The Activity Relations of Perchloric Acid. Summary

The corrected electromotive forces given in Table I are so small as to be negligible in determining the relative activities of the two acids at the same concentration. Thus the largest value (0.00017 volt) would correspond to a difference of only 0.7% in the value of the activity coefficient of the hydrogen ion. The conclusion may therefore be drawn that the activity coefficient of perchloric acid is substantially the same as that of hydrochloric acid up to 1.1 *M;* and the values derived for the latter acid (for example, as summarized by Lewis and Randall[4]) may therefore be employed in mass-action and thermodynamic expressions relating to perchloric acid.

This conclusion is of general interest, inasmuch as it indicates that the behavior of both these acids, including the pronounced minimum in their activity-coefficients in the neighborhood of 0.5 *M*, is primarily determined by the hydrogen ion; the effects of the two anions being apparently relatively small and nearly equal.

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THE SOLUBILITY OF SILVER BROMATE IN SOLUTIONS OF OTHER SALTS AND THE CORRESPONDING ACTIVITY RELATIONS

BY R. H. DALTON, R. POMEROY AND L. E. WEYMOUTH

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Introduction

The activity relations of largely ionized salts in the presence of other ions can be conveniently studied by determining their solubilities in the presence of other salts. Thus, for any salt the ratio of the solubility product in pure water to that in the presence of other ions is equal to the reciprocal of the ratio of the corresponding activity-coefficient products; that is, for a uni-univalent salt whose ions may be assumed to have the same activity coefficient α, we have $\alpha_0^2/\alpha^2 = s^2/s_0^2$ where the zero subscripts refer to the activity and solubility of the salt in pure water. It was the purpose of this investigation to obtain new data concerning this activity effect in the case of silver bromate, in order to test more fully the conclusion drawn by Lewis and Randall[1] that the activity coefficient α of any ion is some function of the sum (called by them the "ionic strength") of the products of the molality c of each ion in the mixture by the square of its valence ν (that

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[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 362.

[1] Lewis and Randall, THIS JOURNAL, 43, 1112 (1921).

is, that $\alpha = f\ (\Sigma\ c\nu^2)$; and especially to verify the validity of the highly important theory of largely ionized salts recently developed by Debye and Hückel.[2] To this end the solubility of silver bromate was determined in solutions of various concentrations of the salts potassium, magnesium, barium and cerium nitrates, sodium, potassium, magnesium and cadmium sulfates, and potassium perchlorate. The first two salts were studied by L. E. Weymouth, the remainder a year later by R. H. Dalton and R. Pomeroy.

This research was carried out at the suggestion and with the advice of Professor A. A. Noyes, and was aided financially by a grant to him from the Carnegie Institution of Washington.

Preparation of the Substances and Solutions

Silver Bromate.—The silver bromate was prepared by pouring a hot 0.6 *N* solution of potassium bromate into an excess of cold 1.3 *N* solution of silver nitrate. The precipitate was collected on a hardened filter, and was washed until, after concentrating the wash water to one-tenth its volume and adding lithium chloride to remove the silver, it gave only a very slight test for potassium with sodium cobaltinitrite. The preparation was dried in an electric oven at 50–60°. Some of this silver bromate (recovered from the saturation mixtures) was recrystallized from boiling water and dried at 105°. A third preparation was made by adding potassium bromate solution in the cold to an excess of silver nitrate solution, washing the precipitate very thoroughly, and drying it at 105°. The first preparation gave a solubility value in millimoles per 1000 g. of water weighed in a vacuum of 8.013 (5 expts.; average deviation of the mean (A. D.) 0.001); the second, 8.097 (5 expts.; A. D., 0.003); and the third, 8.097 (2 expts.; A. D., 0.003). No satisfactory explanation of these results was found. Since before this discrepancy was discovered the preparations were used indiscriminately in the solubility determinations with the added salts, the average value of the solubilities in pure water of the different preparations was adopted.

Potassium Sulfate.—A 0.1 *N* solution of imported salt was standardized by determining the weight of solid in samples of the solution. It gave no test for halide.

Magnesium Nitrate.—A slight excess of a halide-free sample of imported crystallized magnesium carbonate was treated with 16 *N* nitric acid until the solution was saturated. The residue was filtered out, and the solution was made just neutral with nitric acid and diluted. The magnesium content was determined gravimetrically, by weighing it as pyrophosphate, $Mg_2P_2O_7$.

