about eight hours per day for one week, the water (2 liters) being changed each morning. The purpose of the refluxing was the removal of adsorbed and occluded material. The final insoluble product obtained was dried at 110°. Analysis gave 58.07% SrO and 38.78% As_2O_5, and the ratio SrO/As_2O_5, 1.497. This ratio is within the limits of experimental error of the theoretical ratio, 1.502, for the compound $[Sr_3(AsO_4)_2]_3 \cdot Sr(OH)_2$.

Conclusions

1. A phase rule study of the system $SrO-As_2O_5-H_2O$ in the acid range has been made, defining the limits for the existence at 25° of the two acid strontium arsenates.

2. A similar study of the system $PbO-As_2O_5-H_2O$ has determined the conditions for the two acid lead arsenates.

3. A basic strontium arsenate has been prepared giving the ratio, SrO/As_2O_5, corresponding to the formula $[Sr_3(AsO_4)_2]_3 \cdot Sr(OH)_2$.

SEATTLE, WASHINGTON

STUDIES ON HYDRAZINE. THE MOBILITY OF THE HYDRAZINIUM ION AT 25°

BY E. C. GILBERT

Introduction

The conductivity of very few hydrazine salts has been measured, and the mobility of the hydrazinium ion has never been determined accurately. Bredig[1] gives 52 as an approximate value from the conductivity of the chloride. This is shown by the present work to be considerably in error. Two difficulties are met in this problem. In the first place, all hydrazine salts decompose in the presence of platinum black so that polished electrodes must be used. The second and greater difficulty has been the fact that until recently it has been necessary to prepare the salts containing hydrazine and one equivalent of acid by indirect means, generally from those containing two equivalents, and question arises as to the purity of the product. The salts containing two equivalents of acid dissociate almost if not quite completely into the monovalent salt and the free acid, hence are useless from a conductivity standpoint. Perchloric acid and picric acid, however, have been shown to combine directly with hydrazine to form the monovalent salt.[2] Unpublished work by Mr. Eugene Huffman in this Laboratory shows that with these may be included trinitro-m-cresol. This fact and the recent accurate determination of the mobility of the

[1] Bredig, *Z. physik. Chem.*, 13, 212 (1894).

[2] Gilbert, *J. Phys. Chem.*, 33, 1235 (1929).

picrate and trinitro-*m*-cresylate ions by Thomas and Marum[3] affords good opportunity for measurement of the mobility of the monovalent hydrazinium ion.

Experimental Part

Materials.—Hydrazine perchlorate was prepared from the pure acid and base in equivalent proportions and was recrystallized five times from 80–90% alcohol. Analysis showed it to contain one-half molecule of water of crystallization in agreement with previous work of the author. When dried *in vacuo* the salt changes to the anhydrous form.

Anal.   1.3260 g. of $N_2H_5ClO_4 \cdot {}^1/_2H_2O$ in 1 liter of soln. was titrated by the iodic acid method of Bray and Cuy.[4]   Found: 25.00 cc. $\rightleftharpoons$ 18.80, 18.80 and 18.82 cc. of 0.04978 N HIO_3.   Calcd.: 25.00 cc. $\rightleftharpoons$ 18.81 cc.

Hydrazine picrate and trinitro-*m*-cresylate were prepared from the pure base and alcoholic solutions of the acids. The salts were recrystallized twice from alcohol, twice from conductivity water and dried over sulfuric acid. As used the picrate contained one-half molecule of water and the trinitro-*m*-cresylate was anhydrous. Each salt was analyzed by the iodic acid method.

Anal.   2.1973 g. of $N_2H_6OC_6H_2(NO_2)_3 \cdot {}^1/_2H_2O$ in 1 liter.   Found: 25.00 cc. $\rightleftharpoons$ 16.24, 16.24 cc. of 0.05012 N HIO_3.   Calcd.: 25.00 cc. $\rightleftharpoons$ 16.24 cc.   2.8450 g. of N_2H_5-$OC_7H_4(NO_2)_3$ in 1 liter of soln.   Found: 25.00 cc. $\rightleftharpoons$ 20.60, 20.61 cc. of 0.05012 N HIO_3.   Calcd.: 25.00 cc. $\rightleftharpoons$ 20.63 cc.

Sodium picrate was similarly prepared and contained one molecule of water of crystallization.

Potassium perchlorate, "c. p." analyzed, was twice recrystallized from conductivity water and dried *in vacuo*.

