tained is already very pure. It may be recrystallized from a large amount of methyl or ethyl alcohol (absolute). The recrystallized product showed the same physical properties as the unrecrystallized.

D-Glucuronolactone isonicotinyl hydrazone thus prepared is in the form of white plates and rods from methyl alcohol or needles from absolute ethyl alcohol. On heating, it charred and decomposed with foaming between 150 and 160° without any sharp melting point. The decomposition point depends on the rate of heating and the type of apparatus used. The new compound is very soluble in water from which it cannot be recrystallized. It is practically insoluble in cold methyl or ethyl alcohol but slightly soluble in these boiling solvents (100 cc. of methyl alcohol dissolves about 1.2 g. of the product at 66°).

Anal. Calcd. for $C_{12}H_{13}O_6N_3$: C, 48.79; H, 4.45; N, 14.24. Found: C, 48.58, 48.63; H, 4.33, 4.29; N, 14.51, 14.48.

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On Salt Effects and the Temperature Coefficients of Solubility of Benzoic and Phenylacetic Acids in Aqueous Solutions

BY MARTIN A. PAUL

RECEIVED NOVEMBER 14, 1952

Recent publications call attention to the anomalous effect of temperature on the solubility of benzoic acid in water and in aqueous salt solutions.[1,2] The anomalies may be briefly summarized as follows.

(1) The solubility s_0 in water fails to satisfy a linear relationship between log s_0 and $1/T$, such as would be expected of an ideal dilute solution if the heat of solution were not exceptionally temperature sensitive; it increases instead at a much more accelerated rate with increasing temperature.[3]

(2) The solubility s in aqueous salt solutions for a particular salt fails to satisfy the Setschenow equation

$$\log (s_0/s) = K'm_s \qquad (1)$$

Instead, the parameter K' called for by this equation, which is quite generally satisfied by slightly soluble non-electrolytes, shows a tendency to decrease in magnitude with increasing concentration m_s of the electrolyte, this tendency being more marked at higher than at lower temperatures.

(3) The total effect of a given salt on the solubility, whether it salts-out or salts-in the benzoic acid, appears to increase markedly with increasing temperature, in contrast with the rather slight decrease in the salt effect normally observed for other slightly soluble non-electrolytes.

Similar anomalies are shown by phenylacetic acid,[1] with the further anomaly that if one assumes both phenylacetic and benzoic acids to be ideal solutes, then the effects of salts on their respective solubilities appear to differ in magnitude rather more than one would expect in view of their close similarity in molecular size and structure.

These anomalies receive a consistent explanation, as pointed out by Long and McDevit,[4] if one supposes that the solute is not an ideal solute, but deviates from Henry's law in the sense that its activity coefficient with respect to the infinitely dilute solution decreases with increasing concentration. It then "salts-in" itself, so to speak, at the increased concentrations normally accompanying the higher temperatures; the apparent effects of electrolytes on the solubility are thereby enhanced, because any appreciable change in the solute's concentration normally associated with the presence of the electrolyte is accompanied by a further change in the same direction as a result of the changing self interaction. It should be noted that deviation from Henry's law is a natural consequence of failure of the solute to follow Raoult's law, that is, failure of its activity to decrease in exact proportion to its mole fraction over the entire composition range.[5] The only special point at issue is whether such deviations can indeed become significant at the solute concentrations attained in the cases here under consideration.

By making certain simplifying assumptions, we may in fact use the deviation of the temperature coefficient of solubility from ideal-dilute-solution behavior in the pure solvent (as would be embodied by a linear relationship between log s_0 and $1/T$) to calculate a self-interaction parameter for the solute. Such a parameter, k_i', is defined by the first term in a series expansion of log γ' as a function of the molality, m_i

$$\log \gamma' = k_i'm_i \qquad (2)$$

where γ' represents the molal activity coefficient referred to infinite dilution in the pure solvent, water.[6] Let us assume that such an expression can be made to fit the data over the concentration ranges of interest (up to about 0.3 m in the case of benzoic acid and 0.7 m in the case of phenylacetic acid), and that furthermore we may neglect the variation of ΔH, the enthalpy of solution at infinite dilution, with temperature. Then from the thermodynamic equation

$$\frac{\mathrm{d} \ln (s_0\gamma')}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \qquad (3)$$

it follows that

$$\log s_0 + k_i's_0 = -\frac{\Delta H}{2.303RT} + C \qquad (4)$$

where s_0 represents the molal solubility at absolute temperature T and C is an integration constant.

