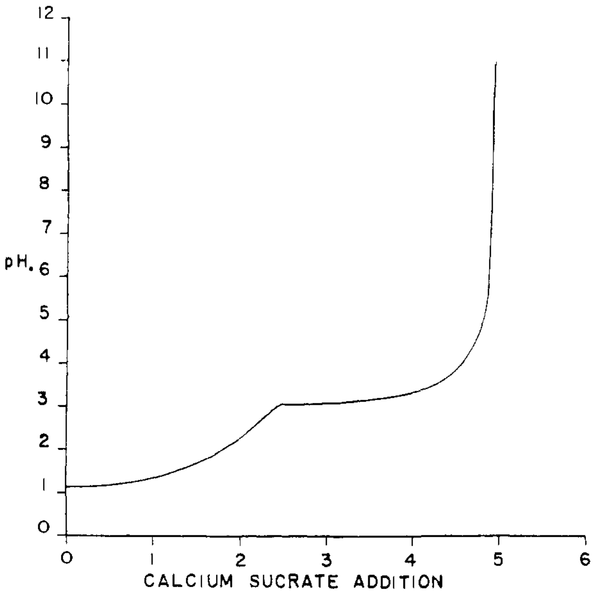

Fig. 1.—*p*H *vs.* neutralization of phosphoric acid by calcium sucrate, liters at 10°.

Prior to converting all the dicalcium phosphate to pyrophosphate, samples were taken for loss-on-ignition determinations at 900°. All samples were found to have a loss-on-ignition of 26.4%, and this is very close to the theoretical 26.2% for the reaction

$$2(CaHPO_4{\cdot}2H_2O) \longrightarrow Ca_2P_2O_7 + 5H_2O$$

It was concluded therefore that the dihydrate of dicalcium phosphate had been made by the reaction between the phosphoric acid and calcium sucrate.

Since pyrophosphate was used as the source of P_2O_5 in the preparation of mixtures for the phase study, chemical analyses were made of this compound rather than of the initial precipitate. Lime was determined by precipitating as calcium oxalate at *p*H 3 and titrating the precipitate dissolved in dilute sulfuric acid against permanganate. The filtrate and washings from the oxalate separation were used to determine the phosphorus. This determination involved a double precipitation of magnesium ammonium phosphate and finally weighing an ignited precipitate as magnesium pyrophosphate.

The calcium pyrophosphate stock used for making the phase study mixtures was found to be of exact stoichiometric composition, that is, 44.1% CaO, 55.9% P_2O_5. No sodium or alkali salts could be detected on a Beckman flame photometer (sensitive to 0.002% Na).

Experiments were carried out to check the effect of (a) temperature and (b) great excess calcium sucrate in the preparation of the dicalcium salt. To study these factors several runs were made in the manner described for the stock material, but varying appropriately the temperature or sucrate excess. Analyses were also made on the resulting products. The experimental results may be summarized as follows.

1. At temperatures up to 20° the neutralization of phosphoric acid proceeds to the second stage of hydrogen displacement only.
2. Above 20° neutralization begins to carry on to the third and final stage.
3. Dicalcium phosphate settles readily and is easily filtered. As soon as the third stage neutralization commences the mixed precipitate becomes gelatinous and difficult to filter.
4. Below 20° excess calcium sucrate does not appear to react appreciably with the precipitated dicalcium phosphate, even after two hours stirring.

In view of the purity of the calcium pyrophosphate obtained by the sucrate method it was considered worthwhile to investigate quantitatively some of its physical properties in order to evaluate data given in the literature.

