and the system was repeatedly frozen in an acetone–Dry Ice bath, then thawed. It was finally stored overnight at 0°. This treatment produced crystals which were recrystallized by dissolving in water, cooling, adding cold acetone with vigorous stirring until an oily layer separated. When seeded, and kept at 0° for two hours, crystals appeared.

Anal. Calcd. for $(tmdH_2)(H_2PO_4)_2$: N, 10.36. Found: N, 10.40; decomposition point, 163°.

1,3-Propanediammonium Monohydrogen Orthophosphate, $(tmdH_2)(HPO_4)\cdot H_2O$.—This was a simple and straightforward preparation. The diamine was added to orthophosphoric acid until *p*H 8 was reached. Gradual addition of cold alcohol to the solution accompanied by vigorous stirring produced crystals. They were purified by recrystallizing twice from water.

Anal. Calcd. for $(tmdH_2)HPO_4\cdot H_2O$: N, 14.73; P, 16.37; H_2O, 9.51. Found: N, 14.73; P, 16.44; H_2O, 9.32 (constant weight at 125°); decomposition point, 225°.

1,3-Propanediammonium Pyrophosphate, $(tmdH_2)_2P_2O_7\cdot 3H_2O$.—This compound was more difficult to crystallize than were previous products which resulted in the alkaline *p*H range. The following procedure was found best. Pyrophosphoric acid was added to the diamine until the *p*H reached 10. Alcohol was added carefully to the resulting solution still at room temperature until an incipient cloudiness just appeared. After cooling this saturated solution in ice for one hour, small acicular crystals appeared. The same technique was followed in the two purifying recrystallizations.

Anal. Calcd. for $(tmdH_2)_2P_2O_7\cdot 3H_2O$: N, 14.72; P, 16.30. Found: N, 14.81; P, 16.14. Attempts to dehydrate the compound in an oven at 105° failed, as it decomposed after losing 82% of its weight; discoloration occurred and the odor of diamine was obvious.

Decomposition point, discoloration evident at 185°, melting and rapid decomposition at 225°.

Diaminobutane Preparations

1,3-Butanediammonium Monohydrogen Orthophosphate, $(dbH_2)(HPO_4)$.—The diamine was added to orthophosphoric acid solution until the *p*H reached 9. While the solution was still at room temperature, alcohol was added slowly and with vigorous stirring until an opaque, fluid, white emulsion formed. The preparation yielded crystals after standing in an ice-bath for 30 minutes. The product was recrystallized twice from water.

Anal. Calcd. for $(dbH_2)HPO_4$: N, 15.05. Found: N, 15.20; decomposition point, discoloration evident at 220°; vigorous decomposition at 232°.

1,3-Butanediammonium Pyrophosphate, $(dbH_2)_2P_2O_7$.—Pyrophosphoric acid was added to the diamine solution until the *p*H had fallen to 10.5. This solution was placed in a vacuum desiccator over ascarite. The preparation was tested daily with silver nitrate to be certain that no significant hydrolysis to orthophosphate had occurred. The system became increasingly viscous, and after one week, a few crystals appeared in the oil. When this thick suspension was stirred, it immediately set to a cold-cream consistency. The material was transferred to a filter and washed thoroughly with alcohol to remove the excess diamine. Purification was accomplished by dissolving the preparation in water, cooling, and adding alcohol until two layers separated. The upper layer was removed and the viscous lower layer seeded with some of the crude product previously obtained. Vigorous stirring induced crystallization.

Anal. Calcd. for $(dbH_2)_2P_2O_7$: N, 15.81. Found: 15.94; decomposition; discoloration evident at 200°, vigorous decomposition and melting at 230°.

Discussion.—During this investigation, extensive efforts were also made to prepare crystalline dihydrogen orthophosphates of 1,2-diaminopropane and 1,3-diaminobutane. The inflection point in the *p*H curve of each of these diamines with orthophosphoric acid indicates that the necessary ions are present in the solution. However all attempts at crystallization led to viscous oils or glasses. Since the corresponding orthophosphates of ethylenediamine and 1,3-diaminopropane do crystallize, it seems very probable that the failure of the former compounds to solidify may be attributed to steric hindrance of the methyl group beyond the amino group.

Similar efforts succeeded in producing only one crystalline dihydrogen pyrophosphate, namely, that of ethylenediamine described above. All the other diacid pyrophosphates of this series were obtained as viscous oils or glasses. Steric factors again offer the most likely explanation for this lack of crystallinity. Support for this view comes from the increasing difficulty of obtaining crystalline tetra-substituted pyrophosphates as the chain length of the diamine increases.