Potassium Perchlorate.—The salt used was a domestic c. p. product. This was recrystallized and dried at 100–110° for several hours. The preparation was free from halides. Two 0.1 *N* solutions were independently prepared by weighing the salt.

Barium Nitrate.—An imported sample was dried at 100–110° to a constant weight. The solutions were made up independently by weighing the salt. They gave no precipitate with silver nitrate.

Sodium Sulfate.—Carefully dried portions of an imported anhydrous salt were weighed directly. The halide content of the dried salt was 0.011%.

Cadmium Sulfate.—A domestic c. p. crystallized product, $3CdSO_4.8H_2O$, was treated with a little sulfuric acid (3 drops of concd. acid to about 200 g. of the salt) and ignited to a constant weight at 350–400°. The anhydrous substance was transferred to a tightly stoppered bottle and samples weighed and dissolved in a known weight of water. The halide content of the dry salt was approximately 0.004%.

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[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

Cerium Nitrate.—A stock solution was made up from a domestic cerium nitrate (hydrated). The most probable impurities were tested for and proved to be absent. The concentration of the solution was determined by evaporating a portion and weighing the cerium dioxide left on ignition.

The Experimental Procedure

Preparation of the Equilibrium Mixtures.—Equilibrium was established by rotating a 4g. sample of solid silver bromate with a 300cc. portion of the solution for at least 16 hours on the horizontal shaft of a rotating apparatus within a thermostat at 25.00° ± 0.05°. The equilibrium was always approached from both a lower and a higher temperature, but no consistent difference was ever observed between the results from the under saturated and the supersaturated sides.

Method of Analysis.—In the work of Weymouth the silver content of the equilibrium mixtures was determined by precipitating it as silver chloride, collecting of the precipitate on an asbestos filter in a perforated crucible, drying in an electric oven, and weighing. In the more extended work of Dalton and Pomeroy, the bottles containing the equilibrium mixtures were placed on a rack in the thermostat, and the solutions were blown by compressed air through hardened filterpaper placed in the exit tube into 250cc. graduated flasks immersed in the bath. After these flasks were weighed (to give the densities of the solutions) their contents were transferred to a beaker; and to each were added 6 cc. of 6 N nitric acid and such a volume (20 cc.) of ammonium bromide solution as contained about 7 equivalents of bromide for each equivalent of silver present. The mixtures were then kept near boiling on a hot plate while a current of air was blown through them. When all the bromine was expelled and the coagulation completed, the precipitates were filtered on asbestos in weighed perforated crucibles, and washed with hot water acidified with nitric acid until free from bromide, and then with 20 cc. of pure water. The precipitates were dried for 2 to 4 hours at 210–220° in a gas oven, then cooled in a desiccator for two hours and weighed with carefully standardized weights. The same crucibles were used without removing the precipitate for ten or twelve consecutive analyses. All weights were corrected for air-buoyancy.

The Solubility Data and the Activity Values

The results are summarized in Table I. Most of the columns are self-explanatory. The values in the third column were obtained by averaging the weights of silver bromide, after correcting them to the average weight of solution in 250 cc. The percentage errors in the fifth column headed "Per cent. A. D." are the average percentage deviations from the mean divided by the square root of the number of determinations. The eighth column headed s/s_0 contains the values of the ratio of the solubility in the solution of the added salt to that in pure water. The activity-coefficient product ratios given in the last column are simply the reciprocals of the squares of the values in the eighth column.

