[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heats of Solution of Alkali Halides and of Hydrogen Chloride in Water–Methyl Alcohol Solutions at 25°[1]

BY CYRIL M. SLANSKY[2]

The entropies of aqueous ions have been determined for nearly all of the common ions.[3] Such a calculation involves considerable experimental data, and for this reason it has been impossible until now to evaluate ionic entropies in non-aqueous solvents. Upon examining the literature it was found that a number of ionic entropies could be calculated for the system water–methyl alcohol, provided heats of solution could be obtained. The determination of the heat of solution at infinite dilution of a number of alkali halide salts and of hydrogen chloride gas in water–methyl alcohol solutions will be given in this research. The calculation of ionic entropies and of the free energies and entropies of solvation of gas ions in water–methyl alcohol solutions will be given in a succeeding paper.

Apparatus.—The calorimeter was designed after the adiabatic, differential type used by Lange and co-workers[4,5,6] for aqueous solutions but altered to fit the needs of acid solutions of non-aqueous solvents. The calorimeter was to be used to measure heats of solution of solids and of gases and also heats of dilution. Time did not permit the measurement of heats of dilution as originally planned. These heats of dilution would have been necessary to obtain heats of solution at infinite dilution had a less sensitive calorimeter been used. Such a calorimeter would have given more satisfactory heats of solution, but the larger samples would have required definite heat of dilution data.

Since small samples were used, the uncertainty in extrapolating to infinite dilution is within experimental error.

Detailed description of the electrical circuits used with this kind of apparatus has been given by Gulbransen and Robinson.[6]

Figure 1 shows the calorimeter without its thermostatically controlled water-bath. The water thermostat was controlled by a sensitive mercury–toluene thermoregulator. The bath was covered and was stirred by two stirrers. The temperature in the water-bath was maintained so constant that no deflection was noted on a Beckmann thermometer over a period of several hours.

In calorimeters of this type it has been the practice in the past to fasten the thermopile in the center of a Dewar flask with a cement such as de Khotinsky and allow the solutions on both sides to come in contact with the junctions. This was impossible for methyl alcohol solutions due to their solvent action; therefore the thermopile was placed between two semi-cylindrical silver-plated copper cans as pictured in Fig. 1. Each of the cans held about 1 liter of solution and was covered to prevent evaporation of the solvent. The contents of each can were identical and consisted of a pure silver stirrer, adiabatic thermocouple, manganin heater, and solvent. In Fig. 1 the contents of only one can are shown. The 1500-junction copper–constantan thermopile was electrically insulated from the cans by several sheets of rice paper and thin coats of a mixture of melted beeswax and rosin. The time lag in reaching temperature equilibrium between the two cans was reasonably small by this arrangement of the thermopile. For example, after one minute of energy input of about 1 calorie it took forty seconds before cooling was registered by the galvanometer and three to five minutes before an equilibrium rate of cooling was reached.

The thermel was connected to a Leeds and Northrup type H. S. galvanometer whose sensitivity was 0.2 microvolt per mm. at a scale distance of 1 meter. This corresponded to a sensitivity of 2.4×10^{-3} cal./mm. or to about 1.5×10^{-6} degree/mm. at the scale distance of seven meters that was used. A reduced sensitivity of about one-sixth maximum was used.

The adiabatic thermocouple consisted of four pairs of copper–constantan couples in each can. The two cans were connected in series to the "adiabatic" galvanometer.

The leads from the thermocouples and thermopile were run through lead-sheathed cables to the galvanometer shunt box and thence to the galvanometers.

The heaters were about 20 ohms of no. 36 double silk covered manganin wire. The resistance wire was placed in small-bore silver tubes, and the tubes then drawn on to the manganin wire to make good heat transfer possible. The ends were soldered within the calorimeter to no. 30 copper leads and the leads brought out the top of the can through a copper tube. The resistance of the heaters was checked against a standard resistance from time to time.

