$$\mathrm{Ag^+ + 2NH_3(aq.) = Ag(NH_3)_2{}^+} \qquad (3)$$

The free energy change for this reaction may be obtained from the following

$$\mathrm{AgCl(s) + 2NH_3(aq.) = Ag(NH_3)_2{}^+ + Cl^-;}\quad \Delta F^\circ = 3472 \text{ cal.}^{6a} \qquad (4)$$

$$\mathrm{Ag^+ + Cl^- = AgCl(s);}\quad \Delta F^\circ = -13{,}329 \text{ cal.}^{3} \qquad (5)$$

The sum of the free energy changes for reactions (4) and (5) gives $\Delta F^\circ_{298.1} = -9857$ cal. for reaction (3). Combining this with $\Delta H^\circ_{298.1}$ gives the change in entropy for reaction (3) to be

$$\Delta S^\circ = (-13{,}400 + 9857)/298.1 = -11.9 \pm 0.5 \text{ e. u.}$$

Reaction (3) may be considered as the replacement of two bound water molecules by ammonia molecules. Since the ammonia molecules are undoubtedly more tightly bound and the entropy of aqueous ammonia is greater than that of water, one would expect a considerable decrease in entropy for this reaction, as is found experimentally.

The heat and free energy of solution of gaseous ammonia in water at 298.1°K. as given in the "International Critical Tables"[6c] are −8290 and −2390 cal., respectively, from which the entropy of solution may be calculated to be $\Delta S^\circ = -19.8$ e. u. Combining this value with the entropy of gaseous ammonia at 298.1°K., 45.9 e. u.,[7] the entropy for $\mathrm{NH_3}$(aq.) is found to be $S^\circ_{298.1} = S^\circ_{\mathrm{NH_3(g)}} + \Delta S^\circ_{\mathrm{sol.}} = 26.1$ e. u. Using this value in combination with the entropy of silver ion[3] and the entropy change for reaction (3) we find the entropy of aqueous silver ammonia complex ion to be

$$S^\circ_{298.1} = 2S_{\mathrm{NH_3(aq.)}} + S_{\mathrm{Ag^+}} + \Delta S^\circ = 58.7 \pm 1.0 \text{ e. u.}$$

Summary

The heat capacity of silver nitrate has been determined from 15 to 300°K., and the entropy of the salt at 298.1°K. has been found to be 33.68 e. u. The heat of solution of silver nitrate in water and in dilute aqueous ammonia has been measured at 298.1°K. The free energy of solution of silver nitrate has been calculated to be −510 cal./mole, and the free energy of formation of the solid from its elements calculated to be −7350 cal./mole. The entropy of aqueous silver ammonia complex ion has been calculated to be 58.7 e. u. at 298.1°K.

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[7] Overstreet and Giauque, THIS JOURNAL, **59**, 254 (1937).

BERKELEY, CALIF. RECEIVED APRIL 5, 1937

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA

Studies on Aging of Fresh Precipitates. XIII. The Aging of Freshly Precipitated Silver Chloride as Indicated by the Adsorption of Wool Violet

BY I. M. KOLTHOFF AND HENRY C. YUTZY[1]

The term "aging" has been used in a collective sense involving any changes occurring in a precipitate after it has been formed. In previous studies with lead sulfate[2] and barium sulfate[3] we have been concerned mainly with the "self-perfection" of micro-crystalline particles, aged under various conditions. In these cases, under the conditions studied, changes in the external surface were found to be relatively small. In the present study, with silver chloride, it was found that upon aging of freshly precipitated silver chloride in the mother liquor, a very pronounced reduction of the total surface occurred.

Changes in the external surface of a precipitate can be followed by measuring the amount of a dye adsorbed upon precipitates of various ages. The dye used, wool violet 4BN, was found to be strongly adsorbed by silver chloride. It consists of a large molecule so that the amount adsorbed is probably a measure of the external surface only. Attempts to make use of smaller molecules in order to measure the internal surface, not accessible to the large dye molecule, were abortive.

The adsorptions of such substances as ammonia, aniline, *p*-nitrophenol, picric acid, urea and others[4] on silver chloride were found to be so small that the difficulty in determining the amounts adsorbed made their use impractical. Attempts to follow the changes in surface by means of photomicrographs were unsuccessful, mainly because the very small particles quickly agglomerated into undistinguishable clumps.

