

THE SELECTIVE REFLECTION OF ORTHO-, META- AND PYRO-PHOSPHATES IN THE INFRA-RED SPECTRUM.

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IT is well known that the reflecting power of certain non-metallic substances varies widely in different parts of the infra-red spectrum. For example, the reflecting power of quartz¹ is practically zero for radiations of wave-length 7.4μ and rises abruptly to 75 per cent. at 8.45μ . The work of Coblentz² and Morse³ shows that not only may carbonates, nitrates and sulphates be distinguished from each other by their selective reflection alone, but also that of the salts of any one acid, those with the heavier bases may in general be separated from those with the lighter, the valence of the bases being the same in all. There was little evidence on salts having a common acid-forming element to show either the effect of a change in the valence of the base, or the effect of a change in the ratio of the weight of the acid forming element to the weight of oxygen combined with it in the acid radical. The series of substances which seemed best adapted to a study of these effects were not obtainable in a form suitable for examination by the usual methods. This paper describes a method by which one may obtain an indication of the selective reflection characteristic of those salts which cannot be had in large crystals. This method has been applied to the examination of sixteen of the ortho-, meta- and pyro-phosphates, and the results are given in the following pages.

PREPARATION OF SURFACES.

A large number of the phosphates were obtainable only in the form of powder precipitates. A few were in the form of minute crystals and one only, sodium meta-phosphate, in a solid mass. On this last a surface large enough for the purpose was polished by rubbing on a surface of ground plate glass. Since the melting point of most phosphates is very high it was impracticable to melt them into solid cakes. The possibility of obtaining reflecting surfaces by the compression of powders was first suggested by Mr. Eimer, of Eimer and Amend, and the practical details of the following process were devised by Dr. E. F. Nichols and Dr. W. S.

¹ *PHYS. REV.*, 1897.² *Investigations of Infra-red Spectrum*, Parts III. and IV., 1906; V., 1908.³ *Astrophysical Journal*, 26, p. 225, 1907.

Day. In Fig. 1, *B* represents a block of hardened and polished steel to which the steel rings, *C* and *C'*, could be tightly screwed. *A* is a steel piston, which slips easily in the rings. The ring *C* contains the powder to be pressed and *C'* acts merely as a guide for the piston. The steel block was ground with emery and water and polished till the top had a fine mirror surface. The rings having been screwed to the block, the

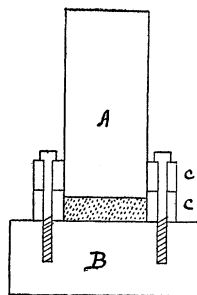


Fig. 1.

lower one, *C*, was filled with the powdered salt and the piston inserted on top of the powder. The piston head was then subjected to a pressure of 42,000 to 52,000 pounds per square inch.¹ After releasing the pressure and withdrawing the piston the steel block was carefully separated from the rings, leaving in the lower ring a solid cake of the compressed powder which sometimes had a very brilliant mirror surface copied from the surface of the polished steel block. In some cases a better surface could be formed by forcing the cake out of

the ring and carefully polishing it in the ordinary way. The salts used were obtained as free from water as possible. To drive off any moisture which might be held in the precipitates and in the case of Na_3PO_4 , to drive off water of crystallization, the substances were heated over a sand-bath. Unless the powder were very fine it was ground in a mortar and after drying was sifted through graded sieves. The finest powder, that passing the 200 per inch mesh, was put in the rings first, that it might form the surface and the coarser parts were used for the main bulk of the cake. When only a small quantity of substance was available it was put in the ring first and the rest of the cake made of a different substance. Only three of the substances used showed any crystalline structure even under the high power microscope. Of these Na_3PO_4 lost its crystalline form with the water of crystallization. The other two, $\text{Zn}_3(\text{PO}_4)_2$ and KPO_3 remained unchanged when heated.

The surfaces obtained by pressure against a plane surface in this way were rather convex, probably a result of the bulging of the powder after the pressure was removed. Sometimes the cake cracked, due to the strain. As most of the pressed cakes of the phosphates were not hard enough to be ground plane and polished, an effort was made to reduce the convexity by pressing on a slightly convex steel surface. But as no two surfaces had the same convexity even when the same pressure was used it was impossible to predict just what curvature would result in any

¹ The pressures were obtained at first by the use of the testing machine in the mechanical engineering laboratories through the kindness of Professor Ira H. Woolson and Mr. J. S. Macgregor. Later a hydraulic press was used in the physics laboratory.