The melting point determined by the Geophysical Laboratory quench method was found to be 1356 ± 2°. This figure is in excellent agreement with the 1353° given by Hill, *et al.*,[4] but is considerably higher than the figure of 1300° given by Trömel, *et al.*,[5] and Barrett and McCaughey.[3]

Hill, *et al.*,[4] state that calcium pyrophosphate transforms from the β- to α-form (*i.e.*, low to high temperature form) at 1140°, but Bale, *et al.*,[6] report a figure of 1270° for this inversion point. The experience of this investigation was that the transformation is extremely sluggish and that the β-form will not transform rapidly to the α until 1250°. Thus, whatever the true transformation temperature is, it would appear that temperatures in the region of 1250° are needed to bring about the transformation in a short period of, say, one hour. It was also noted that molten pyrophosphate had a tendency to supercool and then freeze rapidly to form the low temperature or β-modification.

The refractive indices of the α- and β-forms of pyrophosphate were determined under the petrographic microscope by immersing samples in various oils of known index. The data obtained are as follows and are in agreement with those given by Hill, *et al.*[4]

α-$Ca_2P_2O_7$: biaxial negative, $\alpha = 1.584$, $\gamma = 1.605$
β-$Ca_2P_2O_7$: uniaxial positive, $\omega = 1.630$, $\epsilon = 1.638$

The densities of the two forms were determined on a Berman torsion balance. The α-modification has a density of 2.88 g. per cc., and the β a density of 3.09 g. per cc., both taken at 25°.

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(4) W. L. Hill, G. T. Faust and D. S. Reynolds, *Am. J. Sc.*, **242**, 457, 542 (1944).

(5) G. Trömel, H. J. Harkort and W. Hotop, *Z. anorg. Chem.*, **256**, [6] 253 (1948).

(6) W. F. Bale, J. Bonner, H. C. Hodge, H. Adler, A. R. Wreath and R. Bell, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 491 (1945).

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Copolymer Composition Distribution[1]

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The differential composition distribution function for an ideal copolymer has been given by Wall.[2] The general case has been treated by Skeist using graphical methods which do not require that the instantaneous compositions be given by the copolymer equation 1.[3]

$$\frac{dm_1}{dm_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{M_1 + r_2 M_2} \tag{1}$$

where

m_1 and m_2 are instantaneous polymer mole fractions for species 1 and 2
M_1 and M_2 are instantaneous monomer mole fractions for species 1 and 2
r_1 and r_2 are the reactivity ratios for the more reactive and the less reactive monomers, respectively

The differential composition distribution function has not been given in explicit form for the general case.

For those cases in which the copolymer equation 1 is a valid description of instantaneous composition relationships this equation may be combined with the equation of Rayleigh 2[4] to give an explicit dif-

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(1) Financial assistance was received through the School of Engineering Research of the University of Toronto.

(2) F. T. Wall, This Journal, **63**, 1862 (1941).

(3) I. Skeist, *ibid.*, **68**, 1781 (1946).

(4) Lord Rayleigh, *Phil. Mag.*, **8**, 534 (1902).

ferential composition distribution function as shown in equation 3.

$$\frac{\mathrm{d}M}{M} = \frac{\mathrm{d}M_1}{m_1 - M_1} \qquad (2)$$

where M without subscript signifies total moles of both monomer components.

$$\frac{\mathrm{d}M}{M\,\mathrm{d}m_1} = -\frac{[M_1^2(r_1 + r_2 - 2) - 2M_1(r_2 - 1) + r_2]^3}{[M_1^2(r_1 - 2r_1r_2 + r_2) + 2M_1(r_1 - 1)r_2 + r_2]\,[(r_2 - 1) - (r_1 + r_2 - 2)M_1]M_1(1 - M_1)} \qquad (3)$$

Equation 3 may be used directly to evaluate differential composition distribution curves using as primary data initial and final monomer composition and degree of conversion. For those cases in which it is convenient to determine monomer composition by direct analysis, the degree of conversion may be obtained from the integral composition distribution equation 4.

$$\log\frac{M^0}{M} = \frac{r_2}{1 - r_2}\log\frac{M_1^0}{M_1} + \frac{r_1}{1 - r_1}\log\frac{M_2^0}{M_2} - \frac{1 - r_1r_2}{(1 - r_1)(1 - r_2)}\log\left\{\frac{[2 - r_1 - r_2]M_1^0 + r_2 - 1}{[2 - r_1 - r_2]M_1 + r_2 - 1}\right\} \qquad (4)$$

where superscript ^{0} signifies initial composition or initial total moles of both monomer components.