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[1] From a thesis presented to the Graduate School of the University of Minnesota by H. C. Yutzy in partial fulfilment of the requirements for the degree Doctor of Philosophy, June, 1936.

[2] I. M. Kolthoff and C. Rosenblum, THIS JOURNAL, **56**, 1264 (1934).

[3] G. Noponen, Thesis, Univ. of Minnesota, 1936.

[4] For details see thesis of the junior author.

Experimental

Materials.—The silver nitrate and sodium chloride used were both Mallinckrodt Reagent grade, ground and dried at suitable temperatures.[5] Two solutions of each were prepared: (A) 0.2791 molar and (B) 0.3355 molar. Gravimetric analysis showed the concentrations of these solutions to be accurate to 0.1%. Twenty-five ml. of either solution (A) corresponds to 1.000 g. of silver chloride; 25 ml. of either solution (B) contains enough of that reagent in excess of 25 ml. solution (A), to give a solution 10^{-3} molar in a volume of 100 ml.

The wool violet used was obtained from the National Aniline Company. It was purified by a method described previously.[6] The sodium content was somewhat lower than that used previously (4.0% instead of 5.8%) but was quite constant upon successive crystallizations. In addition the dye contained a small amount of aluminum and a trace of iron. The amount of dye in the residual solution after adsorption was determined colorimetrically by comparison with suitable standard wool violet solutions, and the amount adsorbed calculated as the difference between this figure and the amount added.

Method of Precipitation and Time for Attainment of Adsorption Equilibrium.—In preliminary experiments it soon became apparent that experimental conditions must be controlled carefully to avoid variation between duplicates. After considerable experiment, the following procedure was adopted; it gave fairly reproducible results, even with very fresh precipitates, and seemed satisfactory. In a typical experiment, 25 ml. of sodium chloride (A) together with 25 ml. of water was placed in a 250-ml. bottle, and stirred with a mechanical stirrer having a constant rate of 440 r. p. m. Then, 25 ml. of silver nitrate (A) was added from a pipet (twenty seconds), allowing the stream to fall directly into the solution. After a measured time (hereafter referred to as the "age of the precipitate") 25 ml. of a solution of wool violet of a known strength was added from a pipet and the whole stirred until adsorption equilibrium had been attained—about twenty minutes. The bottle was then centrifuged at 2000 r. p. m. and a sample of the supernatant dye solution removed for analysis.

In order to determine the time for attainment of adsorption equilibrium a series of identical precipitates was prepared and aged for five minutes before the addition of dye. Stirring was continued for various periods of time before centrifuging and analyzing. In this way it was found that a maximum and constant amount of dye was adsorbed within eighteen minutes even in the presence of excess chloride. In all subsequent experiments, reported below, the precipitates were stirred with the dye solution for at least twenty minutes. Upon longer periods of stirring the dye adsorption did not change, indicating that the wool violet prevented further aging of the precipitate. Similar results have been obtained with lead sulfate[2] and barium sulfate.[3]

Adsorption Isotherm.—It was necessary to know the dye concentration in solution above which the surface of the precipitate was saturated. A series of five-minute old precipitates was prepared as described, using 25 ml. of the two solutions (A). After five minutes of aging 25 ml. of dye solutions of different strengths was added; the mixture was stirred for twenty minutes, centrifuged and the supernatant liquid analyzed. Similar experiments were performed using 25 ml. of silver nitrate (A), 25 ml. of sodium chloride (B) (excess chloride 10^{-3} *M*). The data thus obtained are reported in Table I.

Table I

Adsorption of Wool Violet as Function of Final Dye Concentration

Composition of supernatant liquid	Final dye concn., mg./l.	Mg. dye per gram AgCl[a]	
$(Ag^+) = (Cl^-)$	1.2	0.9	
	9.5	4.2	±0.2
	67	4.4	± .1
	208	4.2	± .4
$(Ag^+) = 10^{-3}$ *M*	40	6.0	± .1
	59	5.8	± .1
	194	5.6	± .4
$(Cl^-) = 10^{-3}$ *M*	69	3.2	± .3
	227	2.5	± .3

[a] The possible error in the amount of dye adsorbed is based upon the assumption that the error in the colorimetric determination of the residual dye is 2%.