given case or to wholly correct it. With these curved surfaces the absolute reflecting power was not obtained. But since other conditions made it impossible and as relative values answer our purpose this lack of planeness was not very important. Also the collecting mirrors used in the examination were large enough to receive the beam even if its divergence were slightly increased by the curvature of the salt's surface. Approximately absolute values might at any time be obtained by determining the values at a few wave-lengths distributed along the spectrum and deducing the whole reflection curve from the relative values at the selected wave-lengths. The cakes of the various substance when pressed differed much in appearance and structure. Aluminum and magnesium phosphates, AlPO_3 and $\text{Mg}_3(\text{PO}_4)_2$, for example, in the form of white powder looked alike. After pressing, the AlPO_4 had the appearance of fine white porcelain and was brittle and chipped off in layers like slate, and the surface was very brilliant. But $\text{Mg}_3(\text{PO}_4)_2$ gave a dull surface and showed no pronounced structure.

GENERAL PLAN OF APPARATUS.

The mirror M (Fig. 2) forms an image of the source, N , on the reflecting surface under examination at S . The reflected beam is brought to a focus by the mirror M_2 on the collimator slit C of spectrometer. After passing the slit the beam is rendered parallel by the spectrometer mirror, M_3 , and is then resolved by the prism P , and reflected by the plane mirror M_4 . The portion of the spectrum falling on the second spectrometer mirror M_5 is brought to a focus on the slit, T , which replaces the usual cross wires of the observing telescope of the spectrometer. The energy passing through the slit falls upon the concave mirror, M_6 , and is concentrated on the vane of the radiometer, R .

There are several reasons for forming an image of the source N on the reflecting surface S . In the first place the adjustments are more easily made. Secondly, a smaller surface may be used without loss of energy, and the curvature of the reflecting surface over a small area is likely to be more regularly than over a large one. Moreover, it was possible to choose the best part of the surface, thus avoiding the edges and flaws.

DETAILS OF APPARATUS.

Source.—A Nernst glower, 110 volts and 0.8 ampere, fed by a 120-volt storage battery served as a source. The glower was protected from air currents by an asbestos shield. An ammeter and variable resistance in circuit made it possible to hold the glower current constant in spite of slow fluctuations in the battery voltage and to detect any sudden

change likely to cause error. After adjustment the current usually remained very constant throughout a series of observations.

Spectrometer.—A Schmidt and Haensch spectrometer with Rubens attachment, belonging to the Rumford Committee of the American Academy of Arts and Sciences was used. In place of the customary simple prism the spectrometer table bore the Wadsworth mirror prism arrangement¹ and the different parts of the spectrum could therefore be caused to fall upon the slit *T* (Fig. 2) by rotating the prism table, the arms of the spectrometer remaining fixed. The spectrometer mirrors *M*₃ and *M*₅ had each a focal length of 35 cm. and an aperture of about 4 cm.

Prism.—The sylvite prism *P* had faces 3.2 cm. high and 2.5 cm. broad, and a refracting angle of $38^{\circ} 9' 51''$. Wave-lengths to 20μ may be determined with a sylvite prism of this refracting angle so that the field of observation was extended considerably beyond the limit reached with ordinary 60° rock-salt prism. In order to interpret spectrometer sittings in terms of wave-lengths a curve was drawn with wave-lengths as abscissas and as ordinates, one half the difference between the angles of minimum deviation for the given wave-length and for the sodium line. One half the angle was taken, since with the Wadsworth prism and mirror arrangement the angle of rotation of the prism table is equal to one half the change in the angle of minimum deviation. The values for the angles of minimum deviation for wave-length from $.5\mu$ to 20μ at intervals of $.5\mu$ were calculated from the Ketteler-Helmholtz dispersion formula using the constants for sylvite determined by Rubens.² The adjustment of the spectrometer was repeatedly checked by observing the reading of the spectrometer scale when the *B* line coincided with the telescope slit. The curve for wave-lengths and spectrometer settings was tested by observing the wave-lengths of maximum reflection for quartz and calcite which agreed within experimental errors with the values found by other observers.

Radiometer.—A Nichols radiometer with a sylvite window was used. The mica vanes measured 5 mm. \times .75 mm. and were placed with their outer edges 8 mm. apart. The faces of the vanes were covered with a thin layer of platinum black held on by shellac. The radiometer stood on a shelf supported by a thick inner wall, and under ordinary conditions the vibrations of the building did not affect the readings. Deflections of the radiometer vanes were determined by observing the position of the image of the index lamp, formed on the scale one meter

¹ Phil. Mag., 38, 337, 1894.

