[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE ACTIVITY COEFFICIENT OF SILVER ACETATE

BY F. H. MACDOUGALL

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The activity coefficient of silver acetate was determined by means of measurements of the solubility of the salt in water and in aqueous solutions of potassium nitrate. Of the chief materials used in this investigation, the water was "conductivity" water obtained by distilling ordinary distilled water after the addition of sodium hydroxide and potassium permanganate in a tin-lined copper vessel; the potassium nitrate was Baker's "Analyzed" and was dried at 150° for several hours before using; and the silver acetate was from Mallinckrodt and gave on analysis 64.64, 64.55 and 64.59% of silver compared with 64.64% calculated from the formula.

The solutions of potassium nitrate were prepared by weighing out the water and the salt and were then put into glass-stoppered amber-colored bottles containing an excess of silver acetate. The stoppers were heavily paraffined and the bottles were then rotated in a water-bath at 25.00 ∓ 0.03° for at least seven or eight hours and frequently for twenty-four hours or more.

The saturated solution in a bottle was then examined in the following way: while the bottle was still almost completely immersed in the bath, the stopper was removed and a glass tube with the lower end wrapped in absorbent cotton was inserted. The cotton was tied to the tube by means of platinum wire. By applying suction to the tube approximately 50 cc. of the solution (which originally amounted to about 100 cc.) was transferred to a glass vessel which was now immersed fairly completely in the water-bath. After some minutes two separate portions of about 25 cc. each were withdrawn by means of an accurately calibrated pipet and transferred to weighing bottles. After being weighed, the solutions were washed into 400-cc. beakers, a few drops of nitric acid added, the solutions heated to boiling and then dilute hydrochloric acid was added until there was a slight excess. The beakers were set aside for a number of hours, usually overnight, and then the mixture was filtered using Gooch crucibles. These were then dried in an oven at 150° to constant weight. From the weight of solution delivered by the pipet, the density of the solution was obtained with an accuracy of at least 1 part in 2000. At least two independent experiments were made for each concentration of potassium nitrate, and analyses were made on two separate samples of the solution from each bottle.

Methods of Expressing Composition of Solution.—The composition of the solution saturated with silver acetate is expressed in several ways: first, by giving the molality, m, or moles of silver acetate per 1000 g. of water; second, by giving the molarity, c, or moles per liter of solution, and, third, by giving the mole fraction, x, of Ag^+ or acetate ion, assuming that the silver acetate and the potassium nitrate are completely ionized and taking 18.015 as the molecular weight of water. In addition, I have introduced the term "normalized mole fraction," $|x|$, which, for aqueous solutions, is defined by the equation, $|x| = 55.51\ x$. The advantage arising from the use of this term is that for a given solution the normalized mole fraction is approximately equal to the molarity or the molality.

In Table I is given a summary of the determinations of the solubility of silver acetate in water at 25°.

Table I

Solubility of Silver Acetate in Water at 25°

Author	Year	G. per liter of soln.	Author	Year	G. per liter of soln.
Raupenstrausch[1]	1885	11.21	Hill and Simmons[4]	1909	11.13
Goldschmidt[2]	1898	11.16	Knox and Will[5]	1919	11.13
Jaques[3]	1909	11.07	MacDougall	1929	11.09

Table II gives the solubility of silver acetate in aqueous solutions of potassium nitrate in which the molality of the potassium nitrate ranges from 0 to 3. It will be noted that the solubility of silver acetate expressed as molarity has reached a maximum for a molality of potassium nitrate of

Table II

Solubility of Silver Acetate in Presence of Potassium Nitrate

m = molality; c = molarity, x = mole fraction × 55.51

m, KNO_3	d of satd. soln.	m, AgOAc	c, AgOAc	x, AgOAc
0	1.0047	0.06685	0.06642	0.06669
0.05009	1.0077	.07041	.06978	.07011
.1006	1.0115	.07281	.07204	.07236
.2001	1.0180	.07659	.07547	.07584
.3018	1.0241	.07941	.07791	.07833
.4010	1.0298	.08171	.07982	.08031
.5013	1.0366	.08344	.08124	.08171
.6040	1.0417	.08498	.08233	.08292
.8021	1.0537	.08786	.08449	.08513
1.0155	1.0658	.09019	.08600	.08673
1.2431	1.0784	.09214	.08708	.08791
1.5437	1.0944	.09453	.08828	.08926
2.0371	1.1186	.09750	.08923	.09054
2.5355	1.1426	.09997	.08973	.09130
3.0139	1.1653	.10163	.08960	.09137

[1] Raupenstrauch, *Monatsh.*, **6**, 563 (1885).

[2] Goldschmidt, *Z. physik. Chem.*, **25**, 91 (1898).

[3] Jaques, *Trans. Faraday Soc.*, **5**, 225 (1909).

[4] Hill and Simmons, This Journal, **31**, 821 (1909); *Z. physik. Chem.*, **67**, 594 (1909).

[5] Knox and Will, *J. Chem. Soc.*, **115**, 853 (1919).

about 2.5, that expressed as mole fraction the maximum solubility occurs at a molality of potassium nitrate of about 3 and that expressed as molality the maximum solubility has not been attained in these experiments.