Water having a conductivity of 0.5–0.7×10^{-6} rec. ohm was used. This water was practically freed from carbon dioxide by drawing pure air through it and was freshly prepared each day in Pyrex bottles which have contained nothing but conductivity water for four years. It was protected from the atmosphere by soda-lime towers, and its conductivity taken before and after each run in the same manner as the solutions. No measurable change occurred during the time of a run.

Apparatus.—No apparatus of the splendidly accurate type designed and described by Jones and Josephs[5] or Shedlovsky[6] was available so recourse was had to a conventional circular slide wire of the Kohlrausch type together with special tunable head-phones. Resistance boxes with Curtis type coils were used and were intercompared. The accuracy of these instruments was given by the manufacturer as 0.05%. Following the suggestion of Jones and Josephs the bridge was not shielded but care was taken to avoid contact and lead resistance, inductance, etc. The stirring motor of the thermostat was stopped during the taking of a reading. The source of alternating current was a Leeds and Northrup microphone hummer (frequency 1000) which was kept at a distance and shielded. A

[3] Thomas and Marum, *Z. physik. Chem.*, **143**, 191 (1929).

[4] Bray and Cuy, THIS JOURNAL, **46**, 858 (1924).

[5] Jones and Josephs, *ibid.*, **50**, 1049 (1928).

[6] Shedlovsky, *ibid.*, **52**, 1793 (1930).

condenser was placed in parallel with the resistance box in the customary manner. The cell used for the hydrazine salts was of the Washburn pipet type with polished electrodes and showed a constant of 0.3727 rec. ohm. For comparison and for measurement of the conductivity of potassium perchlorate another cell with black electrodes was used. The use of cells of this type introduced probably the largest source of error in the form of the so-called Parker effect, which Jones and Bollinger[7] have shown conclusively to be due to capacitative shunt and inherent in this and all previous work done with the ordinary Washburn type cell, particularly in a water thermostat, due to the design of the cell. This may amount in an extreme case to 0.3%, but certain facts in regard to our work make it seem probable that the error though present was not so great. In the first place, the conductance of potassium chloride solutions as determined in this cell agreed within 0.1% with the values given in the "International Critical Tables."[8] Secondly, our values for sodium picrate coincide exactly with those of Thomas and Marum,[3] and finally it will be noted from Table V that duplicate results were obtained with two cells, one black and the other polished as to electrodes, on the most dilute solution of potassium perchlorate.

The dilution flasks and pipets were calibrated and intercompared. All flasks were of seasoned Pyrex or special resistance glass. The temperature was maintained at $25 \pm 0.02°$ as measured by a Bureau of Standards calibrated thermometer. Water was used as the immersion medium.

Procedure.—A stock solution $0.006 - 0.01\ M$ was freshly prepared for each run and the others made by appropriate dilution. Each dilution was independent of all others. Dilute solutions were made and measured first before any possible contamination of water or stock solution could occur. Good minima were obtained in the range covered and no decomposition of salts was ever found to take place on the platinum electrodes. The cell constant was determined by the use of potassium chloride solutions prepared according to Parker[9] and by intercomparison with the cell of known constant having black electrodes, which was of the ordinary Freas design. As an additional check the conductivity of a series of potassium chloride solutions was determined and also sodium picrate (see above). Following this the conductance of hydrazine picrate, trinitro-*m*-cresylate, perchlorate and potassium perchlorate was measured.

Results

The results are shown in Tables I–V. The equivalent conductivities were plotted against the square root of the concentration and extrapolated

[7] Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

[8] "International Critical Tables," Vol. VI, 1st ed., 1929, p. 234.

[9] Parker and Parker, THIS JOURNAL, **46**, 312 (1924).

to give Λ_0. The theoretical slopes of the curves were calculated from the equation of Onsager[10] for the conductivity of a binary electrolyte of valence "z."

$$\Lambda_v = \Lambda_0 - \left(\frac{8.18 \times 10^5}{(DT)^{3/2}} \cdot z^2 \cdot \Lambda_0 + \frac{82.0}{(DT)^{1/2} \cdot \eta}\right) \sqrt{C}$$

where D, the dielectric constant of water, was taken as 79 and η the absolute viscosity, as 0.00894. This may be simplified to

$$\Lambda_v = \Lambda_0 - \alpha \sqrt{C}$$

where α is the term in parentheses in the general formula and represents the theoretical limiting slope of the conductivity curve. At 25° $\alpha = (0.2269 \Lambda_0 + 59.78)$. The calculated and experimental values of this slope are compared at the foot of each table. In the last column of Tables I–IV values of Λ_v have been calculated from the equation and may be compared with the experimental values found. Agreement is good with the picrate and cresylate but not so good with the perchlorate.