By means of a substitute resistance the current in the heaters was sufficiently constant during the minute of heating usually employed to require the measurement of only one potential drop across the standard resistance. One minute of energy input for calibration was used, since that corresponded to the average time for a sample of salt to dissolve in the solvent.

The stirrers were turned together at the rate of 180 r. p. m. by means of a small synchronous motor and a combination chain and gear drive.

Materials.—Rubidium chloride and cesium chloride were labeled C. P. and were not purified due to the small amounts at hand. The sample of potassium iodide was obtained

---

[1] From a dissertation presented by the author as partial satisfaction of the requirements for the degree of Doctor of Philosophy at the University of California.

[2] Shell Research Fellow in Chemistry, Academic Year 1939–1940.

[3] W. M. Latimer, K. S. Pitzer and W. V. Smith, THIS JOURNAL, **60**, 1829 (1938).

[4] E. Lange and J. Monheim, *Z. physik. Chem.*, **A149**, 51 (1930).

[5] E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931).

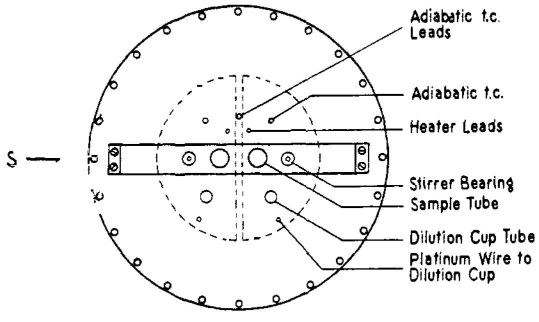
[6] E. A. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934).

from Dr. J. J. Lingane and showed a high degree of purity by analysis based on atomic weight silver. Gravimetric chloride analysis of potassium chloride and sodium chloride showed them to be 100.00 ± 0.05% and 99.83 ± 0.05% pure, respectively. The lithium chloride was Mallinckrodt analytical grade and was not further purified, but was dried.

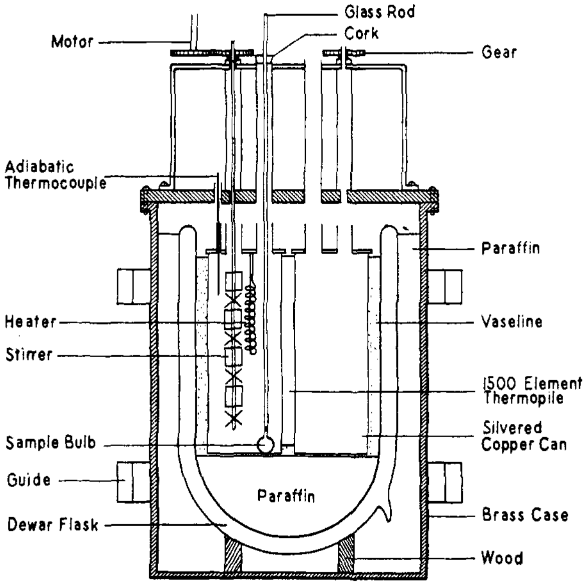
Commercial methyl alcohol was purified by fractionation, treatment with magnesium ribbon, and refractionation. A three-foot (91-cm.) column packed with 1-cm. lengths of 3-mm. glass tubing was used. The density of the final product at 25° was 0.78684 as determined with a pycnometer. The b. p. at 760 mm. pressure was 64.30–64.38°. Values for the density found in the literature vary from 0.78651 to 0.78660.