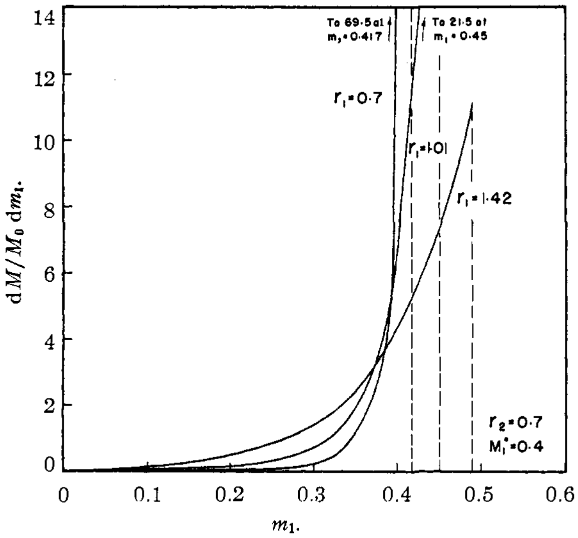

Fig. 1.—Copolymer composition distribution functions for $r_2 > 0.5$.

Equation 4 is similar to the integrated copolymer equation given by Mayo and Lewis.[5]

Combination of equations 3 and 4 gives equation 5.

$$\frac{\mathrm{d}M}{M^0\,\mathrm{d}m_1} = -\left(\frac{M_1^0}{M_1}\right)^{r_2/(r_2-1)}\left(\frac{1 - M_1^0}{1 - M_1}\right)^{r_1/(r_1-1)}\left(\frac{\frac{r_2 - 1}{r_1 + r_2 - 2} - M_1^0}{\frac{r_2 - 1}{r_1 + r_2 - 2} - M_1}\right)^{\frac{1-r_1r_2}{(1-r_1)(1-r_2)}} \times \frac{[M_1^2(r_1 + r_2 - 2) - 2M_1(r_2 - 1) + r_2]^3}{[M_1^2(r_1 - 2r_1r_2 + r_2) + 2M_1(r_1 - 1)r_2 + r_2][(r_2 - 1) - (r_1 + r_2 - 2)M_1]M_1(1 - M_1)} \qquad (5)$$

The equation given by Wall[2] can be derived from equation 5 for the ideal case when $r_1 = 1/r_2$.

For the condition $r_1 = 1/r_2$ Wall has shown that the value of $r_2 = 0.5$ is a critical value for the copolymer composition distribution function at $m_1 \rightarrow 0$. Equation 5 permits the extension of this conclusion to include copolymerizations for which $r_1 \neq 1/r_2$. The value $r_2 = 0.5$ for the less reactive monomer is critical without regard to the value of r_1.

If $r_2 > 0.5$ a differential polymer composition distribution function is obtained which approaches zero as m_1 approaches zero. As shown in Fig. 1 the value of r_1 has a considerable effect on the distribution curves but the intercept is in all cases zero.

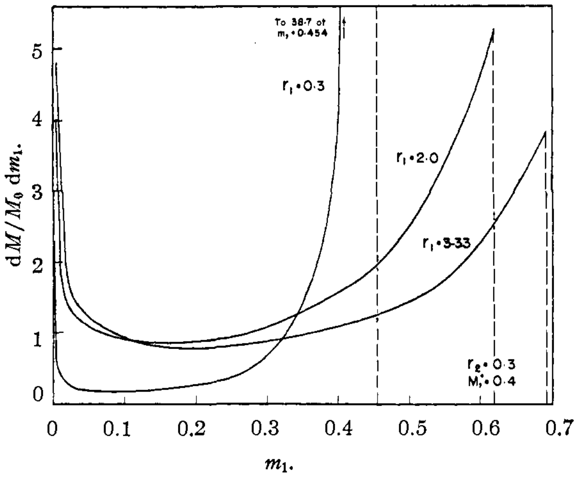

Fig. 2.—Copolymer composition distribution functions for $r_2 < 0.5$.