TABLE I

SOLUBILITY DATA AND ACTIVITY VALUES FOR SILVER BROMATE AT 25°

Added salt								
Nature	Equiv. per kg. water	Mg. AgBr from 250 cc. solution	Number of expts.	Per cent. A. D.	Density at 25°	Millimoles $AgBrO_3$ per kg. water	Solubility ratio s/s_0	$\alpha_{Ag}\alpha_{BrO_3}$ ratio
None	0.00	378.5	12	0.14	0.9990	8.062	1.000	1.000
$KClO_4$	0.10	451.8	5	.02	1.0074	9.706	1.204	0.690
	.05	427.9	2	.03	1.0033	9.190	1.139	.771
	.025	407.4	3	.03	1.0010	8.716	1.081	.853
K_2SO_4	.10	515.5	3	.05	1.0062	11.092	1.377	.529
	.05	467.6	6	.10	1.0028	10.015	1.241	.650
	.025	434.7	6	.18	1.0009	9.292	1.152	.753
$Mg(NO_3)_2$	.10	473.2	8	.12	1.0046	10.090	1.251	.640
	.05	440.2	3	.05	1.0018	9.414	1.169	.732
	.025	417.9	6	.25	1.0003	8.935	1.109	.815
$Ba(NO_3)_2$	.10	484.4	4	.18	1.0098	10.373	1.286	.605
	.05	451.5	2	.00	1.0046	9.655	1.198	.697
	.025	425.2	2	.04	1.0018	9.088	1.128	.788
Na_2SO_4	1.00	...	3	.28	1.0622	18.619	2.310	.188
	0.10	513.3	4	.17	1.0059	10.973	1.360	.541
	.05	466.2	2	.02	1.0025	9.965	1.235	.656
$CdSO_4$	.10	486.7	2	.05	1.0017	10.405	1.291	.601
	.50	623.1	1	...	1.0492	13.349	1.657	.365
$Ce(NO_3)_3$	.025	437.6	2	.22	1.0014	9.336	1.158	.746
	.0125	416.0	2	.14	1.0002	8.888	1.102	.823
KNO_3	.040	259.5[a]	2	.12	....	9.12	1.142	.768
	.100	140.5[b]	3	.29	....	9.92	1.242	.649
	.200	154.9[b]	3	.04	....	11.06	1.382	.522
	.394	346.8[a]	3	.18	....	12.66	1.595	.394
$MgSO_4$	.0200	254.6[a]	2	.12	....	8.92	1.118	.802
	.0510	275.4[a]	3	.12	....	9.67	1.210	.683
	.1000	146.5[b]	4	.13	....	10.3	1.290	.602
	.1988	160.9[b]	4	.13	....	11.38	1.425	.493

[a] Mg. of AgCl from 200 g. of solution.

[b] Mg. of AgCl from 100 g. of solution.

Discussion of the Results

The detailed discussion of the results will be deferred to a later article soon to be published from this Laboratory, in which the other available data on solubility effect will also be studied in relation to the theory of Debye and Hückel.[2] The following conclusions relating to the data here presented may, however, be stated in advance.

Different added salts of the same valence types (namely, potassium nitrate and perchlorate; or potassium sulfate, sodium sulfate, magnesium nitrate and barium nitrate) have effects on the activity-coefficient product of silver bromate that differ by amounts (3 or 10% at 0.05 N) which indicate specific effects of the separate ions that are pronounced enough to deserve recognition as important secondary factors, though they do not invalidate the principle that the valence of the ions has the primary influence.

The added salts of different valence types have on an average, in conformity with the rule of Lewis and Randall[1] nearly equal activating effects when $\Sigma(c\,\nu^2)$ (summated for all kinds of ions in the solution) has the same value (c denoting the molality and ν the valence of any ion). Thus, without entering into the details of the treatment of the results, it may be mentioned that at $^1/_2\,\Sigma\,(c\,\nu^2) = 0.05\,M$ the average value of the ratio of the activity-coefficient products is 0.779 (limits 0.764 – 0.794) for the two uni-univalent salts; 0.766 (limits 0.741–0.804) for the four unibivalent salts; 0.794 for the two bi-bivalent salts; and 0.775 for the uni-trivalent salt.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

ESTERIFICATION EQUILIBRIA IN THE GASEOUS PHASE[1]

BY GRAHAM EDGAR AND WILLIAM H. SCHUYLER[2]

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Introduction

At the Rochester meeting of the American Chemical Society in April, 1921, a paper was presented by Reid and Mulliken containing the results of preliminary experiments upon the use of silica gel in catalyzing the reaction of gaseous acetic acid with gaseous ethyl alcohol to form ethyl acetate, at a temperature of 150°. The yields of ester formed from an equivalent mixture of the two gases were as high as 90% of that which would be formed by complete reaction. It is well known from the work of previous investigators[3,4,5] that in the liquid phase this reaction at any temperature reaches an equilibrium after esterification has proceeded to about 66% of completion. Professor Reid did not offer an explanation of the high yields of ester obtained in his experiments, but in the discussion following the presentation of the paper the opinion was expressed that the

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[1] Preliminary results reported at the Birmingham meeting of the American Chemical Society, April, 1922.

[2] DuPont Fellow in Chemistry.

[3] Berthelot and Péan de Saint-Gilles, *Ann. chim. phys.*, [3] **66,** 64 (1862); [3] **68,** 235 (1863); [5] **14,** 437 (1878).

[4] Menschutkin, *ibid.*, [5] **20,** 305 (1880).

[5] Tobin, *Dissertation*, Bryn Mawr College, **1920.**