occur in five of the gels. In the gel reacted with KOAc, the gel cleaved in multiple "channels" from top to bottom after the supernatant reactant was placed on the gel. Consequently the growth of KHT was rapid and the formations were multitudinous, randomly channelled, very small white crystals. The reason for this cleavage of the gel by KOAc is not known. Similar cleavages of H₂T-N silicate

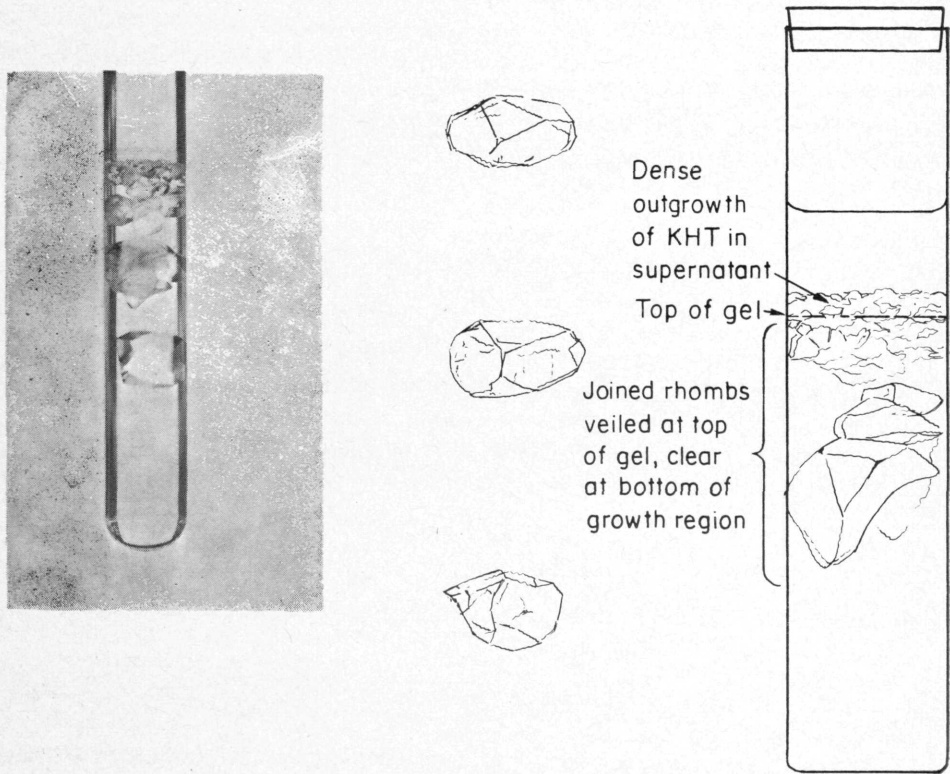


Sp. Gr. "N" silicate	1.039	1.066
Milliequivalents NaOH in silicate	8	20
Millimols H ₂ T used	100	150
Excess H ₂ T, millimols	96	140
Milliequivalents KCl used	200	360
Excess K ⁺ , meq	100	210
Excess H ⁺ as HCl, meq	92	130
Millimols KHT formable	100	150
Gm KHT per 100 ml gel	47	47

FIGURE 6. Formations of KHT Crystals in Gels Made With 10N H₂T and Two Concentrations of N Sodium Silicate and Reacted With Excess KCl.

gels have been noted when LiCl, NaCl, and NaI have been used as external reactants in other experiments.

The gel reacted with KI soon developed a pale yellow color which darkened progressively to a deep brown. This is caused by the oxidation of HI by tartrate



7-1

7-2

7-3

	<u>7-1 & 7-2</u>	<u>7-3</u>
	N	E
Silicate		
Sp. Gr. silicate	1.059	1.060
Milliequivalents NaOH in silicate	4.8	9
Millimols H ₂ T used	60	135
Excess H ⁺ T, millimols	57.6	130.5
Milliequivalents KCl used	75	150
Excess KCl, meq	15	15
Excess H ⁺ as HCl, meq	28.8	65.3
Millimols KHT formable	60	135
Gm KHT per 100 ml gel	56.3	67.5

FIGURE 7. Formations of KHT Crystals in Gels Made With 15N and 18N H₂T.

to form I_2 . Apparently I_2 has little or no oxidative effect on KHT, because the crystals of KHT do not change in size or appearance during the months when progressively more and more I_2 is liberated. This is in marked contrast to a H_2T -N silicate gel system which, when reacted with K_2CrO_4 , resulted in a redox forming Cr^{3+} (green). Also a gas (presumably CO_2), which formed lens-like cleavages in the gel, was generated from oxidation of the tartrate radical. Needless to say, no crystals of KHT formed in the gel reacted with K_2CrO_4 .

A gel made with 1.048 sp gr E silicate and 8N H_2T in a 300-mm test tube was reacted with excess KCl. All of the crystals' growths are rhombohedral. None has an elongated dimension. While most of the smaller rhombohedra near the top of the gel are veiled, most of the larger (1 to 2 cm) crystals in the middle of the gel and below are clear, veil-free, and essentially perfect in shape. Distortions appear in the shape of the clear rhombohedra only where the wall of the test tube interfered with crystal growth.

Gels Made With 10N H_2T

Two gels were made with equal volumes of 10N H_2T and N silicate. After gelling, both systems were reacted with excess KCl slurried in water. Figure 6 shows the rhombohedral shape of the crystal formations of KHT. In each gel are clear, essentially perfectly shaped rhombohedra, which range up to 2 cm in size. The concentration of silicate influenced the number of nucleation sites, but did not affect the size and distribution of the KHT crystals.

Gels Made With 15N H_2T

A gel made with 15N H_2T and 1.059 sp gr N sodium silicate was reacted with excess KCl. Figure 7-1 shows the crystal formations of KHT which grew in this gel. In the top half of the gel, which was like water in clarity, only veiled rhombohedra grew, probably because of the rapid rate of growth. However, in the lower half of the gel, only one rhombohedron grew, fully 1.5 cm in size, perfect in form and entirely clear. This rhombohedron is sketched in Figure 7-2.

Gels Made With 18N H_2T

A gel made with 18N H_2T and 1.060 sp gr E sodium silicate was reacted with excess KCl. Figure 7-3 shows that the growth of KHT included several rhombohedra which were clear and perfectly shaped, and one which was about 2 cm in size. There was also a growth of small, loose rhombohedra of KHT in the supernatant. In gels made with weaker H_2T , all of the KHT formed was in the gel body.

It has been shown that there is a progressive improvement in the shape, clarity, and rhombohedral perfection of the KHT crystals formed as the strength of the H_2T , used with 1.039 to 1.066 sp gr sodium silicate to prepare gels for subsequent reaction with K^+ , is increased from 1 N to 15N. It has been shown also that when 18N H_2T is used to prepare a gel, clear, perfectly shaped, rhombohedral crystals still are formed in the gel, but there is also a simultaneous growth of small KHT crystals in the supernatant liquor, suggesting that optimum conditions for in-gel growth have been passed in this system.

REFERENCES

- Holmes, H. N. 1917. The formation of crystals in gels. *J. Phys. Chem.* 21: 709-33.
———. 1917. The formation of crystals in gels. *J. Franklin Inst.* 184: 743-73.