² Wied. Ann., 60, 418, 1897; 60, 724, 1897.

distant, by a small concave mirror fastened at the lower extremity of the suspended system.

Adjustment of the Surface.—The surface to be examined was clamped behind one of the openings, S_2 (Fig. 2), in an upright brass plate mounted on a small car which slid smoothly on the carefully planed ways of a bedplate. At a second opening, S_1 , was placed a plane silvered mirror used as a standard reflector. The back of the upright plate was plane

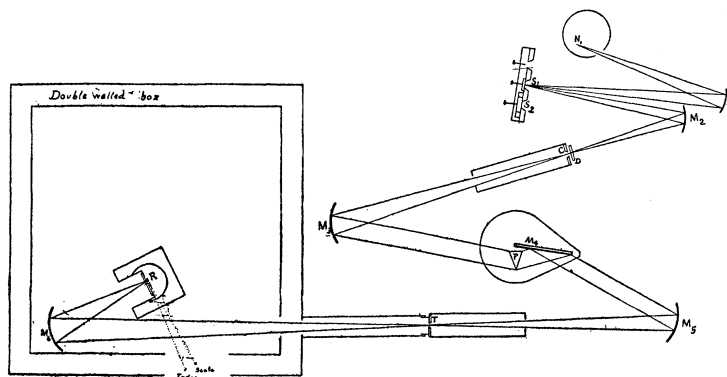


Fig. 2.

so that either the surface whose reflection was to be studied or the standard could be brought successively into the same position by sliding the car along the ways between properly adjusted stops. In the case of plane bright surfaces this adjustment was tested by observing in a telescope provided with cross wires, the position of the image of an incandescent lamp filament reflected first from one and then from the other surface. The adjustment of the more brilliant surfaces was made slightly more exact by the use of three screws which passed through the upright plate and pressed against the silver surface, making it possible to change the angle of the silver until it was in the same plane with the other surface. The adjustment required was in each case so small that but a slight error was introduced by not making the finer adjustment for the duller surfaces after they were clamped in place.

Purification of the Spectrum.—In the preliminary work the energy in the region 18μ to 20μ was found to be unexpectedly great, and it was suspected that this was due, in part at least, to stray energy of shorter wave-lengths. To test this, observations were made on the transparency of quartz, fluorite and rock salt at 20μ where these salts, in plates of the thickness used, were known to be almost entirely opaque. It was found that of the apparent energy at 20μ 70 per cent. was transmitted by quartz, 78 per cent. by fluorite, and 82 per cent. by rock salt.

Of the remaining 18 per cent. not transmitted by rock salt, perhaps 5 to 12 per cent. might be accounted for by diffuse¹ reflection from the surface, and this might also consist of short waves. Therefore, only a remainder of not more than 13 per cent. of the total energy could be considered to be of wave-length 20μ . To get rid of as much as possible of this stray energy, shutters of the three above-mentioned substances were mounted so that either one could be placed in front of the collimator slit at *D* (Fig. 2). Between 4μ and 10μ a plate of quartz 3.5 mm. thick was used, between 10μ and 17μ a plate of fluorite 3 mm. thick, and beyond 17μ a plate of rock salt 4 mm. thick. In the last part of the work the quartz plate was being used for other purposes and a piece of plate glass made a satisfactory substitute.

Method of Making Observations.—When the shutter was in front of the slit, *C*, the energy to which the shutter was transparent produced a deflection of the radiometer suspension and the position of the spot of light on the scale was read. When the shutter was raised the additional deflection was that due to the energy which the shutter formerly cut out and the turning point of the index image on the scale gave a second reading. The shutter was lowered as soon as the extreme swing was reached and the turning point on the backward swing was used. The difference between the second reading and the mean of the first and last is proportional to the energy of the wave-length for which the spectrometer was set and for convenience is called the deflection. The usual order of observing was to take first such a set of readings with the silver surface in the reflecting position. This was followed by three or more sets in which the surface being studied replaced the standard silver surface. In order to make sure that the energy from the Nernst glower had remained constant, a second set of observations was made on the silver surface. If the deflection differed from the first, or if the deflections were small, more observations were made. When the deflections were small the time of a large deflection was determined and the same time allowed between removing or replacing the shutter and reading the scale. Assuming the reflection of silver to be total² the ratio of the average deflection with the salt surface in place to that with the standard silver surface in place is called the percentage of reflection. The slit widths were varied from .1 mm. at 4μ corresponding to an interval of $.23\mu$, to 1 mm. corresponding to an interval of $.43\mu$ at 20μ . Care was taken to make no changes in the material used for a shutter, or in the slit widths, at a part of the spectrum where the percentage of reflection was changing rapidly.