Apparently an equilibrium dye concentration of 70 mg. per liter is sufficient to ensure saturation of the surface even in the unfavorable case in which chloride ion is in excess.

Variation in Dye Adsorption with Age of the Silver Chloride.—Three series of precipitates were prepared as described: one in excess of chloride (a); one in excess of silver (b); the third as equivalent bodies (c). After the periods of shaking given below as the "age," 25 ml. of wool violet solution (400 mg. per liter) was added and the whole stirred for twenty minutes, after which the samples were centrifuged and analyzed for residual dye. The resulting data are presented in Table II.

Table II

Change of Dye Adsorption with Age

Mg. dye per gram AgCl[(z)]

AgCl	5 min.	30 min.	60 min.	3 hr.	11 hr.	18 hr.	8 days
							0.5^x
(a) In 10^{-3} *M* Cl^-	2.9	2.1	1.9	...	...	1.4	0.5^y
(b) In 10^{-3} *M*	5.8				3.2		1.4^x
Ag^+	6.0	5.5	4.6	3.3	3.2	2.1	1.2^y
(c) As equiv.	4.2, 4.9	3.0, 3.3					0.9^x
body	4.4, 4.2	3.6	2.5	...	1.9	1.8	0.8^y

[x] Violently shaken during aging; [y] not shaken during aging; [z] estimated error is ±0.2 mg. per gram.

These data have been plotted in Fig. 1. They show a rapid decrease in the amount of dye adsorbed as the precipitate ages. Evidently the rate of aging in excess of silver is considerably slower than in excess of chloride. It was found immaterial whether the precipitates were aged with shaking or allowed to stand quietly.

Effect of Order of Precipitation.—In the experiments just reported, the precipitates in series (a) were prepared by adding chloride to silver; those in series (b) and (c)

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[5] I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York, 1929, pp. 87, 222.

[6] I. M. Kolthoff, W. von Fischer and C. Rosenblum, This Journal, **56**, 832 (1934).

TABLE III

EFFECT OF EXCESS LATTICE ION ON AGING AND ADSORPTION

Precipitant	Precipitated	Added after aging	Lattice ion in excess During aging	Lattice ion in excess During adsorption	Mg. dye per gram AgCl[a]	Av.
$AgNO_3$ (B)	NaCl (A)	1 ml. 1 *N* NaCl	Ag^+	$Ag^+ = Cl^-$	3.7 3.9	3.8
NaCl (B)	$AgNO_3$ (A)	1 ml. 1 *N* $AgNO_3$	Cl^-	$Ag^+ = Cl^-$	1.6 1.7	1.7
$AgNO_3$ (A)	NaCl (A)	1 ml. 1 *N* NaCl	$Ag^+ = Cl^-$	Cl^-	2.5 2.6	2.5
$AgNO_3$ (A)	NaCl (A)	1 ml. 1 *N* $AgNO_3$	$Ag^+ = Cl^-$	Ag^+	2.4 3.1	(2.7)
$AgNO_3$ (A)	NaCl (A)		$Ag^+ = Cl^-$	$Ag^+ = Cl^-$	2.5	2.5
NaCl (B)	$AgNO_3$ (A)		Cl^-	Cl^-	1.9	1.9
$AgNO_3$ (B)	NaCl (A)		Ag^+	Ag^+	4.6	4.6

[a] Estimated error is ±0.1–0.2 mg. per gram.

TABLE IV

EFFECT OF DISSOLVED LATTICE IONS ON ADSORPTION

Precipitant	Precipitated	Aged in	Dye ads. in	Mg. dye per gram at the age of 5 min.	30 min.	1 hour
NaCl (B)	$AgNO_3$ (A)	10^{-3} *M* NaCl	10^{-3} *M* $AgNO_3$	4.8	2.8	1.8
NaCl (B)	$AgNO_3$ (A)	10^{-3} *M* NaCl	10^{-3} *M* NaCl	2.9	2.1	1.9
$AgNO_3$ (B)	NaCl (A)	10^{-3} *M* $AgNO_3$	10^{-3} *M* $AgNO_3$	5.9	5.5	4.6

were precipitated in the reverse order—silver was added to chloride. A few precipitates were made using the same solutions as in (a) Table II, but reversing the order of mixing. The amounts of dye adsorbed after various periods of aging were found to be identical with those given in Table II. Consequently, within the experimental error, the effect of order of mixing of the silver and chloride solutions upon the adsorption of dye by the precipitate is negligible upon rapid precipitation.