Exhaustive attempts were also made to prepare the tertiary orthophosphates, particularly of ethylenediamine. Even protracted refluxing of $(enH_2)HPO_4$ with undiluted ethylenediamine produced no reaction. The most logical reason for this lack of reaction probably resides in the weakness of the third dissociation constant of the acid, and the energy necessary to arrange a stable lattice consisting of the ions in question.

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The Molar Refractions of Some Complex Ions in Solution

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The molar refractions of ionic compounds in aqueous solution have been studied[1,2] and ionic refractions have been derived from such data. Complex ions have not been extensively investigated, however. We have measured the refractive indices of aqueous solutions of several compounds containing complex fluoride ions by use of an interferometer. The molar refractions of the salts have been found and ionic refractions estimated.

The refractive indices at 20° of solutions of the various electrolytes studied are shown in Table I for several concentrations. The molar refraction of the solute was found by the method of Halverstadt and Kumler[3] and values are included in Table I. The squares of the refractive indices of the solutions and the specific volumes of the solutions were each plotted *versus* the weight fraction of solute, w_2. From the slopes a and b of the resulting straight lines, along with the intercepts ${n_1}^2$ and v_1 at infinite dilution, the molar refraction MR was calculated by use of the equation

$$MR = M_2\left\{\frac{3av_1}{({n_1}^2+2)^2} + (v_1+b)\,\frac{{n_1}^2-1}{{n_1}^2+2}\right\}$$

where M_2 is the molecular weight of the solute. Although our values of MR are for λ = 5461 A., and so are not strictly comparable with the more common values of MR_{D} in tables, the differences are only about 1% which is less than the probable error of measurement.

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(1) K. Fajans and G. Joos, *Z. Physik*, **23**, 46 (1924), *et seq.*

(2) A. Heydweiller, *Physik. Z.*, **26**, 526 (1925).

(3) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

TABLE I

REFRACTIVE INDICES OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES AT 20° AND MOLAR REFRACTIONS OF DISSOLVED SALTS

w_2	n^a
Sodium chloride	
0	1.334468
.001121	1.334665
.002239	1.334924
.004470	1.335263
.005583	1.335465
.008904	1.335818
.011123	1.336483
MR = 9.40 cc./mole	
Potassium chloride	
0.001908	1.334735
.005711	1.335300
.009495	1.335830
.014201	1.336508
MR = 11.68	
Ammonium chloride	
0.001899	1.334794
.002846	1.334976
.004740	1.335293
.009466	1.336157
MR = 12.86	
Ammonium fluoborate	
0.00286	1.334403
.00714	1.334304
.01483	1.334148
.02128	1.333991
MR = 11.08	
Sodium fluosilicate	
0.000502	1.334498
.000753	1.334513
.001254	1.334530
.002506	1.334603
.003754	1.334661
MR = 13.20	
Potassium fluosilicate	
0.000277	1.334484
.000551	1.334496
.000827	1.334513
.001102	1.334521
MR = 17.40	
w_2	n
Sodium fluoride	
0.000945	1.334598
.001417	1.334662
.002360	1.334791
.004708	1.335111
.007043	1.335416
MR = 2.60	
Fluoboric acid	
0.003569	1.334356
.008892	1.334184
.017692	1.333860
.026430	1.333508
.035064	1.333260
MR = 6.14	
Sodium fluoborate	
0.00497	1.334400
.00709	1.334375
.01012	1.334334
.01211	1.334301
.01989	1.334200
MR = 7.63	
Potassium fluotitanate	
0.002075	1.334583
.002593	1.334616
.004146	1.334680
.005179	1.334739
MR = 26.68	
Potassium ferricyanide[b]	
0	1.333221
.001610	1.336408
.003185	1.340058
.004728	1.342814
.006238	1.345994
MR = 60.91	
Potassium ferrocyanide[b]	
0	1.333221
.001750	1.336674
.003466	1.340142
.005414	1.343422
.006781	1.346707
MR = 69.06	

[a] λ = 5461 Å. [b] Measurements made with immersion refractometer, λ = 5893 Å.