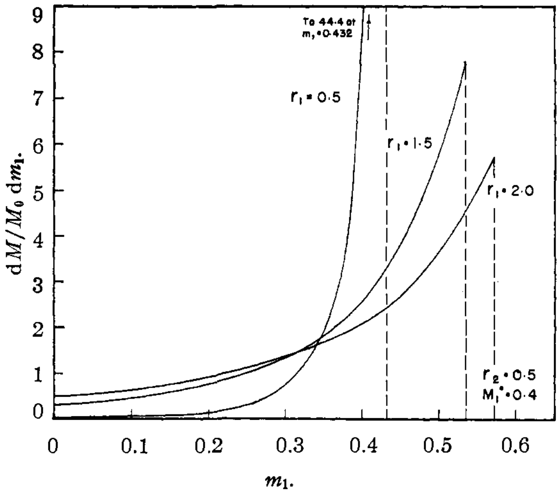

Fig. 3.—Copolymer composition distribution function for $r_2 = 0.5$.

For $r_2 < 0.5$ the function becomes very large as m_1 approaches zero. This conclusion is independent of the value of r_1 but it may be seen that the fraction of the copolymer which is composed of ap-

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(5) F. R. Mayo and F. M. Lewis, THIS JOURNAL, 66, 1594 (1944).

proximately pure monomer 2 is greatly dependent on the value of r_1.

The values obtained for the function when $r_2 = 0.5$ precisely are shown in Fig. 3. These composition distributions are of little practical significance since r_2 values only slightly greater or less than 0.5 result in functions of the form shown in Figs. 1 and 2, respectively.

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The Dimeric Nature and Crystallographic Unit Cell of Ammonium 6-Molybdochromiate[1]

BY C. WROE WOLFE, MURRY L. BLOCK
AND LOUIS C. W. BAKER[2]

RECEIVED OCTOBER 21, 1954

Elsewhere in this issue[3] a detailed argument, based on chemical evidence, is presented concerning the formulas and structures of the isomorphous heteropoly 6-molybdate anions of trivalent Cr, Fe, Co and Al. The formula therein proposed for these anions is $[(XO_6Mo_6O_{15})_n]^{-3n}$, where X represents the trivalent atom and n is an undetermined integer which is probably small.

The structural argument[3] makes it clear that a monomeric formula is extremely improbable. The crystallographic evidence described below shows that there are two empirical formulas per simplest crystallographic unit cell in the ammonium salt of the chromic complex. Therefore, $n = 2$; and the correct formula for the compound is $(NH_4)_6[(CrO_6Mo_6O_{15})_2]\cdot 20H_2O$.

Isomorphism of this Cr compound with the corresponding Fe, Co and Al compounds was previously strongly indicated by chemical evidence[3] and mixed crystal formation.[4] It is further supported by our observation that the powder X-ray patterns of the four salts are extremely similar.[1]

The results described below lend further strong support to the structure which was postulated previously[3] for these anions, because the unit cell is of appropriate size and shape to contain that specific structure.

Experimental

Samples of the ammonium salts of the Cr, Fe, Co and Al complexes were prepared[1,3] and analyzed.

Anal. Calcd. for $(NH_4)_6[(CrO_6Mo_6O_{15})_2]\cdot 20H_2O$: Mo, 48.1; Cr, 4.35; N, 3.52. Found: Mo, 48.2; Cr, 4.39; N, 3.68. The analytical results for the other salts were equally satisfactory.