Effect of Dissolved Lattice Ions upon Aging and Adsorption.—The results of the various series in Table II are not quite comparable, since the dye adsorption took place in series (a) in excess of chloride, in series (b) in excess of silver and in (c) in an equivalent solution.[7] Especially from Fig. 1 it is clear that a fresh precipitate adsorbs more dye from 0.001 *N* silver solution than from 0.001 *M* chloride solution on the saturated surface.

In the following experiments several precipitates were prepared in the standard way and aged for one hour in the presence of excess of lattice ions or as equivalent bodies. A suitable amount of silver or chloride solution was then added to determine the dye adsorption on the precipitates under comparable conditions. The dye solution (25 ml. of a solution containing 400 mg. of wool violet per liter) was added and the amount adsorbed determined as before. Table III gives a summary of the preparation and aging of the precipitates and the amounts of dye adsorbed.

It is apparent that, in the case of precipitates more than one hour old, the dye adsorption is more or less independent of the presence of dissolved silver or chloride ions, the amount of dye adsorbed by these precipitates being dependent only upon the type of ion present in solution *during aging.*

By special experiments it was shown that the dye adsorption on aged precipitates is, partly at least, an exchange: $AgCl + {}^1/_2W.V.^- \longrightarrow Ag^1/_2W.V. + Cl^-$. In addition, a fresh precipitate adsorbs an extra amount of dye probably in the form of silver wool violet, from a solution containing an excess of silver. Apparently, this kind of adsorption occurs on active surface only, the magnitude of the latter decreasing rapidly on aging. From the results given in Table IV it is seen that the fresh precipitate adsorbs almost twice as much dye from 0.001 *M* silver as from 0.001 *M* chloride solution; after one hour of aging in 0.001 *M* silver or in some other solution, the dye adsorption is the same from both media.

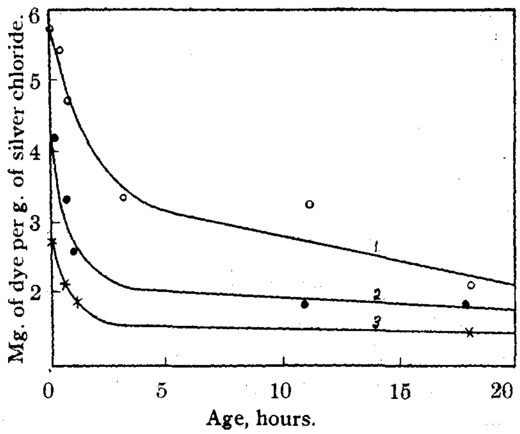

Fig. 1.—Aging measured by dye adsorption: 1, aged in 0.001 *M* silver; 2, aged as an equivalent body; 3, aged in 0.001 *M* chloride.

Aging in Other Solvents.—Aging experiments were carried out in absolute ethanol and in ammonia solutions of various concentrations.

Aging in Ethanol.—(a) Approximately 4 g. of silver chloride was prepared by adding 100 ml. of silver nitrate (B) to 100 ml. of sodium chloride (A) plus 100 ml. of water. After three minutes of stirring, the silver chloride was washed by decantation and filtered on a sintered glass funnel. After washing with water and several times with absolute alcohol, the precipitate was divided among several bottles containing 100 ml. of an alcoholic solution, 0.001 *M* to lithium chloride (chosen because of its greater

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[7] The terms "equivalent solution" and "equivalent body" are used here in an approximate sense. It is recognized, both from the viewpoint of experimental technique and with regard to the location of the isoelectric point of silver chloride [for silver iodide see E. J. W. Verwey, *Chem. Rev.*, **16**, 363 (1935); I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **58**, 1528 (1936)] that the designation of "equivalent body" (Series C, Table II) is only a close approximation.

solubility in alcohol). The precipitate at this point was fifteen minutes old. After shaking for various periods of time, the precipitates were filtered, washed with water and added to 75 ml. of an aqueous dye solution (125 mg. dye per liter). After thirty minutes of shaking, the amount of dye adsorbed was determined as before, and the silver chloride collected, dried and weighed.