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(1) T. J. Morrison, *Trans. Faraday Soc.*, **40**, 43 (1944).

(2) J. O'M. Bockris, J. Bowler-Reed and J. A. Kitchener, *ibid.*, **47**, 184 (1951).

(3) See ref. 2, where the empirical equation, $\ln s_0 = A + 0.0357\,T$, is given for the molal solubility between 25 and 85° in water containing 0.01 m sodium benzoate to repress ionization. If benzoic acid were an ideal solute, the implied enthalpy of solution would have the form $0.0357\,RT^2$, corresponding to a heat capacity difference between solute in infinitely dilute solution and in the pure crystalline state of magnitude $0.142\,T$ cal./mole deg. While the heat capacity of crystalline benzoic acid is 42.5 and that of the pure liquid, 63.2 cal./mole deg. (at the melting point, from data quoted in the "International Critical Tables"), it seems likely that the partial molal heat capacity in dilute aqueous solution is much closer to that of the crystalline solid, since the comparatively high value for the pure liquid no doubt corresponds with extensive dimerization undergoing decrease with rising temperature.

(4) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

(5) This is made clear in the discussion and diagram given by J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 12.

(6) See ref. 4; primes will be used to distinguish symbols based on moles per kilogram of water as concentration measure from corresponding symbols used by Long and McDevit based on moles per liter of solution. The "solvent" in the present instance is actually a 0.01 m aqueous solution of sodium benzoate or sodium phenylacetate, respectively.

From a plot of the quantity ($\log s_0 + \Delta H/2.303RT$) *vs.* s_0, it should be possible to derive the value of k_i' as the negative of the slope of the resulting curve, the plot being linear if in addition to the conditions previously assumed, it turns out that k_i' itself is practically constant with temperature. Such a plot for benzoic acid, with ΔH = 6500 cal./mole,[7] is presented in Fig. 1, based on the solubility data of Morrison[1] and of Ward and Cooper.[8] One sees that between 25° (the lowest temperature included) and 85°, the plot is indeed quite linear, the two highest points, at 88.3 and 88.6°, respectively, showing a trend away from linearity.

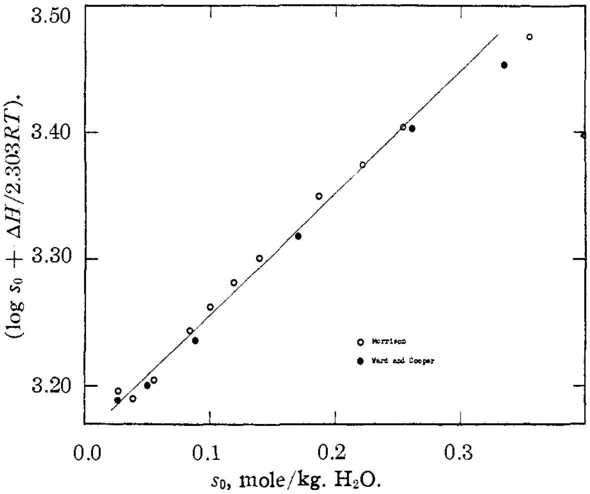

Fig. 1.—($\log s_0 + \Delta H/2.303\ RT$) *vs.* s_0 for benzoic acid in water: ○, Morrison; ●, Ward and Cooper.

From the slope of the linear relationship indicated by Fig. 1, we obtain a value of the self-interaction parameter k_i' for benzoic acid of about −0.96. This value may seem rather large as compared for example with the value of −0.25 for mandelic acid derived by McDevit and Long (using a different principle),[9] but independent evidence is available from boiling point elevation data reported by Peddle and Turner.[10] These authors, working with benzoic acid concentrations in the range 0.5–0.6 *m*, discovered enormous deviations from ideal behavior, such as to lead them in fact to the conclusion that the solute was practically completely associated into dimeric molecules. This conclusion is at variance with the essentially ideal behavior actually shown by benzoic acid in dilute aqueous solutions toward ionization equilibria and partition with other non-aqueous liquid phases; if extensive dimerization existed in 0.5 *m* solutions, the law of mass action would call for a still appreciable degree of association even in 0.01 *m* solutions, quite contrary to experience. But while the boiling point elevation data cannot be fitted precisely by means of a simple linear equation such as eq. (2) representing the deviation from ideality, yet the indicated activity coefficients do have magnitudes consistent with k_i' values of order −0.9. By contrast, the behavior of mandelic acid is almost ideal.[10]