Discussion of Experimental Results

On the basis of the theory of Debye we may write

$$-\log_{10} f = \log_{10} x - \log_{10} x_0 = \frac{0.5045\ S^{1/2}}{1 + 0.3283 \times 10^8\ aS^{1/2}} = \frac{0.5045\ S^{1/2}}{1 + AS^{1/2}} \qquad \text{(I)}$$

where f is the mean activity coefficient of silver and acetate ions in the saturated solution or, more briefly, the activity coefficient of silver acetate $S_c = \Sigma C_i Z_i^2/2$ is the ionic strength of the solution in which an ion of the i-th kind has a valence of z_i and a molarity, C_i; a is an "average" diameter to be assigned to the silver and acetate ions in the solutions investigated, and x is the "normalized" mole fraction of either silver or acetate ions. We may interpret x_0 as the value of x which would be obtained for a saturated solution of silver acetate in case the silver and acetate ions were ideal; or in terms of the Debye equation, x_0 is the value of x extrapolated to a solution of zero ionic strength. Corresponding to x_0 there will be a value m_0 and a value c_0, defining thus three activity coefficients, *viz.*

$$f = \frac{x_0}{x} \quad \gamma = \frac{m_0}{m} \quad \gamma_c = \frac{c_0}{c} \qquad \text{(II)}$$

From two sets of corresponding values of x and S_c, it is possible, using Equation I, to find a value of x_0 and a value of A (or a). Table III contains the values of A and x_0, obtained using in every case the values of x and S_c for $m = 0$ with respect to potassium nitrate combined successively with the values of x and S_c for each of the solutions containing potassium nitrate.

TABLE III

A AND x_0 FROM $m_{KNO_3} = 0$ AND THE VALUE OF m_{KNO_3} IN FIRST COLUMN

m, KNO_3	S_c	A	x_0	m, KNO_3	S_c	A	x_0
0.05009	0.1194	1.4274	0.05358	0.8021	0.8558	1.4120	0.05355
.1006	.1715	1.4789	.05369	1.0155	1.0543	1.4405	.05361
.2001	.2727	1.4297	.05359	1.2431	1.2619	1.4625	.05366
.3018	.3740	1.4493	.05363	1.5437	1.5300	1.4763	.05369
.4010	.4716	1.4079	.05354	2.0371	1.9535	1.5138	.05376
.5013	.5694	1.4266	.05358	2.5355	2.3655	1.5497	.05384
.6040	.6675	1.4388	.05360	3.0139	2.7469	1.6021	.05396

It will be evident from Table III that up to an ionic strength of at least unity the values of A are sensibly constant but that above this ionic strength the values of A obtained exhibit an upward drift. The mean of the first ten values of A is 1.4311, which does not differ appreciably from the third value of the table (1.4297). The latter value of A and the corresponding value of x_0, *viz.*, 0.05359, were used in the following calculations. From $A = 1.430$, we have $a = 4.35 \times 10^{-8}$ cm. The extrapolated density of the solution corresponding to $x_0 = 0.05359$ is 1.0032. Moreover, we find from this value of x_0 and the density $m_0 = 0.05369$, $C_0 = 0.05338$. Table IV contains the observed values of x and the values of x calculated by Equation I. It will be seen that this equation gives excellent results up to an ionic strength of greater than one.

Finally, I give in Table V, the observed activity coefficients of silver acetate based on the values x_0, m_0 and c_0 already obtained.

By adding to the right-hand side of Equation I a term proportional to the ionic strength, it is possible to obtain an expression which will reproduce the experimental results even in the high ionic strengths. This point will not be discussed further in this paper.

Table IV

Observed and Calculated Values of x with $A = 1.430$ and $x_0 = 0.05359$

S_0	x, obs.	x, calcd.	S_0	x, obs.	x, calcd.
0.06642	0.06669	0.06669	0.8558	0.08513	0.08492
.1194	.07011	.07010	1.0543	.08673	.08688
.1715	.07236	.07249	1.2619	.08791	.08841
.2727	.07584	.07584	1.5300	.08926	.09004
.3740	.07833	.07828	1.9535	.09054	.09209
.4716	.08031	.08014	2.3655	.09130	.09367
.5694	.08171	.08169	2.7469	.09137	.09488
.6675	.08292	.08301			

Table V

Activity Coefficient of Silver Acetate at 25° in Solutions of Potassium Nitrate

S_0 Ionic strength	f	γ	γ_c	S_0 Ionic strength	f	γ	γ_c
0.06642	0.804	0.803	0.804	0.8558	0.629	0.611	0.632
.1194	.764	.763	.765	1.0543	.618	.595	.621
.1715	.741	.737	.741	1.2619	.610	.583	.613
.2727	.707	.701	.707	1.5300	.600	.568	.605
.3740	.684	.676	.685	1.954	.592	.551	.598
.4716	.667	.657	.669	2.366	.587	.537	.595
.5694	.656	.644	.657	2.747	.586	.528	.596
.6675	.646	.632	.648				

Summary

Measurements have been made of the solubility at 25° of silver acetate in water and in aqueous solutions of potassium nitrate up to a molality of 3.014. The Debye expression for the activity coefficient using an ionic diameter of 4.35×10^{-8} cm. represents the experimental facts up to an ionic strength of over one. The activity coefficients of silver acetate in the various solutions are presented in tabular form.

Minneapolis, Minnesota