(b) Similar experiments were carried out except that the silver chloride was aged in an alcoholic solution being 0.001 M in silver nitrate. The results obtained are given in Table V.

TABLE V

AGING IN ETHANOL

Age in hours	1	2.3	6	21
Mg. dye adsorbed p. 1 g. AgCl: in 10^{-3} M LiCl	1.9	...	1.6	0.4
Mg. dye adsorbed p. 1 g. AgCl: in 10^{-3} M $AgNO_3$	3.5	2.8	2.3	2.5

Aging in Ammonia Solutions.—Precipitates were prepared as described in (a) above but, after filtration and washing with water, the silver chloride was added in portions to bottles containing ammonia in various concentrations. After shaking for the periods of time indicated in Table VI, filtration and washing, the dye adsorption was determined as before.

TABLE VI

AGING IN AMMONIA SOLUTIONS

Age in hours	0.7	1.5	3	0.17	2	28	0.17	2	28
Concentration of ammonia, molar	1	1	1	0.1	0.1	0.1	0.01	0.01	0.01
Mg. of dye p. 1 g. AgCl	0.6	0.2	0.2	2.3	1.4	0.6	2.7	2.1	1.0

A comparison of the absolute values of the dye adsorption after aging in alcohol or ammonium hydroxide with similar values previously reported after aging in water is of doubtful value because of the difference in conditions of precipitation and because of the filtrations necessary in the alcohol and ammonia experiments.

Discussion

The external surface of a silver chloride precipitate, rapidly formed at room temperature, decreases relatively rapidly when the solid is kept in the mother liquor. When the aging medium contains 0.001 M Cl^-, the changes observed are much more pronounced than in 0.001 M Ag^+; the rate of aging in a solution containing approximately equivalent amounts of Ag^+ and Cl^- is intermediate between these two. It is difficult to account for this behavior upon the basis of an "Ostwald ripening."

In the first place it was shown that the same amounts of dye were adsorbed whether the suspensions were aged with shaking or were allowed to stand quietly. Moreover, the solubility of silver chloride in either 0.001 M chloride or 0.001 M silver solution is less than in a solution containing equivalent amounts of the two ions.[8] It seems plausible to explain the mechanism of the aging in the following way. The primary particles of the precipitate form loose aggregates by sharing a mutual sheath of solvent.[9] The imperfect particles of the primary precipitate perfect themselves rapidly as a result of repeated recrystallizations by way of the liquid films around them.[2,3] During this rapid perfection lattice material may deposit in the liquid film between the particles in an agglomerate, thus building bridges and cementing these particles together. Eventually, the entire liquid space between the particles in an agglomerate may be filled up with lattice material, resulting in the formation of imperfect crystals with a mosaic structure. The surface as measured by the dye adsorption decreases in consequence of this cementing process. According to the above picture the speed of aging is determined by the solubility of the lattice material in the film around the particles and not by that in the bulk of the solution. It is readily seen that silver chloride ages less rapidly as a "silver body" than as an "equivalent body." Although the solubility of silver chloride in 0.001 M chloride solution is less than in water, it ages more rapidly in the former medium. This we explain by the fact that the adsorbed chloride in the liquid film around the particles is present in such a high concentration as to increase the solubility of the silver chloride in the liquid sheath as a result of complex formation ($AgCl_2^-$). The speed of aging was found to increase slightly with increasing chloride concentration and to decrease with increasing silver concentration.

The speed of aging of silver chloride in 0.001 M alcoholic silver nitrate is much less than in water. This was to be expected as the solubility of silver chloride in ethanol is about 100 times less than in water.[10] On the other hand, the speed of aging is very pronounced again in 0.001 M solution of chloride in ethanol. This promoting effect of chloride is explained in the same manner as above in aqueous medium. Ammonia promotes the aging very strongly, the effect increasing with increasing ammonia concentration. This may be attributed to an Ostwald ripening, although it is reasonable to assume that ammonia promotes the perfection and subsequent cementing very strongly.