TABLE I

CONDUCTIVITY OF SODIUM PICRATE AT 25°

Concn., mole/liter	100 $\sqrt{C}$	Corr. sp. cond. × 10⁴	Found	Equiv. cond. T. and M.[a]	I. C. T.	Calcd.
0.002977	5.46	2.295	77.1	77.2	80.3	77.0
.001486	3.87	1.166	78.4	78.4	81.6	78.3
.0007445	2.73	0.590	79.2	79.2	...	79.2
.0005946	2.44	.472	79.4	79.46	83.0	79.4
(.0)	...	...	81.3	81.3		

[a] Data of Thomas and Marum. α: calcd., 78.1; found, 75.8.

TABLE II

CONDUCTIVITY OF HYDRAZINE PICRATE AT 25°

Concn., mole/liter	100 $\sqrt{C}$	Corr. sp. cond. × 10⁴	Equiv. cond. Found	Calcd.
0.006554	8.09	5.386	82.2	82.0
.004086	6.39	3.400	83.2	83.4
.004076	6.38	3.396	83.3	
.003707	6.09	3.105	83.6	83.6
.003277	5.72	2.743	83.7	83.9
.002043	4.52	1.731	84.7	84.9
.002038	4.51	1.730	84.9	
.001634	4.04	1.390	85.1	85.3
.001630	4.04	1.389	85.2	
.001311	3.62	1.122	85.6	85.6
.000817	2.86	0.705	86.3	86.2
.000815	2.85	.703	86.3	86.3
.000327	1.81	.284	86.9	87.0
.000326	1.81	.283	86.8	
(.0)			88.5	

α: calcd., 79.9; found, 81.1.

[10] Onsager, *Physik. Z.*, **28**, 277 (1927).

TABLE III

CONDUCTIVITY OF HYDRAZINE TRINITRO-*m*-CRESYLATE AT 25°

Concn., mole/liter	100 $\sqrt{C}$	Corr. sp. cond. $\times 10^4$	Equiv. cond. Found	Calcd.
0.00401	6.33	3.308	82.5	82.4
.00400	6.32	3.297	82.4	
.00363	6.02	2.994	82.5	82.7
.002005	4.48	1.681	83.9	83.9
.00200	4.47	1.679	83.9	
.001337	3.66	1.128	84.4	84.6
.000805	2.83	0.685	85.1	85.2
.000729	2.69	.620	85.4	85.36
.000668	2.59	.570	85.3	85.44
.000334	1.83	.287	85.9	86.0
(.0)			87.5	

α: calcd., **79.7**; found, 81.1.

TABLE IV

CONDUCTIVITY OF HYDRAZINE PERCHLORATE AT 25°

Concn., mole/liter	100 $\sqrt{C}$	Corr. sp. cond. $\times 10^4$	Equiv. cond. Found	Calcd.
0.005651	7.52	6.650	117.7	118.6
.004244	6.52	5.041	118.8	119.4
.002826	5.32	3.388	119.9	120.5
.002122	4.61	2.559	120.6	121.1
.001413	3.76	1.716	121.5	121.9
.0008489	2.91	1.037	122.2	122.6
.000565	2.38	0.693	122.6	123.1
.0003396	1.84	.419	123.5	123.6
.000226	1.50	.280	123.9	123.9
(.0)			125.2	

α: calcd., **88.2**; found, 100.0.

TABLE V

CONDUCTIVITY OF POTASSIUM PERCHLORATE AT 25°

Concn., mole/liter	100 $\sqrt{C}$	Corr. sp. cond. $\times 10^4$	Equiv. cond. Found	I. C. T.
0.008664	9.31	11.280	130.3	
.007294	8.54	9.560	131.1	
.004332	6.58	5.760	132.9	
.002166	4.65	2.920	134.9	
.0007294	2.70	0.9984	136.9	
.0003466	1.86	.478	137.9	
.0002918	1.71	.4026	138.0	
.0002918[a]	1.71	.4031	138.1	
(.0)			140.0	
.010	10.0			131.7
.005	7.06			134.4
.002	4.47			137.3
.001	3.16			139.1

[a] Unplatinized cell.

Within the limit of error all the curves were straight lines below concentrations of 0.004–0.005 M.

