but sufficient hydrolysis is caused by atmospheric moisture so that the odor of phosphine may be observed.

A sample of high purity aluminum phosphide reacts readily with water to release phosphine and with acid or alkaline solutions the reaction rate is higher. Ordinarily the evolved gas does not ignite spontaneously in the air as does the impure phosphine generated from hot, concentrated alkaline solutions reacting with yellow phosphorus. The ignition temperature is low—about 100°—however, and combustion of the gas is easy to initiate. When small portions of the phosphide are dropped onto the surface of aqua regia, explosive reaction and combustion of evolved gases occur. When the vapors above the aqua regia become rich in the fumes from the acid mixture and air is excluded, dissolution of the phosphide is not accompanied by the pyrotechnics which otherwise occur. Aluminum phosphide is decomposed by dry hydrogen chloride so that this reagent cannot be used to remove elemental aluminum from an aluminum phosphide preparation. The simultaneous evolution of phosphine and aluminum chloride from interaction of hydrogen chloride and the phosphide results in the formation of yellow to orange deposits which may be of the solid phosphorus hydrides as previously described.[11]

Summary

Five different binary combinations of aluminum and phosphorus have been reported in the literature. Evidence is presented in this paper to support the belief that only the one compound, AlP, exists and that the previously reported products have been mixtures of AlP with free aluminum and aluminum oxide. An analytical procedure has been used which permits determination of phosphide phosphorus, free aluminum, and total aluminum. Preparations have been made with over 90% AlP. Aluminum phosphide is dark gray to yellowish-gray in color, crystalline, and it does not melt nor thermally decompose at temperatures up to 1000°. It is readily hydrolyzed and reacts with water, acids, or bases to give phosphine.

NEW KENSINGTON, PA. RECEIVED JULY 24, 1944

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF INDIANA UNIVERSITY]

Isotonic Solutions: Activity Coefficients of Sodium Bromate and Potassium Chlorate

BY JAMES HOMER JONES AND H. R. FRONING[1]

Physical measurements on aqueous solutions of sodium bromate are very limited. No measurements of activity coefficients by any method were revealed by the literature search. Scatchard[1a] and co-workers have determined the activity coefficients of potassium chlorate in aqueous solution from freezing point measurements. The solubility of the saturated solution is only about 0.25 molal at the freezing point, whereas, it is 0.7000 molal[2] at 25°.

This investigation was undertaken to obtain the activity coefficients of sodium bromate and potassium chlorate in aqueous solution at 25°. The method and apparatus have been described in an earlier paper.[3]

Experimental

Purification of Materials: Sodium Chloride.—This has been described previously.[3]

Sodium Bromate and Potassium Chlorate.—Reagent grade sodium bromate and potassium chlorate were recrystallized from conductivity water. The hot solutions were filtered through sintered glass filters to remove any insoluble material. Two successive crops of crystals were collected from each solution. The salts were partially dried in an oven at 100°, the lumps broken up, and the drying completed in a vacuum desiccator over solid potassium hydroxide.

Preparation of Solutions.—All solutions were made up directly by weight. The samples of the salt were always reheated for two to three hours before they were weighed. The samples were weighed in two ways. Part of the samples were weighed into the cups from weight burets. In the other cases, 2 ml. of the solution was pipetted into the weighed cups and the cups covered and immediately reweighed. The precision in weighing was at least ±0.5 mg.

Data Obtained

The concentrations of solutions of sodium bromate and potassium chlorate that were isotonic with solutions of sodium chloride of known molality were determined from about 0.2 molal to saturation of the least soluble salt. The results are collected in Table I. In this table, R_0 refers to the observed ratios of M_{NaCl}/M_x, M_x to the molality of either sodium bromate or potassium chlorate, and R_s to the ratios above as read from a smoothed curve through the experimental points. The fourth column gives the difference between the observed ratios and the smoothed curve value corresponding. The deviations from the smoothed curve are seen to be well within the allowable experimental error. The concentration of sodium bromate or potassium chlorate isotonic with the concentration of sodium chloride listed can be obtained readily by dividing column 1 by the corresponding ratio given in column 2.

