Chemical Studies On Ion Emission from Solids. II. A Method of Micro-Determination of An Alkali Salt in Aqueous Solution by Measuring Positive-Ion Emission

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(Received May 28, 1953)

Commercial alumina-coated tungsten filament operating as a heater in a vacuum tube, emits positive ions at about 800°C. They consist of sodium and potassium ions, as shown mass-spectrographically by H. Inoue[1] in our laboratory. The emission decays[2] with respect to time nearly exponentially. To the filament thus freed from alkalis by long heating was mounted* a known amount (about one mg.) of aqueous sodium chloride solutions in various ranges of concentration. The total number of positive ions emitted from the filament by heating was measured and plotted against the concentration of sodium. The resulting smooth curve may be used for determining the extremely low concentration of sodium, only one milligram of sample solution (e.g. a rain drop) being required.

1) The results were read at the Meeting of the Chemical Society of Japan (Kinki-Branch), Oct., 1949.

2) N. Sasaki and T. Yuasa, *J. Chem. Soc. Japan*, **73**, 273 (1952).

* The weight of a small amount of a volatile liquid such as the sample solution mounted to the filament was determined by a method to be described elsewhere.

Experimental

A piece of alumina-coated tungsten filament, 60 mm. in length and 0.051 mm. in diameter, was mounted as anode along the axis of a cylindrical cathode of 15 mm. diameter by screw-binders for convenient dismounting. The ions reaching to the cathode were measured by a galvanometer (1.1×10^{-11} amp./mm.) under the following conditions—applied voltage being 60 V., temperature of the filament about 750°C, pressure about 10^{-5} mm.Hg. Further details of the apparatus were explained in the previous report.[2] For preparing sample solutions only quartz apparatus was used to avoid any contamination of alkalis.

Determination of the Total Number of Positive Ions Emitted.—Aqueous sodium chloride solutions of various ranges of known concentration were prepared as standard using distilled water. Reading of the galvanometer was taken fifteen seconds after the heating current of filament was switched in. The current-time curves of some representative results (No (3), (5), (7), (12), (14)) are shown in Fig. 1. The total number of

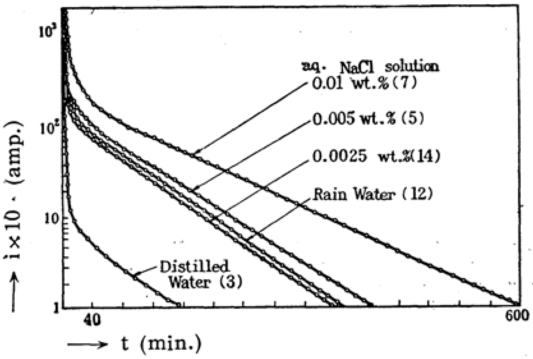

Fig. 1.—Emission Current-time curve

positive ions for each solution was obtained by integrating the emission currents with respect to ime (Table I). They give a smooth curve when plotted against the concentration (Fig. 2).

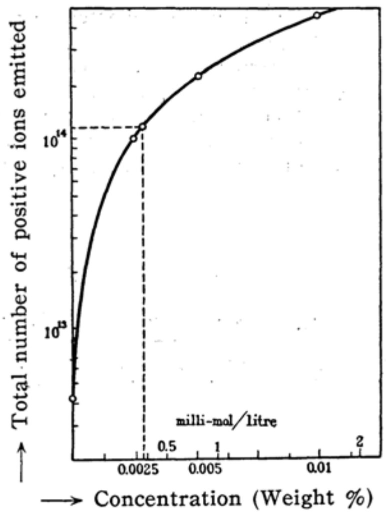

Fig. 2.—Total number of positive ions VS. Concentration curve

TABLE I

Samples	Order of measurement	Weights of the samples applied (W) in mg.	Total number of positive ions emitted (N)	N/W	Means
NaCl aq. soln.	(7)	0.864	3.70×10^{14}	4.28×10^{14}	
0.01 wt. %	(8)	1.093	4.77×10^{14}	4.36×10^{14}	4.29×10^{14}
	(9)	0.870	3.70×10^{14}	4.25×10^{14}	
	(4)	1.016	2.00×10^{14}	1.96×10^{14}	
0.005 wt. %	(5)	0.907	1.86×10^{14}	2.05×10^{14}	2.05×10^{14}
	(6)	0.851	1.82×10^{14}	2.13×10^{14}	
	(13)	0.901	8.41×10^{13}	0.93×10^{14}	
0.0025 wt. %	(14)	1.078	1.10×10^{14}	1.02×10^{14}	1.01×10^{14}
	(15)	0.924	9.98×10^{13}	1.08×10^{14}	
	(1)	0.909	3.75×10^{12}	4.12×10^{12}	
Distilled Water	(2)	1.091	4.64×10^{12}	4.25×10^{12}	4.19×10^{12}
	(3)	1.007	4.23×10^{12}	4.20×10^{12}	
	(10)	1.005	4.23×10^{12}	4.20×10^{12}	
Rain Water	(11)	1.013	1.17×10^{14}	1.15×10^{14}	1.13×10^{14}
	(12)	1.062	1.18×10^{14}	1.11×10^{14}	

The total number of positive ions emitted from one mg. of distilled water is nearly equal to the probable errors of N/W of aqueous sodium chloride solutions of various ranges of concentration, so that no correction was made for the blank value of distilled water.

The ratios of N/W to N_0, the total number of sodium ions contained in one mg. of solutions, are strikingly constant for wide ranges of concentration, namely, 0.38, 0.39 and 0.41 respectively for 0.0025, 0.005 and 0.01 weight per cent aqueous sodium chloride solutions. The rest of sodium ions seem to have evaporated as neutral molecules or atoms.

Similar measurements were made with aqueous potassium chloride solutions and a calibration curve of the same type was obtained.

Ionic emission from mixed KCl–NaCl solutions have been found greater than those calculated by the additive law. Ionic emission from more complicated mixtures was investigated by H. A. Barton and coworkers[3], and B. Toubes and coworker[4], finding that only alkali metal ions were emitted at about 800°–1000°C from the mixture of alkali and alkaline earth salts, while the alkaline earth salts required higher temperatures to produce emission.

Analysis of rain water in Nagoya and Kiryu Cities has been carried out by K. Sugahara[5], and S. Muto[6] respectively. The results show that the most important constituents are sodium and chloride ions with minor constituents such as K, Fe, Al, Ca, Mg, SO_4 and SiO_2.

3) H. A. Barton, G. P. Harnwell, and C. H. Kunsman, *Phys. Rev.*, **27**, 739 (1926).
4) B. Toubes and G. K. Rollefson, *J. Chem. Phys.*, **8**, 495 (1940).
5) K. Sugahara, *Kagaku (Science)*, **18**, 485 (1948).
6) S. Muto, *J. Chem. Soc. Japan*, **74**, 420 (1953).

A few rain drops were collected in a quartz vessel in Kyoto City, February 25,1953 and submitted to measurement. The result obtained $N/W = 1.13 \times 10^{14}$ consists of sodium ions with a small portion of potassium ions. If we neglect the effect of the other salts and simply make use of the calibration curve in Fig. 2, N/W may be turned into a more familiar quantity 0.48 millimol./litre.

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