The conductivity of sodium picrate given by Thomas and Marum[3] from which the mobility of the picrate ion is determined was different from that given in the "International Critical Tables"[11] (hereafter abbreviated as I. C. T.) by three or four units, so it was necessary to determine which data to accept. Our results for sodium picrate, Table I, fall directly on the curve of Thomas and Marum, hence it is believed that the previously recorded data are in error. More serious than this are the discrepancies found in the value of the mobility of the perchlorate ion as calculated from various perchlorates whose conductivity is given in the I. C. T.[12] Extrapolation of the conductivity data for sodium, lithium, potassium, silver and thallous perchlorate to obtain Λ_0 followed by subtraction of the mobility of the cation from the same source[13] gives, respectively, ca. 76.3, 76.8, 70.4, 68.5 and 72.6 for the mobility of the perchlorate ion. It was therefore thought advisable to check one of these. Potassium perchlorate was chosen and results are shown in Table V. The measured conductivities fall considerably below those given in the I. C. T. Duplicate results were obtained by the use of both a platinized and an unplatinized conductivity cell. Extrapolation gives $\Lambda_0 = 140.0$. Taking the mobility of the potassium ion as 73.9, this gives 66.1 for that of the perchlorate ion at 25°. This is lower than any value calculated from the data referred to above. Ferguson and Vogel[14] calculated 54.80 for the mobility of the perchlorate ion at 18°. Assuming a temperature coefficient equal to that of the chloride ion gives a calculated mobility of 63.0 at 25°. Their ionic mobilities while consistent among themselves vary considerably from those of the I. C. T. and so are not strictly comparable with them.

Based on a mobility for the chloride ion of 76.3, which agrees fairly well with that of the I. C. T. (76.1), Thomas and Marum calculate the mobility of the trinitro-m-cresylate ion as 29.1 and of the picrate ion as 30.1. Using these values together with $\Lambda_0 = 88.5$ for hydrazine picrate and 87.5 for hydrazine trinitro-m-cresylate, the value 58.4 is obtained in each instance for the mobility of the hydrazinium ion at 25°. Taking $\Lambda_0 = 125.2$ for hydrazine perchlorate and 66.1 for the perchlorate ion gives 59.1 for the mobility of the hydrazinium ion. Not quite so much reliance is placed on this value, as the hydrazine perchlorate was of necessity recrystallized from alcohol by reason of its high solubility in water. In addition to this, use of the I. C. T. value of the mobility of the chloride ion instead of that used by Thomas and Marum operates to bring the values for the hydrazin-

[11] Ref. 8, p. 250.
[12] Ref. 8, pp. 242–253.
[13] Ref. 8, p. 230.
[14] Ferguson and Vogel, *Phil. Mag.*, **4**, 233, 300 (1927).

ium ion closer together. In view of this small uncertainty it is thought fairer to leave the values as recorded above, *i. e.*, 58.6 and 59.1.

Summary

The conductivities of hydrazine picrate, trinitro-*m*-cresylate and perchlorate have been measured at 25°, likewise sodium picrate and potassium perchlorate. At low concentration the slope of the curve obtained by plotting equivalent conductivity against square root of the concentration is quite close to that calculated from the equation of Onsager.

From these results the mobility of the hydrazinium ion has been calculated.

CORVALLIS, OREGON

DENSITIES, AND PARTIAL MOLAL VOLUMES OF AMMONIA, FOR THE AMMINES OF CALCIUM AND BARIUM CHLORIDES

BY LOUIS J. GILLESPIE AND HAROLD T. GERRY

Introduction

Density data for ammines and the consequent knowledge of the partial molal volume of ammonia in such compounds have been limited to compounds which have comparatively low vapor pressures, such as those of the cobalt, chromium, iron and manganese salts.[1] Such compounds may be isolated in quite a pure state, and density data may be obtained for pure compounds with little modification from the procedure used with ordinary solids.

In the case of compounds such as the ammines of the alkaline earth halides, where dissociation pressures run as high as two and one-half atmospheres in the case of barium chloride octammine at room temperature, such methods are not applicable. In such cases the pure compound is difficult to prepare, and once it is prepared it is likely to lose a considerable quantity of ammonia, forming a mixture of compounds during the process of the density measurements.

However, it is not necessary to work with pure ammines. The vapor pressure curves show that at equilibrium between a salt and ammonia, at any composition other than that of the compounds, there will be two solid phases, either the ammonia-free salt and an ammine or a mixture of two ammines. Consider the case of a salt MX forming two ammines: MX·-

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[1] Biltz and Birk, *Z. anorg. Chem.*, **134**, 125 (1921); Clark, Quick and Harkins, THIS JOURNAL, **42**, 2483 (1920); Birk, *Z. anorg. Chem.*, **158**, 111 (1926).