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(8) G. S. Forbes and H. I. Cole, THIS JOURNAL, **43**, 2492 (1921).

(9) *Cf.* also S. E. Sheppard and R. H. Lambert, *Colloid Symposium Monograph*, **6**, 265 (1928).

(10) D. McFarlane and H. Hartley, *Phil. Mag.*, **13**, 425 (1932).

Summary

1. Silver chloride precipitated at room temperature and aged in the mother liquor is subject to a rapid decrease of the surface as measured by the adsorption of wool violet. The aging is most pronounced in 0.001 *M* chloride in water as well as in ethanol, less as an equivalent body and the least in 0.001 *M* silver solution.

2. An explanation has been offered of the fact that silver chloride ages more rapidly as a "chloride body" than as an "equivalent body." Evidence has been presented that the Ostwald ripening is of subordinate significance.

3. Ammonia promotes the aging, the effect increasing with the concentration of ammonia.

4. Freshly precipitated silver chloride adsorbs about twice the amount of wool violet from a solution containing an excess of silver as from a solution containing an excess of chloride on the saturated surface. After one hour of aging the amount of dye adsorbed on the saturated surface is independent of the kind of lattice ion present in excess in the solution. An interpretation of this behavior has been presented.

MINNEAPOLIS, MINN. RECEIVED MARCH 11, 1937

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

The Vapor Pressures and Activity Coefficients of Aqueous Solutions of Ammonium Chloride at 25°[1]

BY J. N. PEARCE[2] AND G. G. PUMPLIN

Continuing the investigation of activity coefficients of salts in aqueous solution by the dynamic vapor pressure method devised by Pearce and Snow, as previously discussed,[3,4] the results on ammonium chloride solutions are here reported. The attempt to apply the method to cupric sulfate solutions gave anomalous results. The apparatus used was exactly the same as reported by Pearce and Blackman.[4]

Reagent grade ammonium chloride, purified by three recrystallizations, was made up into a nearly saturated solution, which was carefully analyzed gravimetrically for its chloride content by precipitation as silver chloride. Solutions of the required molality were made up on the weight-molal basis by dilution of the concentrated solution with conductivity water.

The essential data are collected in Table I. The values of p given are the mean of three or more independent determinations, with a maximum deviation of 0.004 mm. from the mean. The symbols used have their familiar significance. The activity of the water, a_1, is calculated directly from the fact that $a_1 = p/p^0$.

The geometric mean activity coefficients of the ions, $\gamma_{\pm}$, were calculated from the activity of the solvent by means of the relation[5]

$$\log \gamma_{\pm} = \frac{-h}{2.303} - \frac{2}{2.303}\int_0^{m^{1/2}} \frac{h}{m^{1/2}}\, dm^{1/2}$$

where $h = (55.51 \ln a_1/\nu m) + 1$, and νm is the total number of ions furnished by m moles of solute.

Randall[6] has shown that for uni-univalent salts, a plot of $h/m^{1/2}$ against the square root of the molality has the limiting value of 0.394 at $m = 0$ for 25°. This plot is shown in Fig. 1. To calculate the value of the activity coefficient of any solution of molality m, the value of the integral from $m = 0$ to m was determined, using a polar planimeter.

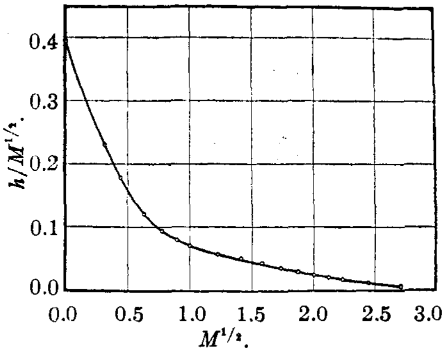

Fig. 1.

The change in free energy accompanying the transfer of one mole of ammonium chloride from

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[1] Part of the dissertation presented to the Graduate College of the State University of Iowa by Gerald G. Pumplin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Deceased Nov. 14, 1936.

[3] Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932); **55**, 3075 (1933).

[4] Pearce and Blackman, *ibid.*, **57**, 24 (1935).

[5] Randall and White, *ibid.*, **48**, 2514 (1926).

[6] Randall, *ibid.*, **48**, 2512 (1926).