¹ Pogg. Ann., 138, 174, 1869.

² E. Hagen and H. Rubens, Ann. die Phys., II., 73, 1903.

The results are plotted in the accompanying curves in which wave-lengths are chosen as abscissas and percentages of reflection as ordinates. Of the sixteen substances examined ten were ortho-phosphates, two meta-phosphates, and four pyro-phosphates, the typical formulas being respectively R_3PO_4 , RPO_3 and $R_4P_2O_7$, where R represents a monovalent base.

ORTHO-PHOSPHATES.

The reflection curves for the ortho-phosphates are shown in Figs. 3 and 4. The maxima occur in two distinct parts of the spectrum, one between 9μ and 11μ which for convenience will be referred to as the first region, and the other beyond 16μ or in the second region of maximum reflection. Between these two regions there are no reflection maxima. The curves for the three ortho-phosphates having monovalent bases are put together in Fig. 3. They seem to form a typical set showing clearly that the first point of maximum reflection occurs farther toward the long waves as the atomic weight of the base increases (at. wts. Li = 7, Na = 23, Ag = 108). Of all the salts examined Ag_3PO_4 has the highest and Li_3PO_4 the next highest percentage of reflection. The bases of these two are monovalent and belong to the same chemical group. That the high reflection cannot be attributed to this is shown by the fact that though sodium is also in this group the reflecting power of Na_3PO_4 is one of the lowest. A fourth member of this chemical group, K_3PO_4 , was so deliquescent that it was impossible to examine it. All three curves for this monovalent series have two maxima in the second region, each of the two for Ag_3PO_4 being at longer wave-lengths than the corresponding one for Li_3PO_4 . But the second for Na_3PO_4 is at a shorter wave-length than the second for Li_3PO_4 .

The ortho-phosphates with divalent and trivalent bases are represented by the curves in Fig. 4. They are arranged in the order of the weights of the bases combined with one atomic weight of phosphorus beginning at the bottom with the smallest weight. When the weight of the base is changed these show in general a change in the first region wave-length selectively reflected, similar to that observed in the case of the monovalent series. $Zn_3(PO_4)_2$, and perhaps $Sr_3(PO_4)_2$ with two maxima, are exceptions. There is less regularity in the change of position of the maxima in the second region and the reflection bands are in general more complex. There seems to be no very distinctive difference between the curves for the monovalent and divalent ortho-phosphates. The bases in the latter series—magnesium, calcium, zinc, strontium and lead—belong, with the exception of lead, to the second chemical group. $Sr_3(PO_4)_2$ and $Mg_3(PO_4)_2$ have each two points of maximum reflection in the first region. There

is a rather doubtful indication of a second maximum on the left slope of the first band in $\text{Zn}_3(\text{PO}_4)_2$ but none with $\text{Ca}_3(\text{PO}_4)_2$. The general form of the curve for $\text{Pb}_3(\text{PO}_4)_2$ is very similar to the others, although lead belongs to a different chemical group.

Only two representatives of the ortho-phosphates with trivalent bases could be obtained, AlPO_4 and BiPO_4 . An effort was made to add BPO_4 to the list, but it proved unstable at a certain stage in its preparation. AlPO_4 had a very low reflecting power even at the wave-lengths for which the reflection was greatest, although the surface was one of the brightest obtained. There was one rather irregular maximum in the first region, and a probable one beyond 20μ . BiPO_4 , on the other hand, has high and complex maxima in both regions.

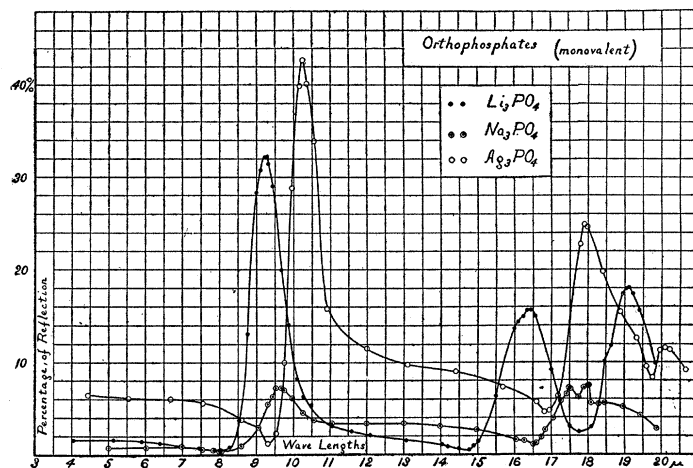


Fig. 3.

