

that the melting point of the salt determines approximately the span of the curve), and the maximum vapor pressure is determined by the temperature coefficient of solubility, particularly in the first half of the temperature range. Thus for salts such as sodium iodide, where there is a marked increase in solubility with temperature in the region 100–300°, the maximum vapor pressure is low; for sodium chloride, when the rate of increase of solubility is relatively small, the maximum pressure is high; whereas for potassium chloride which exhibits an intermediate temperature coefficient, a moderate maximum vapor pressure is found.

The similarity in behavior of these inorganic systems is brought out by the curve showing similar negative deviation from Raoult's law (Fig. 10). Although the deviation from the straight line is appreciable in the plot of  $p/p_0$  for water against the mole fraction,  $N$ , for salt most of the points fall on a smooth curve showing that changes in water vapor pressures at high temperatures are determined largely by mole fraction.

If melting point and solubility curves (Fig. 1) are examined approximations may be made of the positions of the curves for saturated solutions in the  $P$ - $T$  system. Such a survey indicates several salts as unclassifiable. It, therefore, seems desir-

able that further work be done on such salts as magnesium sulfate and sodium fluoride to determine whether critical phenomena obtain (Class I) or the vapor pressure curves are continuous (Class II).

### Summary

1. Vapor pressure data within the temperature range 150–650° are reported for saturated aqueous solutions of sodium chloride, sodium bromide, sodium iodide, potassium chloride, and potassium iodide, together with some data for sodium sulfate, sodium carbonate, calcium nitrate, boric oxide, and for a mixture of potassium chloride and sodium bromide.

2. Critical conditions near the critical point for water are confirmed for sodium carbonate, and for sodium sulfate.

3. Continuous curves are obtained for saturated solutions of highly soluble salts, showing maximum vapor pressures (up to 390 atmospheres for sodium chloride at 550°) at temperatures intermediate between the triple points of water and of salt, and no critical region.

4. The maximum vapor pressure appears to be less, the greater the initial temperature coefficient of solubility, and the lower the melting point of the salt.

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## Radio Halogen Exchanges in the Phosphorus Halides

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### Introduction

In several cases radio indicators have been used in a qualitative way for the determination of bond equivalence or non-equivalence. Using radiobromine, Roginsky and Gopstein<sup>1</sup> came to the conclusion that the two bromine atoms in solid cupric bromide are not equally reactive. Grinberg and Filinov<sup>2</sup> as a result of their exchange work concluded that probably the bromine bonds in  $K_2PtBr_4$  and  $K_2PtBr_6$  are equivalent, and Andersen<sup>3</sup> proved that the sulfur atoms in thio-

sulfate ion are not equivalent. It is of considerable interest to investigate halogen exchanges in the phosphorus halides, especially the case of phosphorus pentachloride, since some investigations<sup>4</sup> seem to indicate that the bonds are not all equivalent, at least not in the gas phase. It was decided to study these investigations in solution, and carbon tetrachloride was considered a convenient solvent to work in, since the amount of dissociation of the pentahalides in this solvent can be estimated from existing literature.<sup>5</sup>

### Experimental

**Materials.**—Phosphorus tribromide was made by dropping bromine on phosphorus under carbon tetrachloride

\* This work constitutes a portion of a thesis to be submitted by W. Koskoski in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the Johns Hopkins University.

(1) S. Roginsky and N. Gopstein, *Physik. Z. Sowjetunion*, **7**, 672 (1935).

(2) A. A. Grinberg and F. M. Filinov, *Compt. rend. acad. sci. U. R. S. S.*, **23**, 912 (1939).

(3) E. B. Andersen, *Z. physik Chem.*, **B32**, 237 (1936).

(4) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 109.