Pycnometer densities of powdered samples of the salts were found to be: (av. in g./cc.) Cr cpd., 2.866; Fe cpd., 2.874; Co cpd., 2.878; and Al cpd., 2.767.

The pure Fe and Al compounds were obtained only as microcrystalline precipitates. Bigger crystals of the Cr and Co compounds may be grown, and a number of attempts were made to obtain material suitable for complete single crystal work. However, these crystals tend to develop well in two crystallographic directions while the development in the third direction is less satisfactory. The net result of this circumstance is that one of the crystallographic angles (β^*) could be determined only by indirect calculation. Doubt is not cast on the value obtained for the volume and content of the unit cell, however, because this volume was calculated from appropriate simultaneous equations[5] which do not utilize β^*

$$V = \frac{d_{100}d_{010}c_0}{\sin\gamma^*} \quad \text{and} \quad V = \frac{d_{001}d_{010}a_0}{\sin\alpha^*}$$

In appearance, the crystals of the chromic compound are small, flat rhombs. They proved to be triclinic. Rotation and zero and first layer line X-ray diffraction photographs were taken about the short diagonal of the rhombic platey face, about the long diagonal of this face, and about one of the edges. The results are summarized in Table I.

Although the simplest crystallographic unit cell contains two empirical formulas, it was found more convenient, for purposes of crystallographic calculation, to consider a body-centered triclinic unit cell containing four empirical formulas. The results given below in Table I are in terms of this larger body-centered cell rather than the smallest crystallographic unit cell.

TABLE I

CRYSTALLOGRAPHIC DATA FOR AMMONIUM 6-MOLYBDOCHROMIATE

Crystal system, triclinic; space group, $I\bar{1}$
a_0 = 12.0 Å. = periodicity of acute bisectrix
c_0 = 10.8 Å. = periodicity of obtuse bisectrix
D_{100} = D of acute bisectrix = 11.8 Å.
D_{010} = D of platey direction = 21.2 Å.
D_{001} = D of obtuse bisectrix = 10.7 Å.
α^* = 85°32′ = angle between 010 and 001
β^* = approx. 90° = angle between 100 and 001[6]
γ^* = 77°04′ = angle between 010 and 100
Av. vol. of body-centered unit cell = 2760 ± 15 Å.^{3}
Mol. wt. of body-centered unit cell = 4765
No. of empirical formula units per body-centered cell = 3.98
No. of empirical formula units per simplest crystallographic unit cell = 1.99

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[1] Abstracted from portions of a thesis, presented by Murry L. Block to the Graduate School of Boston University in partial fulfillment of the requirements for the A.M. degree in chemistry.

[2] Addressee for reprint requests.

[3] L. C. W. Baker, G. Foster, W. Tan, F. Scholnick and T. P. McCutcheon, THIS JOURNAL, **77**, 2136 (1955).

[4] G. A. Barbieri, *Atti. Acad. Lincei*, [5], **23i**, 338 (1914).

[5] C. W. Wolfe, *Am. Mineralogist*, **26**, 134 (1941).

[6] The value of β^* was calculated by using the relationship

$$V^* = a^*b^*c^* \times \sqrt{1 - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^* + 2\cos\alpha^*\cos\beta^*\cos\gamma^*}$$

wherein

$$V^* = \frac{1}{V},\ a^* = \frac{1}{d_{100}},\ b^* = \frac{1}{d_{010}},\ \text{and}\ c^* = \frac{1}{d_{001}}.$$

Body-centered unit cell volumes below 2750.5 Å.^{3} give imaginary values for β^*. When the volume employed is 2750.53 Å.^{3}, β^* = 90°00′. The largest cell volume ever indicated by any of the experimental measurements was 2767 Å.^{3}, for which β^* may be either 82°47′ or 95°14′. The best experimental results and the majority of the results give values for β^* which are very much closer to 90°.