It has not been possible with the data obtained to find any distinctive characteristics in the reflection curves which may be ascribed to the chemical group to which the base belongs. Neither have any simple hypotheses suggested themselves which are adequate to interpret the effect of the valence of the base on the complexity of the curves. There seems, however, to be a tendency for the curves to become more complex as the valence of the base increases.

META-PHOSPHATES.

The two meta-phosphates examined, NaPO_3 and KPO_3 , have monovalent bases. Both curves (Fig. 5) have three reflection maxima between 7μ and 12μ , the middle one being the lowest. NaPO_3 was examined to

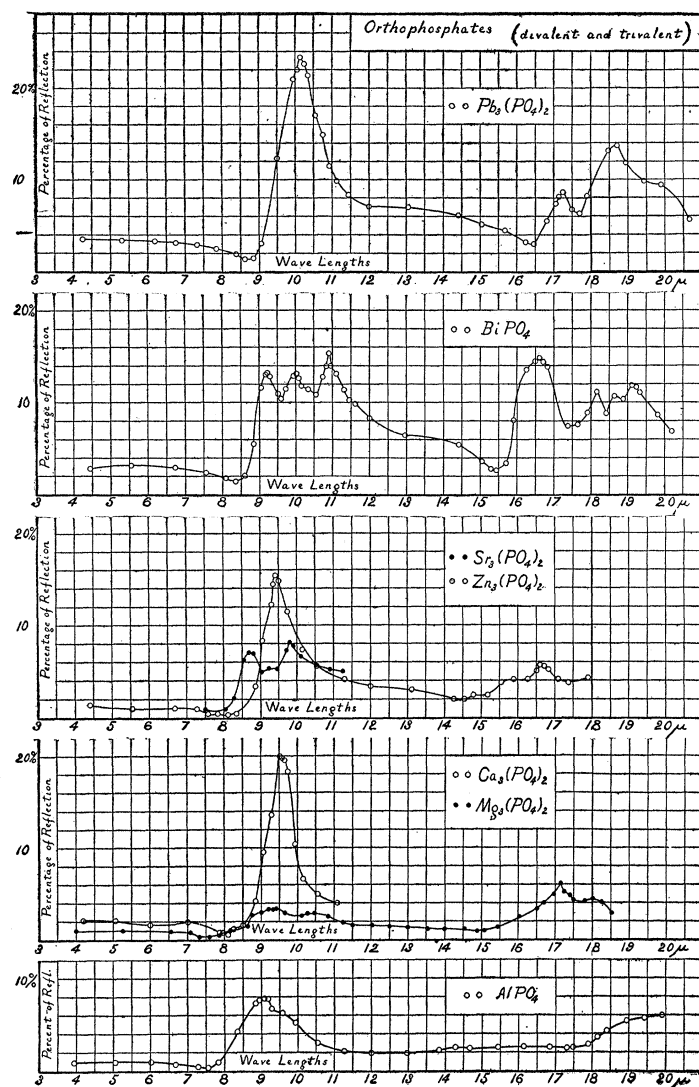


Fig. 4.

20 μ and shows a single maximum at 19 μ . KPO_3 shows resonance for radiation of greater frequency than does NaPO_3 though K has an atomic weight of 39 and Na only 23. Thus an increase in atomic weight of the base is accompanied by a decrease of the wave-length, for which the reflection is a maximum, instead of an increase, as is usually the case. Several different forms of sodium meta-phosphate are known, however, having the formulas NaPO_3 , $\text{Na}_2\text{P}_2\text{O}_6$, etc., so the sodium meta-phosphate

and the potassium meta-phosphate examined might not have been similar. The NaPO_3 was amorphous or glassy, and KPO_3 crystalline. The first maximum for NaPO_3 at 7.9μ lies close to that found by Coblenz at 8.0μ .

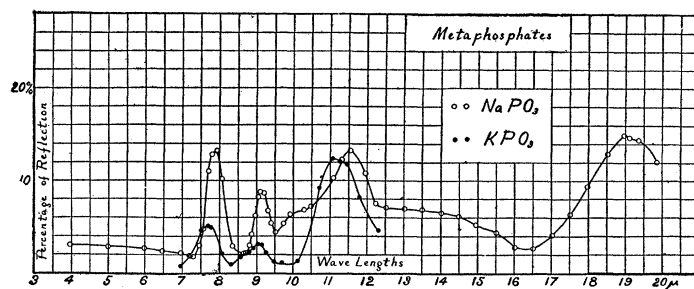


Fig. 5.