Ionic refractivities have been derived from those of the salts by choosing the value 8.26 cc./mole for the ionic refraction of chloride ion; this is essentially the same as the figure used by Heydweiller and leads to values of the other ions which agree well, on the average, with the ionic refractivities of Heydweiller (for aqueous solutions) and those of Shockley, *et al.*[4] (for crystals). The set of ionic refractivities obtained are shown in Table II. The ionic refractivities of fluoborate, fluosilicate and fluotitanate ions are about equal to the sums of the atomic refractions of the constituent atoms when the usual atomic refractivities are employed with no correction for change in oxidation number (calculated for BF_4^-, 6.3; for SiF_6^-, 10.4; for TiF_6^-, 19.2). Since an increase in polarizability should result from the negative charge on the ion the expected increase must be approximately cancelled by a decrease in polarizability of the central atom as the coördination number is increased.

TABLE II

REFRACTIVITIES OF IONS IN DILUTE AQUEOUS SOLUTION

Ion[b]	MR^a	Ion	MR
BF_4^{-1}	6.45	K^+	3.32
SiF_6^{-2}	10.8	Na^+	1.20
TiF_6^{-2}	20.0	NH_4^+	4.60
$Fe(CN)_6^{-3}$	51.0	H^+	−0.30
$Fe(CN)_6^{-4}$	55.8	F^-	1.40
		Cl^-	8.26

[a] At λ = 5461 Å. for all except ferrocyanide and ferricyanide for which λ = 5893 Å. [b] The refractivities of BF_4^{-1}, SiF_6^{-2}, $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$ computed from data on crystalline compounds are 6.50, 10.81, 47.3 and 53.9, respectively.

The refractivities of ferrocyanide and ferricyanide ions were measured to provide an example where the effect of ionic charge could be separated from that of change of coördination number. The increase of 4.83 cc./mole represents the effect of increasing the negative charge on the ferricyanide ion by one unit. For smaller ions the magnitude of the effect should be smaller but the only data available for such a comparison are the two cations Cu^+ (1.6) and Cu^{++} (0.5) reported by Shockley, *et al.*[3]

Experimental

Materials.—Potassium chloride, sodium chloride, ammonium chloride, sodium fluosilicate and potassium fluosilicate were J. T. Baker Analyzed, C.P. grade; potassium bifluoride, sodium fluoride, potassium ferrocyanide and potassium ferricyanide were Merck reagent grade; fluoboric acid, potassium fluoborate, sodium fluoborate, ammonium fluoborate were Baker and Adamson products; potassium fluotitanate was a student preparation. All salts were recrystallized several times from conductivity water before use.

Apparatus and Method.—Refractive indices were measured with a dipping refractometer (potassium ferrocyanide and ferricyanide) or with an interferometer (all the remaining materials). The design and operation of the Rayleigh-type interferometer employed have been described.[5] For this work cells were constructed by machining two troughs in a Monel block and cementing an optically flat glass plate to each side. The cell was held in an aluminum block through which water at 20° was circulated. The path length was 0.9611 cm. or, for some work, 2.3706 cm., and pure water was always the reference liquid.

When the interferometer was used to measure the difference between the refractive index of a solution and that of pure water, calibrated compensating plates were employed. The rotation of the compensating plates necessary to equalize the optical paths through solvent and through solution and compensating plates was measured and, from a graphical calibration curve for the compensating plates, the corresponding refractive index difference was obtained. The zero-order fringe was located using a white light source but actual measurements were made with monochromatic radiation (λ = 5461 Å.) from a General Electric AH-4 lamp and interference-type filter. It is possible to make an error of one or more fringes when this method is used since the solvent,

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(4) J. R. Tessman, A. H. Kahn and W. Shockley, *Phys. Rev.*, **92**, 890 (1953).

(5) J. G. Malik, J. L. Speirs and M. T. Rogers, *J. Chem. Educ.*, **30**, 437 (1953); J. G. Malik, Doctoral Thesis, Michigan State College, 1954.

solution and compensating plates have different dispersions. To correct for such gain or loss of fringes plots were made[4] of the compensator plate reading *versus* concentration of each solute, at closely spaced values of concentration, and the necessary correction determined from the graph. The refractive indices are all relative to the refractive index of water for which an average of literature values, n^{20} = 1.334468 at λ = 5461 Å., was selected. The refractive indices of potassium ferrocyanide and ferricyanide were determined with a Bausch and Lomb immersion refractometer at λ = 5893 Å., n^{20}D = 1.333221 for pure water.

Densities were measured with a modified Ostwald pycnometer. The probable error in the refractive indices is about 1×10^{-5} and in the molar refractions about ±2% (chlorides) or ±4% (fluorides).