(5) J. H. Kastle and W. A. Beatty, *Am. Chem. J.*, **21**, 392 (1899); S. U. Pickering, *Ber.*, **24**, 1469 (1891).

and the tribromide was then purified by distillation. The tri- and pentachlorides of phosphorus used in this work were simply distilled from stock reagents, and in some of the cases the pentachloride was made from pure trichloride and chlorine. The carbon tetrachloride was dried over phosphorus pentoxide, and it was filtered and distilled just before use. The radiochlorine and bromine were made by bombarding chloroform and *n*-butyl bromide, respectively, with slow neutrons from the deuterium-deuterium disintegration apparatus in this Laboratory. After irradiation the activity was extracted with water containing a trace of carrier and this aqueous solution was evaporated to a small volume. In the case of radiobromine, the solution was permitted to stand for forty-eight hours or longer, so that only the thirty-four hour activity remained in appreciable amount. This solution containing the activity was acidified with sulfuric acid to suppress the hydrolysis of the halogen, and it was then shaken up with a solution of the desired halogen in carbon tetrachloride. Since the exchange between halide ion and halogen is fast, the activity was rapidly transferred to the halogen in the carbon tetrachloride solution. The solution containing the radio-halogen was then separated from the water and dried with anhydrous calcium sulfate or in some cases with phosphorus pentoxide.

**Procedure.**—Equal volumes of solutions of known concentrations were mixed in a reaction vessel and at measured time intervals samples were pipetted out and the halogen was pumped off. The phosphorus halide was hydrolyzed in basic solution and then acidified with nitric acid. The resulting halide ion was then determined by the Volhard method. The concentration of the halogen in the carbon tetrachloride solution was determined by converting the halogen to the halide ion by shaking with an alkaline solution of sodium nitrite. The halide ion was then determined by the Volhard method. The precipitates containing the activity were then collected on one-inch filter papers in a Hirsch funnel, washed with water, acetone, dried, mounted and examined for activity. In each case about equal amounts of silver halide were present so that the absorptions were about the same. The activities were measured with a ball point counter having a flat mica window, 2.86 cm. in diameter and with a thickness of 3.2 mg./sq. cm. The filter papers were mounted on flat glass plates which could be placed about 4.8 mm. below the mica window in an exactly reproducible position. The counter was surrounded with about 5 cm. of lead on all sides and gave a background of about fifteen counts per minute. A high speed scale-of-eight circuit of the type described by Lifschutz<sup>6</sup> was used with the counter.

The separation of the chlorine or bromine from the phosphorus halide was also made with mercury. Bromine and chlorine react rapidly with mercury, whereas the phosphorus trihalides react slowly. Phosphorus pentachloride reacts with mercury to give the trichloride and mercury chloride. The mercury halide could then be filtered off and the trihalide could be hydrolyzed, analyzed for activity and halide ion concentration.

### Results

Table I is an example of the typical results obtained in the exchange between phosphorus

(6) H. Lifschutz, *Rev. Sci. Instruments*, **10**, 21 (1939).

halides and radio halogens in carbon tetrachloride solution at 23°. The first and second columns give the time in minutes and activities in counts/min. found in the case of the phosphorus tribromide-radiobromine exchange. The concentration of the tribromide was 0.0309 *M* and that

TABLE I

<i>t</i> , min.	PBr <sub>3</sub> Counts/ min.	<i>t</i> , min.	PCl <sub>3</sub> Counts/ min.	<i>t</i> , min.	PCl <sub>5</sub> Counts/ min.
0	355	0	330	0	440
3.2	199	5	174	2.5	180
10.7	197	10	166	12.5	190
30	191	27.5	170	25	175

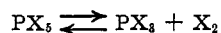
of the bromine was 0.0404 *M*. The table gives the activities as found in the tribromide at the recorded times. The activity recorded under zero time is the total activity in any one sample. The separations were made by pumping off the bromine and also by using mercury to remove the bromine. The results were the same in each case. The average of the ratios of the activity in the phosphorus tribromide to that in the bromine is 1.23 whereas the ratio as predicted from the concentrations of the amount of halogen in each compound is 1.15. Therefore it is apparent that the exchange in this case is rapid and complete in less than three minutes.