PYRO-PHOSPHATES.

Four pyro-phosphates were examined, three with monovalent bases, $\text{Na}_4\text{P}_2\text{O}_7$, $\text{K}_4\text{P}_2\text{O}_7$, $\text{Ag}_4\text{P}_2\text{O}_7$, and one with divalent base, $\text{Pb}_2\text{P}_2\text{O}_7$. A

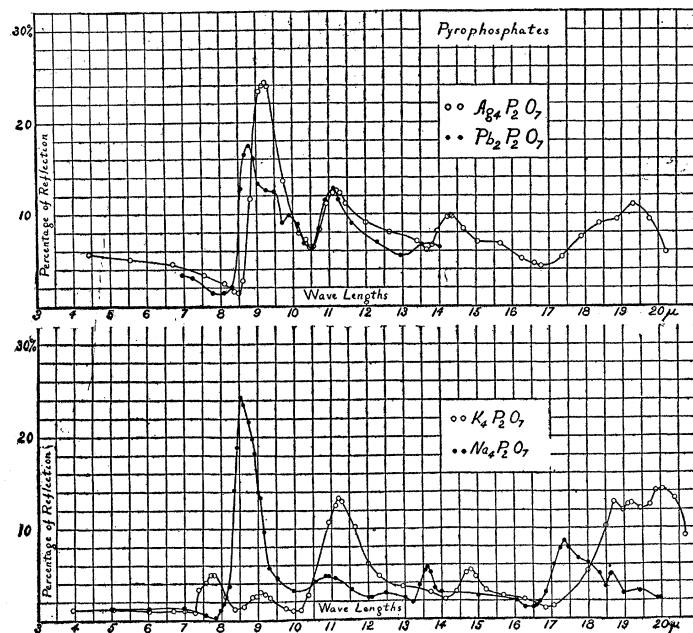


Fig. 6.

distinguishing feature of these curves (Fig. 6) is that they have no region of low or continuously decreasing reflection between 12μ and 15μ as do all the other phosphates examined. Instead, the pyro-phosphates

have in this region one or two points of pronounced selective reflection. The highest points in the $K_4P_2O_7$ curve are at longer waves than the apparently corresponding ones for $Na_4P_2O_7$ with the lighter base, but if all the maxima are taken in regular order without regard to height, the difference is in the opposite sense. There is a somewhat similar correspondence between $Pb_2P_2O_7$ and $Ag_4P_2O_7$; but the two sets cannot be reduced to one depending on the effect of the weights of the bases.

Little more can be said than that these salts with more complex chemical formulas have more free periods of vibration to which they respond than do the simpler molecules. The table is given to assist the reader in locating the more important maxima. The values of the wave-lengths in the last column are taken directly from the curves.

TABLE.

I., Ortho-phosphates; II., Meta-phosphates; III., Pyro-phosphates.

	Chemical Formula of Salt.	Valence of Base.	Atomic Weight of Base.	Weight of Base Combined with One At. Wt. of P.	Wave-lengths of Reflection Maxima.
I.	Li_3PO_4	1	7	21	9.25, 16.4-19.1
	$AlPO_4$	3	27	27	9.1, (20)
	$Mg_3(PO_4)_2$	2	24	36	9.4, 10.5, 17.1
	$Ca_3(PO_4)_2$	2	40	60	9.5,
	Na_3PO_4	1	23	69	9.6, 17.5-18.0
	$Zn_3(PO_4)_2$	2	65	98	9.4, 16.6
	$Sr_3(PO_4)_2$	2	87	130	8.7-9.8
	Bi_3PO_4	3	207	207	9.2-10.0, 16.6-18.15
	$Pb_3(PO_4)_2$	2	206	309	10.15, 17.25-18.7
	Ag_3PO_4	1	108	324	10.25, 17.9-20.1
II.	$NaPO_3$	1	23	23	7.9-9.15-11.6, 19.0
	KPO_3	1	39	39	7.7-9.1-11.1
III.	$Na_4P_2O_7$	1	23	46	8.5-10.9, 12.5-13.6, 17.4-18.7
	$K_4P_2O_7$	1	39	78	7.75-9.05, 11.2-14.8, 18.7-19.15, 20.0
	$Pb_4P_2O_7$				
	$Pb_2P_2O_7$	2	206	206	8.-89.5, 9.9-11.1, 13.5
	$Ag_4P_2O_7$	1	108	216	9.2-11.2, 14.3-19.3