When ΔH values are lacking, as seems to be the case for phenylacetic acid, we may still fit a three-constant equation of the form

$$\log s_0 = -k_i's_0 - (A/T) + C \qquad (5)$$

to the solubility data; the best value so found for the constant A then represents the mean value of $\Delta H/2.303R$ over the given temperature range, assuming of course that eq. (2) correctly represents the form of the deviation from ideal behavior. Applying this method to Morrison's solubility data for phenylacetic acid,[1] we find for the solid, which melts under water at 47°, that from just three experimental points (at 25, 35 and 45°), $k_i' = -0.59$ and ΔH = 5520 cal./mole; it is noteworthy that even over such a short interval of temperature, $\log s_0$ itself departs significantly from linearity as a function of $1/T$. From six experimental points for the liquid ranging between 41 and 87°, we obtain by the method of least squares, $k_i' = -0.57$ and ΔH = 1745 cal./mole. The agreement between the k_i' values indicated by the two sets of data is excellent, and Fig. 2, in which ($\log s_0 - 0.58s_0$) is plotted against $1/T$ for both solid and liquid, shows how well eq. (5) fits the data with k_i' assigned the average value, −0.58. It is gratifying to note that boiling point elevation data for this compound in aqueous solutions at concentrations

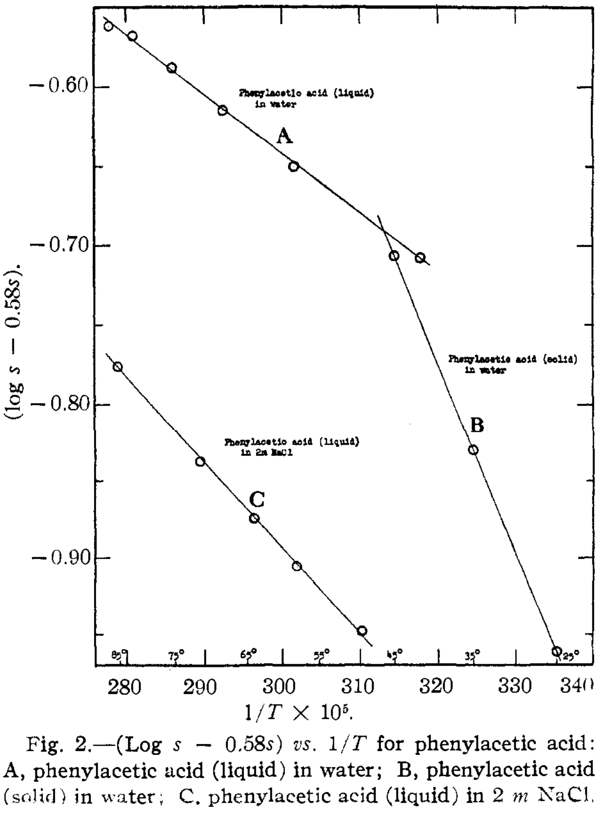

Fig. 2.—($\log s - 0.58s$) *vs.* $1/T$ for phenylacetic acid: A, phenylacetic acid (liquid) in water; B, phenylacetic acid (solid) in water; C, phenylacetic acid (liquid) in 2 *m* NaCl.

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[7] "International Critical Tables," from direct calorimetric investigation at 20° by M. Berthelot.

[8] H. L. Ward and S. S. Cooper, *J. Phys. Chem.*, **34**, 1484 (1930). These data in pure water, after correction for ionization, are in substantial agreement with those of Morrison in 0.01 *m* sodium benzoate solutions; the data in ref. 2 are in agreement at the lower temperatures, but deviate in the direction of lower solubilities at the higher temperatures.

[9] W. F. McDevit and F. A. Long, THIS JOURNAL, **74**, 1090 (1952).