The third and fourth columns of Table I give the corresponding results for phosphorus trichloride and radiochlorine exchange. The concentration of the phosphorus trichloride was 0.0421 *M* and that of the chlorine was 0.0589 *M*. The predicted ratio is 1.07 and the average value obtained from the ratio of the activities was 1.06, indicating again that the exchange is rapid and complete.

The fifth and sixth columns give the results for the pentachloride-chlorine exchange. The activity recorded is that found in the phosphorus trichloride after the mercury treatment. The concentration of the pentachloride was 0.0276 *M* and the chlorine was 0.0295 *M*. The predicted ratio is 1.40 whereas the average of the values found is 1.34. Again the exchange is rapid and complete.

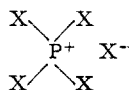
### Discussion of Results

The phosphorus pentahalides are known to be dissociated in solution



the pentabromide being dissociated to a much greater extent under comparable conditions than

the pentachloride. The exchange proceeds through this equilibrium and if the bonds are not equivalent one might expect in an extreme case to have complete exchange of two halide atoms and none on the other three, or one might expect the two halide atoms to exchange at different rates from the other three. However, if the exchange is rapid and complete, the five halide atoms are probably equally reactive. There is still the possibility that the halide atoms are exchanging at different rates which are too fast to measure. The observation of a rapid exchange would be in harmony with Pauling's interpretation of the  $PX_5$  structure for if there are five resonating forms where the four covalent bonds resonate among the five positions, making all bonds in the molecules equivalent in bond type



one would expect the exchange to be very rapid, in fact, too rapid to be measured by ordinary means. The present measurements indicate that the exchanges between radiochlorine and the phosphorus tri- and pentachlorides and between

radiobromine and phosphorus tribromide are rapid and complete in less than three minutes, and hence it may be concluded that in carbon tetrachloride solution when  $PX_3$  reacts with  $X_2$  the two new bonds formed probably do not differ in reactivity from the other three.

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### Summary

Exchanges between radiobromine and phosphorus tribromide, between radiochlorine and phosphorus trichloride and between radiochlorine and phosphorus pentachloride have been studied in carbon tetrachloride solution. All of the exchanges studied were found to be rapid and complete in less than three minutes, and the conclusion was drawn that five halide atoms in phosphorus pentachloride and pentabromide are probably all equally reactive.

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## Reactions Involving Oxygen, Amalgams and Hydrogen Peroxide

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As in many analogous cases, hydrogen peroxide is formed from molecular oxygen when base-metal amalgams are shaken with acid solutions in contact with air. The hydrogen peroxide thus formed can be reduced to water by these amalgams; and the possibility of this reaction warrants the belief that *steady states* ought to be established, in which hydrogen peroxide disappears as rapidly as it is formed—thus remaining at constant concentration, while oxygen and the base metal are consumed. Reaction systems of this kind have been investigated briefly as a natural sequel to recent studies of the reactivities of amalgams<sup>1</sup>; the results, though admittedly incomplete, are presented here as an invitation to further investigation.

In all oxygen experiments, approximately 25 cc. of amalgam was shaken with 40 or 50 cc. of 1

*N* sulfuric or perchloric acid in contact with air. Amalgam concentrations were calculated from measured electromotive forces. Hydrogen peroxide was determined spectrophotometrically as peroxytitanic acid. When necessary, the separatory funnel was opened to the air at suitable intervals to replenish the oxygen consumed.<sup>2</sup>

**Stoichiometry.**—A few experiments in stoichiometry were carried out by way of orientation: 0.001% amalgams were shaken to exhaustion, whereupon the hydrogen peroxide formed was determined. The ratio of the metal consumed to hydrogen peroxide produced (both expressed in equivalents) could then be calculated, for the metal initially present in the amalgam was known. When this ratio is unity, stoichiometric reduction of oxygen to hydrogen peroxide has evidently occurred; the more this ratio exceeds unity, the greater the proportion of oxygen that has been

(1) (a) Liebhafsky, *THIS JOURNAL*, **59**, 452 (1937); (b) Liebhafsky and Winslow, *ibid.*, **63**, 3137 (1941).

(2) For complete experimental details, see refs. 1a and 1b.