Fig. 7 shows the position of the most prominent reflection maxima for the ortho-phosphates plotted with wave-lengths as abscissas and as ordinates the weights of the bases united with one atomic weight of phosphorus. To show the magnitude of the deviations from exact proportionality between the wave-lengths and weights of the bases, a straight line has been drawn through the Li_3PO_4 and Ag_3PO_4 maxima in the first

region. It is seen from this figure that the deviations do not bear any constant relation to the valence of the base. In the second region two lines have been drawn which include between them all except one of the principal maxima. This region of selective reflection is nearly 3μ broad

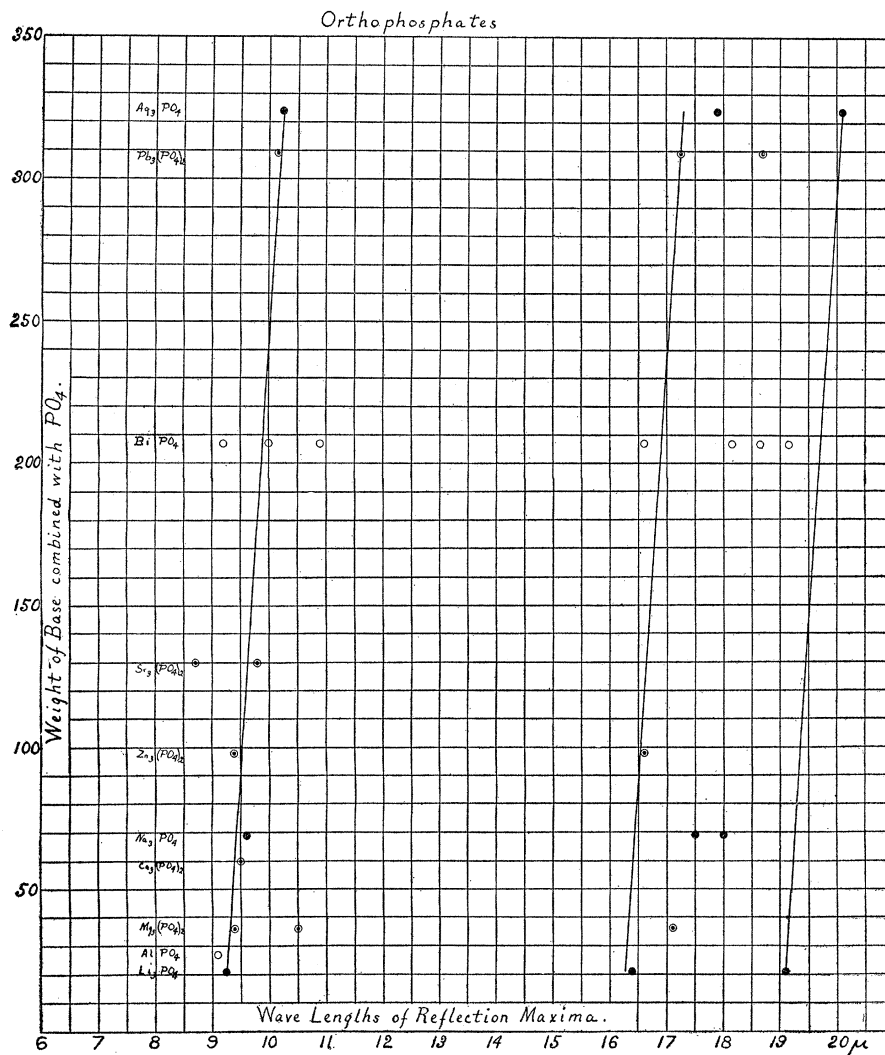


Fig. 7.

and shows a general shift to the long waves with increasing weight of base, though no correspondence between individual maxima can be traced.

It has been shown that¹ a change in the atomic weight of the element

¹ *Astrophysical Journal*, 26, p. 240, 1907.