[10] C. J. Peddle and W. E. S. Turner, *J. Chem. Soc.*, **99**, 685 (1911); the data were corrected by the authors for the slight but not insignificant volatility of the solute.

between 0.4 and 0.7 m are consistent with a k_i' value of order -0.6,[10] though as in the case of benzoic acid, it is not possible to fit the data exactly by means of a linear deviation function such as is described by eq. (2). The difference between the indicated ΔH values for solid and liquid agrees quite well with the latent heat of fusion of pure phenylacetic acid, 3890 cal./mole, derived from its cryoscopic constant at the normal melting point.[11]

These results have an important bearing on the interpretation of salt effects. For benzoic acid, the solubility at 25° is sufficiently low (0.027 mole/kg. H_2O) so that self interaction cannot be very influential at that temperature, the indicated value of the molal activity coefficient in the saturated aqueous solution being 0.94. For phenylacetic acid, the value of 0.84 (corresponding with solubility of 0.130 mole/kg. H_2O) deviates sufficiently from unity, however, to cast doubt on the applicability of the Setschenow equation, eq. (1), or at least on the interpretation of K' in that equation as the true salting-out parameter for the electrolyte. For both benzoic and phenylacetic acids, self interaction must have a profound effect on the temperature coefficients of salt effects, as is indeed indicated by the abnormal increase previously mentioned in the apparent effects of salts on the solubilities at the higher temperatures.[1,2]

Long and McDevit[4] have shown that in cases of this kind, one may often represent the activity coefficient of the non-electrolyte in the form

$$\log \gamma' = k_i' m_i + k_s' m_s \qquad (6)$$

where k_s' represents the true salting-out parameter for the electrolyte, while the other symbols have the same significance as before. In this generalization of eq. (2), it is assumed essentially that k_i' and k_s' are independent of each other, or what amounts to the same thing, that terms involving $m_i m_s$ as well as terms involving higher powers of m_i and m_s in the series expansion of log γ' may be neglected. It follows that in the saturated solutions

$$(\log s_0 + k_i' s_0) - (\log s + k_i' s) = k_s' m_s \qquad (7)$$

If k_i' has been established, one may readily apply this equation to evaluate k_s' from solubility data.

Applying eq. (7) to Morrison's solubility data for benzoic and phenylacetic acids,[1] using the k_i' values previously derived, one obtains k_s' values for different electrolytes which are indeed quite independent of the electrolyte's concentration. This is shown by the data for phenylacetic acid in NaCl solutions plotted in Fig. 3. It should be recalled that a plot of log (s_0/s) itself against m_s, as suggested by eq. (1), is definitely not linear, particularly at the higher temperatures. Figure 2 shows how well (log $s + k_i's$) for a particular salt concentration conforms to a straight line when plotted against $1/T$; the negative of the slope in this case, multiplied by $2.303R$, evidently represents the enthalpy of solution at infinite dilution in the salt solution of given concentration. The data for benzoic acid in solutions of NaCl, the only electrolyte for which Morrison reports more than one salt concentration for this solute, do not conform so well at 25° to the linear form (7) as his data for phenylacetic acid, but the indicated experimental error is of order ±0.02 unit in log s;[12] at higher temperatures, where the higher solubilities reduce the relative experimental error, eq. (7) appears to give an entirely satisfactory account of the data.

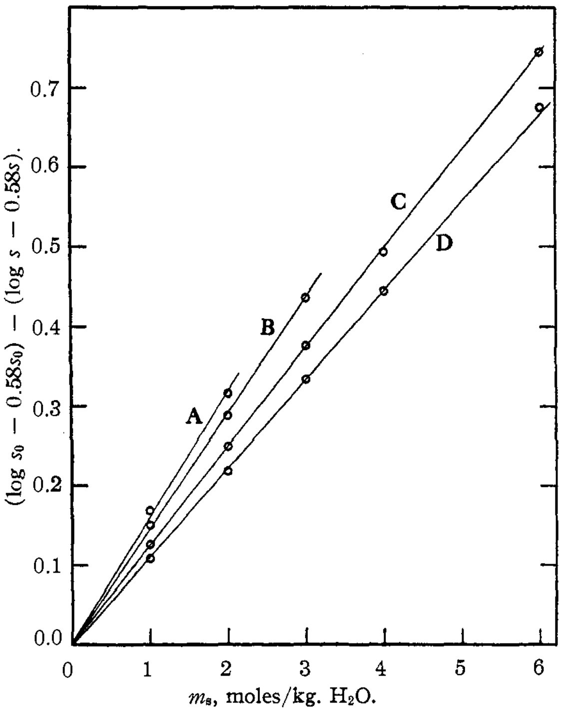

Fig. 3.—$(\text{Log } s_0 - 0.58s_0) - (\log s - 0.58s)$ *vs.* m_s for phenylacetic acid in aqueous NaCl solutions: A, 25°; B, 45°; C, 65°; D, 85°.