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[1] Taken from a thesis submitted to the Graduate School, Indiana University, in partial fulfillment of the requirements for the degree of Master of Arts.

[1a] Scatchard, Prentiss and P. T. Jones, THIS JOURNAL, **56**, 805 (1934).

[2] Swenson and Ricci, *ibid.*, **61**, 1974 (1939).

[3] J. H. Jones, *ibid.*, **65**, 1353 (1943).

TABLE I

RATIOS OF CONCENTRATIONS THAT ARE ISOTONIC

Concn. of NaCl	R_0	R_s	$R_s - R_0$
	Sodium Bromate		
0.2232	0.9652	0.9666	+0.0014
.4386	.9430	.9428	− .0002
.5184	.9343	.9345	+ .0002
.5163	.9330	.9343	+ .0013
.5950	.9264	.9260	− .0004
.7134	.9145	.9138	− .0007
.9777	.8877	.8869	− .0008
1.0181	.8816	.8819	+ .0003
1.3771	.8487	.8495	+ .0008
1.4622	.8432	.8431	− .0001
1.5058	.8408	.8397	− .0011
1.5270	.8383	.8382	− .0001
1.6660	.8285	.8283	− .0002
1.7457	.8224	.8229	+ .0005
1.7906	.8202	.8200	− .0002
2.0701	.8020	.8020	± .0000
	Potassium Chlorate		
0.2043	0.9566	0.9565	+0.0001
.2459	.9486	.9478	+ .0008
.3910	.9164	.9168	− .0004
.4321	.9093	.9078	+ .0015
.4210	.9091	.9107	− .0016
.5354	.8875	.8862	+ .0013
.5641	.8777	.8800	− .0023

Treatment of Data

The osmotic coefficients were calculated from experimental data using the equation $\phi(\text{X}) = \phi(\text{NaCl})M(\text{NaCl})/M(\text{X})$, where ϕ is the osmotic coefficient and M the molality of the isotonic solutions. The values for sodium chloride are those of Scatchard, Hamer and Wood.[4] A large scale plot was used to obtain values at rounded concentrations.

The activity coefficients were evaluated by two independent methods. The original equation of Robinson and Sinclair[5] was used. In this equation, r refers to the reference salt (sodium chloride) and x refers to either sodium bromate or potassium chlorate. The activity coefficients were also evaluated by the graphical integration of the equation

$$\log \gamma_x = \log \gamma_r + \log \frac{M_r}{M_x} + \frac{2}{2.3026} \int_0^{a_r^{1/2}} \frac{\frac{M_r}{M_x} - 1}{a_r^{1/2}}\, \mathrm{d}\, a_r^{1/2} \quad (1)$$

$$-\ln \gamma_{\pm} = (1 - \phi) + 2 \int_0^m \frac{(1 - \phi)}{M^{1/2}}\, \mathrm{d}\, M^{1/2} \quad (2)$$

as outlined by Harned and Owen.[6] The extrapolation of this equation was based on an a-parameter of 3.5 Å. for potassium chlorate and 4.1 Å. for sodium bromate as evaluated from the experimental data at the lower concentrations.

The activity coefficients and osmotic coefficients are tabulated in Table II.