combined with oxygen in the acid radical seems to have a greater effect on the position of the reflection band than an equal change in the atomic weight of the base. A comparison of the curves for phosphates with those for sulphates¹ shows that in all cases the first region bands for the ortho-phosphates are at longer wave-lengths, on an average fully $.7\mu$, than those for the corresponding sulphates. This difference cannot be attributed to a difference only in the atomic weights of phosphorus and sulphur for the two have approximately the same weights, that for sulphur being slightly larger ($S = 32.0$, $P = 31.0$). Neither does it seem that a difference in the weights of the bases can account for more than a small part of the difference in wave-lengths selectively reflected. This is certainly true if we may for example assume that K_2 and K_3 in K_2SO_4 and K_3PO_4 act similarly to bases of atomic weights 2×39 and 3×39 respectively. If we should assume that oxygen is the determining element and that the position of the reflection maxima is due to the loading of the oxygen atom with atoms in combination with it, it might be inferred that not only would the precise position be affected by the weight of the base and the acid forming element, but also that the strength of the bonds and the arrangements of the atoms in the molecule would have some influence. Phosphorus has a much stronger affinity for oxygen than has sulphur, for the oxides of phosphorus are decomposed with greater difficulty. What relation this bears to the selective reflection of the solid salts it is impossible to determine with present data.

Merritt² and Königsburger³ both found that between $.1\mu$ and 5.5μ the absorption in doubly refracting media depended upon the plane of polarization of the incident energy. Later it was observed that the reflection maxima of calcite and aragonite⁴ in the 11μ region differed by $.24\mu$ though both calcite and aragonite had the same chemical formula, $CaCO_3$. There were also decided differences in the heights of the reflection maxima, which could not be attributed to a difference in polish. This showed conclusively that the crystal form as well as the chemical composition must be taken into account even when dealing with radiations of wave-lengths over 10μ . More recently the dependence of the selective reflection on both the crystal form and the orientation of the section examined has been very carefully studied by Nyswander⁵ in the case of calcite and aragonite using polarized light.

In order to obtain a complete analysis of the dependence of free reso-

¹ Investigations of Infra-red Spectra, Parts IV. and VI.

² *PHYS. REV.*, 2, 424, 1895.

³ *Ann. der Phys.*, 61, 687, 1897.

⁴ *Astrophysical Journal*, 11., 225, 1907.

⁵ *PHYS. REV.*, 28, 4, p. 291, 1909.

nance periods upon the chemical composition of a salt it will be necessary to examine the substance in crystal form and with polarized light. It is, as has already been stated, impossible to find suitable crystal sections of an extended series of salts which have the desired variations in chemical composition. While pressed surfaces cannot give the absolute values of reflection, the minute crystalline structures when present must have all possible orientations and therefore all the free resonance periods of sufficient strength must appear in the resulting curves. A comparison of the relative heights of the reflection maxima observed with pressed surfaces is certainly more trustworthy than such a comparison when crystal sections cut at random are used. For example, the almost complete disappearance of the second region maximum in the witherite examined by Morse¹ is undoubtedly due to the chance orientation of the crystal section. The use of pressed surfaces makes possible the examination of a great number of large and complicated series of salts like the phosphates here described. And the data thus obtained promise eventually to be of much value in selecting the crystal sections best suited to a more complete investigation of the problem.

The main results here presented may be summarized as follows:

1. A surface suitable for the qualitative study of selective reflection in the infra-red spectrum may be produced on a substance which is available only in the form of fine powder, if this powder is subjected to great pressure.
2. The method of making the pressed surfaces described has made it possible to compare the reflection in the infra-red spectrum of extended series of salts, such as phosphates, chromates or chlorates in which a common acid forming element is combined with different weights of oxygen. Data on the selective reflection of phosphates are here given.
3. A comparison of Figs. 3 and 4 for ortho-phosphates with Fig. 5 for meta-phosphates and Fig. 6 for pyro-phosphates shows that each group has a more or less characteristic selective reflection which easily distinguishes it from the other groups of phosphates as well as from salts of other acids, carbonates, nitrates, and sulphates.
4. The data on phosphates alone are an insufficient basis for the formulation of any exact relation between the valence of the base, or the chemical group to which it belongs, and the selective reflection characteristic of the salts of a given acid radical. But in general an increase in the weight of the base combined with the given acid radical containing phosphorus causes the reflection maxima to be moved toward the longer waves, as has been found with salts of other acids.

¹ Astrophysical Journal, 26, p. 240, 1907.

5. A comparison of sulphates and phosphates shows that phosphorus has a greater effect on the free resonance periods than sulphur for some reason not connected with the relative atomic weights since the reflection maxima occur for longer waves in the phosphates, although phosphorus and sulphur for the rough purposes in hand have practically the same atomic weight.

In conclusion the writer wishes to thank Mr. B. L. Murray, of Merck and Company, for aid in the selection of the phosphates used. She also wishes to thank Dr. L. B. Morse for his interest and assistance throughout the work. And she especially wishes to acknowledge her great indebtedness to Dr. E. F. Nichols who suggested the investigation, and under whose direction it was carried out.

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