Table I summarizes average k_s' values so derived for the electrolytes studied by Morrison.[1] One sees that with the possible exception of KNO_3, for which the salt effects are very small and therefore subject to large relative error, the salting-out parameters show what appears to be the normal gradual decrease with increasing temperature. One sees furthermore that there is little difference between the salting-out parameters for the two non-electrolytes. While the data of Bockris, Bowler-Reed and Kitchener for the salting-in of benzoic acid by tetraethylammonium iodide[2] are not given in sufficient detail to permit calculation, there appears to be no doubt that self interaction is sufficient to account for the marked increase they observed in the apparent effect of the salt between

TABLE I

SALTING-OUT PARAMETER, k_s', AT t, °C.

Salt	25	35	45	55	65	75	85
			Benzoic acid				
NaCl	0.160	0.151	0.143	0.135	0.129	0.122	0.116
KCl	.123	.117	.112	.106	.102	.097	.092
NH_4Cl	.098	.087	.076	.066	.057	.047	.039
KNO_3	.011	.017	.023	.029	.034	.039	.043
			Phenylacetic acid				
NaCl	0.162	0.151	0.143	0.133	0.124	0.117	0.110
KCl	...	...	.103	.097	.091	.087	.081
$NaNO_3$	...	...	.058	.054	.050	.047	.043
KNO_3	...	...	.026	.027	.027	.026	.026

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[11] "International Critical Tables."

[12] The data of other authors at this temperature, however, apparently conform quite well with the Setschenow equation, eq. (1); for references, see ref. 4.

60 and 85° as compared with the much smaller increase between 25 and 50°.

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A New Synthesis of *n*-Heptafluoropropyl Grignard Reagent

BY O. R. PIERCE, A. F. MEINERS AND E. T. MCBEE

RECEIVED FEBRUARY 6, 1953

The synthesis and reactions of *n*-heptafluoropropylmagnesium iodide have been reported in recent literature,[1-3] and in all cases the Grignard reagent was prepared by reaction of 1-iodoheptafluoropropane with magnesium metal. In this Laboratory, a Grignard reagent has been prepared in good yield from this iodide by reaction with phenylmagnesium bromide in diethyl ether at 0–10°. The reagent obtained was found to give a normal addition reaction with acetone in high yield, employing simultaneous addition of the phenyl Grignard reagent and acetone to a solution of the iodide. A study of the scope of this rather unusual Grignard exchange reaction is in progress.

Experimental

In a typical experiment, a 3-necked round bottom flask was equipped with a mercury-sealed Hershberg stirrer and two closed circuit addition funnels. A mercury bubble counter and Dry Ice-cooled vapor traps were attached to one of the addition funnels and dry nitrogen was introduced through the other. The flask was flamed with a Bunsen burner and, on cooling, 59.2 g. (0.2 mole) of 1-iodoheptafluoropropane in 250 ml. of anhydrous ether was added to the flask. The flask and contents were then cooled by means of an ice-water bath. Into one of the addition funnels was placed 110 ml. of 1.88 *M* phenylmagnesium bromide (0.207 mole) in ether, and into the other was placed 17.4 g. (0.3 mole) of acetone (commercial grade, 99%) in an equal volume of anhydrous ether. The Grignard reagent and the acetone were then added simultaneously to the ether solution of 1-iodoheptafluoropropane. A white flocculent precipitate formed as soon as a few drops had been added. The addition was conducted over a period of four hours and the reaction mixture was stirred at ice-bath temperatures for an additional eight hours. The reaction mixture was then light yellow in color and contained a considerable quantity of the white flocculent material. No escaping gas was observed and no material condensed in the vapor trap.