TABLE II

ACTIVITY[a] AND OSMOTIC COEFFICIENTS

Molality	Sodium Bromate ϕ	Sodium Bromate $\gamma(1)$	Sodium Bromate $\gamma(2)$	Potassium Chlorate ϕ	Potassium Chlorate $\gamma(1)$	Potassium Chlorate $\gamma(2)$
0.2	0.8981	0.696	0.692	0.8876	0.681	0.678
.3	.8851	.656	.654	.8677	.634	.632
.4	.8749	.628	.625	.8499	.598	.596
.5	.8663	.605	.602	.8333	.568	.566
.6	.8585	.586	.583	.8173	.542	.540
.7	.8519	.570	.566	.8017	.519	.516
.8	.8456	.555	.551		(satd.)	
.9	.8396	.542	.538			
1.0	.8352	.529	.526			
1.2	.8239	.506	.504			
1.4	.8152	.488	.486			
1.6	.8063	.470	.469			
1.8	.8000	.458	.456			
2.0	.7965	.446	.445			
2.2	.7931	.437	.435			
2.4	.7904	.428	.426			
2.6	.7883	.419	.418			
2.612 (satd.)	.7881	.418	.418			

[a] The numbers after γ refer to equations 1 and 2, respectively.

Discussion of Data

The data on potassium chlorate are not as consistent as those for sodium bromate. A straight line seems to be the best line that can be drawn

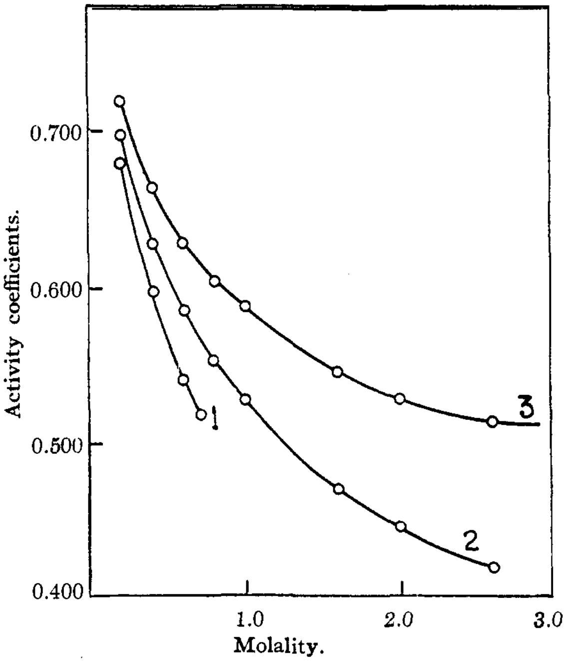

Fig. 1.—Activity coefficients *vs.* Molality: Curve 1, $KClO_3$; Curve 2, $NaBrO_3$; Curve 3, $NaClO_3$ (see ref. 3).

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(4) Scatchard, Hamer and Wood, THIS JOURNAL, **60**, 3069 (1938).

(5) Robinson and Sinclair, *ibid.*, **56**, 1830 (1934).

(6) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 292.

through the experimental points. The value for the activity coefficient of potassium chlorate at 0.2 molal of Scatchard and co-workers[1a] from freezing point data is 0.665. Our values at 0.2 molal and 25° are 0.681 and 0.678 from equations (1) and (2), respectively. This difference is of the correct order of magnitude.

The values for the activity coefficients of sodium bromate and potassium chlorate at 0.2 molal from equation (1) are about 0.5% higher than those yielded by equation (2). This agreement is considered satisfactory.

The solubility of sodium bromate at 25° was determined after the method proposed by Scatchard.[1a] A mean value of 2.612 molal was found. The solubility calculated from the work by Ricci[7] is 2.614 molal. The two values are probably within experimental error of the two measurements.

The general trend of the activity coefficients with concentration can be shown by means of a graph of activity coefficients *vs.* molality. Such a graph is shown in Fig. 1.

Summary

The concentrations of isotonic solutions of sodium bromate–sodium chloride and potassium chlorate–sodium chloride were determined from about 0.2 molal to saturation.

The solubility of sodium bromate in water at 25° was measured.

From the observed molalities and ratios of the isotonic solutions the activity coefficients and osmotic coefficients were calculated by comparison with sodium chloride.