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The Lead Styphnate Jelly[1]

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During the course of investigations to determine a method of preparation of the pure, explosive normal lead salt of styphnic acid (2,4,6-trinitroresorcinol) we noted that a jelly may result from solutions of soluble styphnate and a lead salt mixed at room temperatures. We undertook preliminary studies of the nature of this jelly both because of its possible chemical and physical relationship to the desired salt and to determine other useful characteristics of this novel heavy metal–organic jelly of potentially explosive constitution. We noted that Miles[2] employed lead nitrate and magnesium styphnate; however, solutions of lead acetate and styphnic acid formed a jelly.[3] Using resorcinol or its mono- or dinitro derivatives in place of styphnic acid, we found no jellies under comparable conditions. Salts of zinc and magnesium did not form jellies with styphnic acid solutions.

We found that the jelly was translucent and slightly yellow when freshly prepared, and became more opaque and yellow on standing. It was made sufficiently rigid to permit slicing or the inversion of its container without textural change. Agitation converted the jelly to a gelatinous precipitate which did not regain its original rigidity.

We observed that by mixing at room temperatures, saturated solutions of lead acetate trihydrate and styphnic acid formed the jelly directly. The addition of molar lead nitrate to a solution of styphnic acid saturated at 20° did not form the jelly until the addition of base sufficient to bring the *p*H to 2.8. As the *p*H of the styphnate solution was raised, the yield of gel became greater, with an increasing proportion of gelatinous precipitate mixed with the jelly. With styphnate solutions of *p*H greater than 5.5, addition of the lead nitrate did not cause the formation of the jelly, giving way to a more granular, yellow precipitate. In every instance observed, hardening of the jelly caused a sharp drop in *p*H.

We found the sequence of addition and the concentration of reagents to be critical. For example, the jelly was produced by the dropwise addition of 2 *M* sodium hydroxide to a solution of a rapidly agitated, saturated solution of styphnic acid containing more than a quarter equivalent of lead nitrate. Sufficient base was added to bring the *p*H to 3.7. However, when a 0.1 *M* lead nitrate solution was added dropwise to a rapidly agitated, saturated solution of styphnic acid which was previously brought to a *p*H of 3.7 by addition of sodium hydroxide, crystals precipitated without any apparent preliminary gelation. Furthermore, when two equivalents of 1 *M* lead nitrate were added rapidly to an unagitated styphnic acid solution at *p*H 3.7, the jelly was obtained again.

The jelly, prepared by a special method, gave way to fibrous crystals on standing, Miles reported. He analyzed the crystals for PbO and loss of water and found them to be a normal salt of lead styphnate which was able to lose two moles of water. These fibers spontaneously decomposed to the common monohydrate[4] of the normal salt of lead styphnate, $PbC_6H(NO_2)_3O_2 \cdot H_2O$, usually called normal lead styphnate. This normal salt was also obtained directly by allowing the usual preparation of the jelly to stand at room temperature. Purer preparations of the normal salt are prepared by crystallization from hot solutions of *p*H 2 to 5 with or without the temporary jelly formation.[5]

Our attempts to isolate the dried component of the jelly by freeze–drying techniques have only yielded crystals of the impure normal salt. We suspected that shrinking and washing the jelly to remove possible reactants might keep the component of the jelly in its occurring chemical form. We obtained a yellow powder by shrinking the jelly with 1,4-dioxane, washing it briefly with water and alcohol, and drying it with ether. Under the microscope the powder appeared amorphous and gave an X-ray diffraction powder pattern lacking the many orientation planes of the normal and basic[6] lead styphnates.

Several analyses of the powders showed a variation in content of Pb, C, N and in loss of water of successive preparations, with no indication of a stoichiometric relation. The minimum lead obtained was 52.3% in contrast to 43.1% for the fibrous crystals of Miles. The amount of lead in the powder increased toward 60% with increased *p*H of the jelly's preparation medium. X-Ray powder patterns of successive preparations were not comparable, none showing strong orientation. The slight solubility and chemical sensitivity of the powder sharply limited the investigation of its solution properties.

Attempts to crystallize the gel component from the powder resulted in the following observations.

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(1) A contribution from the Institute of Science & Technology, University of Arkansas, Fayetteville, Arkansas. Studies supported by U. S. Navy Bureau of Ordnance, Contract NOrd 10,417.

(2) F. D. Miles, *J. Chem. Soc.*, 2532 (1931).

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