The reaction mixture was then hydrolyzed with 300 ml. of ice-cold 10% sulfuric acid. The solid completely dissolved and the mixture was separated into two sharply divided portions. The ether layer was separated and washed once with water. The water layer was extracted three times with ether and the ether portions were combined and dried with Drierite. The ether was distilled through a short column (14 mm. barrel, stainless steel, "heli-pak" packing) and the residue was rectified through the same column. After a short forerun (2–3 cc.), 29.6 g. of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol[1-3] boiling at 107–108° was obtained, representing a 65% yield based on the 1-iodoheptafluoropropane. Also, 33.8 g. of iodobenzene was formed, which raises to 83% the accounting of the 1-iodoheptafluoropropane.

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[1] O. R. Pierce and M. Levine, THIS JOURNAL, **73**, 1254 (1951).

[2] A. L. Henne and W. Francis, private communication.

[3] R. N. Haszeldine, *J. Chem. Soc.*, 3423 (1952).

The Fluoroplatinates. I. Lanthanum, Cerium, Praseodymium and Neodymium Fluoroplatinates

BY THEODORE P. PERROS[1] AND CHARLES R. NAESER

RECEIVED JANUARY 9, 1953

During the investigation of the effect of fluorine on certain rare earth fluorides, the reaction between fluorine, platinum and a rare earth fluoride was noted. The product was determined to be the fluorine analog of the chloroplatinates, namely, a fluoroplatinate. This is the first of a series of papers dealing with the preparation and properties of compounds containing the fluoroplatinate ion.

Of the platinum complexes having the general formula $(PtX_6)^{-2}$ in which X is a halogen, a number of compounds have been prepared which contain either chlorine, bromine or iodine as X. With regard to fluorine, there is only one original reference citing the preparation and properties of a compound containing the complex $(PtF_6)^{-2}$. This is the work of Schlesinger and Tapley[2] who prepared K_2PtF_6. This compound was formed by heating finely divided platinum with $3KF \cdot HF \cdot PbF_4$ in a platinum boat. Their efforts to prepare other fluoroplatinic salts were unsuccessful.

In this investigation the fluoroplatinates of lanthanum, cerium, praseodymium and neodymium were prepared and some of their physical properties determined. The rare earth fluoroplatinates were prepared by treating an intimate mixture of platinum and the respective fluoride with elemental fluorine at 525°.

Experimental Methods and Materials

Rare Earth Fluorides.—The rare earth oxides from which the rare earth fluorides were prepared, were a part of the Welsbach collection. Only trace amounts of the neighboring rare earth elements were found in each respective rare earth oxide. The rare earth trifluorides were prepared by precipitation from rare earth chloride solutions with hydrofluoric acid. Absolute alcohol was used to wash the precipitates.

Platinum.—The platinum foil from which the platinum boats were fashioned was 0.0015 inch thick. The boat had the dimensions 4.8 cm. × 1.0 cm. × 0.7 cm.

Fluorine.—Fluorine was prepared by the electrolysis of molten potassium bifluoride. The fluorine generator was constructed according to the description given by Von Wartenburg.[3] The anode was made of carbon.

Reaction Tube.—Fluorination was carried out in a nickel tube, 14" in length, 7/8" inside diameter and 1/8" in thickness. During the runs, the tube was heated in a calibrated electric combustion furnace. The connections between the nickel tube and the fluorine inlet consisted of plaster of Paris stoppers.

The Rare Earth Fluoroplatinates.—All samples were prepared by identical procedures. A rare earth fluoride was spread evenly in a thin layer on the bottom of a platinum boat. Several strips of platinum foil were placed lengthwise on top of the layer of salts, and then covered with another thin layer of the rare earth fluoride. This process was repeated until the capacity of the boat had been reached. The sample was then placed in the reaction tube. While the tube was being heated to 525°, the system was flushed with dry air. The sample was fluorinated for five hours. In each instance, after the completion of a run, the platinum foil had disappeared in the formation of the fluoroplatinate. The rare earth fluoroplatinates are soluble in water and thus

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[1] Abstracted from a portion of the thesis submitted by Theodore P. Perros in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] H. Schlesinger and M. Tapley, THIS JOURNAL, **46**, 276 (1924).

[3] H. Von Wartenburg, *Z. anorg. allgem. Chem.*, **244**, 377 (1940).