BLOOMINGTON, IND. RECEIVED APRIL 21, 1944

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[7] Ricci, THIS JOURNAL, **56**, 303 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF EMORY UNIVERSITY]

The Addition of 4-Mercaptobiphenyl to a Series of 1-Olefins

BY CHARLES T. LESTER, GEORGE F. RODGERS[1] AND E. EMMET REID

The addition of mercaptans to olefins has been investigated in several different laboratories and its mechanism thoroughly discussed.[2] The additions reported have covered a wide range of both olefins and mercaptans. Most of the resulting sulfides have been low melting solids or liquids.

It seemed to us that, if a mercaptan were used which would give high melting sulfides, the sulfides might be of some interest as a means of identification of the olefins. We have found that 4-mercaptobiphenyl[3] gives high melting solids with styrene and olefins from 1-hexene through 1-heptadecene. All of these products are white crystals, easily purified. The identity of each sulfide has been established by a mixed melting point determination with the sulfide obtained by the reaction of mercaptobiphenyl with the corresponding alkyl bromide. The melting points were taken in duplicate in a Hershberg[4] apparatus[5] with a calibrated Anschütz thermometer. The rate of heating was regulated to produce an increase in temperature of one degree every three minutes. The melting points are recorded in Table I.

TABLE I

MELTING POINTS OF ALKYL BIPHENYL SULFIDES

1 Alkyl group	2 Prepared by addition, °C.	3 Prepared by alkylation, °C.	4 2 and 3 mixed, °C.
Hexyl	75.1–75.7	75.4–76.0	74.8–75.7
Heptyl	83.2–83.9	82.5–83.5	82.4–83.5
Octyl	81.8–82.4	82.3–82.9	81.8–82.6
Nonyl	88.4–88.9	88.2–88.7	87.7–88.7
Decyl	87.2–87.5	86.5–87.2	86.8–87.3
Undecyl	92.1–93.0	91.8–92.8	91.8–92.8
Dodecyl	91.1–91.6	91.2–91.7	91.0–91.5
Tridecyl	95.6–96.3	94.5–95.5	95.4–95.9
Tetradecyl	94.2–94.6	94.5–95.2	94.0–94.6
Pentadecyl	98.4–98.8	98.0–98.7	97.9–98.7
Hexadecyl	97.0–97.7	96.7–97.4	96.6–97.3
Heptadecyl	99.7–100.6	100.1–100.9	99.7–100.7
Phenylethyl	78.1–80.2	77.8–80.0	77.4–79.6

The close proximity of the melting points of the members of the series is disappointing. We had hoped these solids might serve as derivatives for the identification of the olefins.

In Table II are recorded mixed melting points of different members of the series. While a defi-

TABLE II

MIXED MELTING POINTS OF HOMOLOGOUS ALKYL BIPHENYL SULFIDES

	°C.
Hexyl and heptyl	74.6–77.0
Octyl and nonyl	79.3–82.8
Nonyl and decyl	83.0–85.4
Decyl and undecyl	87.0–88.5
Undecyl and dodecyl	87.7–89.0
Dodecyl and tridecyl	90.7–92.0
Tetradecyl and pentadecyl	92.0–94.4
Hexadecyl and heptadecyl	96.0–97.5

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(1) Taken from the thesis submitted by George F. Rodgers in partial fulfillment of the requirements for a degree of Master of Science.

(2) (a) Posner, *Ber.*, **38**, 649 (1905); (b) Carothers, THIS JOURNAL, **55**, 2008 (1933); (c) Kharasch, Read and Mayo, *Chem. and Industry*, **57**, 752 (1938); (d) Jones and Reid, THIS JOURNAL, **60**, 2452 (1938); (e) Ipatieff, *et al.*, *ibid.*, **60**, 2737 (1938); **61**, 71 (1939).

(3) Gabriel and Deutsch, *Ber.*, **13**, 386–391 (1880).

(4) Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936).

(5) Loaned to us through the kindness of the Callaway Institute of LaGrange, Georgia.