Hydrogen chloride gas was prepared in an all-glass apparatus by the action of concentrated sulfuric acid on C. P. sodium chloride. The gas was bubbled through concentrated sulfuric acid twice, passed through a large spray trap filled with glass wool and finally stored over concentrated sulfuric acid in a glass bulb. The gas was put under slight pressure by forcing concentrated sulfuric acid into the bulb and dispensed into a gas buret as needed. A 25-ml. gas buret was used to measure a known amount of gas into the calorimeter through a capillary tube of 0.15-ml. capacity. It was found impossible to dispense hydrogen chloride gas accurately when minute droplets of solvent remained on the walls of the capillary. To prevent the solvent from sucking back up the capillary a three-way stopcock was used and a small amount of dry air to clear the capillary. No appreciable heat effect was noted when a few ml. of air was passed into the solvent before a heat of solution run. The sensitivity of the sensitive galvanometer was further reduced for hydrochloric acid solutions, and the heat effect from solvent evaporation was within experimental error. Air was not eliminated from the hydrochloric acid solutions. In water the reaction between oxygen, hydrochloric acid and silver is very slow and would not affect the heat of solution. The reaction seems to be speeded up in methyl alcohol solutions, but does not affect the results appreciably because temperature equilibrium is rapidly attained for the solution process.

Experimental Procedure.—For a series of runs both calorimeter cans were filled with the same volume of solvent, and the temperature of the solvent and of the water-bath allowed to become the same. The sensitive galvanometer was read at one-minute intervals until either a very small steady drift or a zero drift was obtained. Then a known quantity of electrical energy was measured through the heater of the can to be calibrated and the deflection of the galvanometer recorded at one-minute intervals for seven to ten minutes after the heating. The logarithm of the difference between the observed galvanometer reading and the reading at zero drift was plotted against time. At equilibrium in cooling this plot gave a straight line. When the equilibrium drift before and after heating was extrapolated to the middle of the heating period, the correct galvanometer deflection was obtained. The galvanometer deflections during calibration were plotted against the energy in calories, and a straight line was obtained. One calorie was taken equal to 4.1833 international joules.



TOP VIEW
SHOWING OUTLET FROM ONE CAN



Sec. elev. approx. at —S.

Fig. 1.—Differential calorimeter.

A heat of solution was run as nearly the same as the calibration as was possible. This was necessary, because the calorimeter was not adiabatic. Thirty to one hundred milligrams of solid salt was weighed into a thin-walled glass bulb of about 1-ml. capacity, and the bulb fused on a solid glass rod. The resulting concentration of salt was from 0.0005 to 0.001 *M*. The bulb was allowed to come to thermal equilibrium in the calorimeter before breaking. The drifts before and after breaking the sample bulb were extrapolated to half a minute from the beginning of solution. When empty sample bulbs were broken, no appreciable effect was noted. In the case of hydrogen chloride gas 5 to 8 ml. of gas was used per determination. Within experimental accuracy it was found unnecessary to use a fresh sample of solvent for each alkali halide salt. That is, the ΔH° of sodium chloride in water was very nearly independent of the salt already present in solution in the calorimeter. With the small amount of sample used it was possible to run several salts before changing the solvent. Hydrogen chloride runs were made in the absence of salts.

The apparatus was checked in aqueous solution by measuring the heats of solution of potassium chloride, sodium chloride, and hydrogen chloride. Table I shows the heats of solution at infinite dilution and at 25° using two different heaters. The probable errors given cover a number of determinations. Heats of dilution for aqueous solutions were taken from Young and Seligman.[9]

TABLE I

$\Delta H^{\circ}_{298.1^{\circ}\mathrm{K.}}$ IN WATER IN CAL. PER MOLE

	Heater 1	Heater 2	Literature
KCl	4080 ± 40	4065 ± 50	4118[7]
NaCl	930 ± 10	915 ± 5	916[6]
HCl	−17820 ± 400		−17880[8]

TABLE II

HEATS OF SOLUTION AT INFINITE DILUTION AT 298.1°K. IN WATER–METHYL ALCOHOL SOLUTIONS, CAL./MOLE OF SOLUTE[a]

Wt. % CH_3OH	0	20.86	44.18	76.0	100
Mol. % CH_3OH	0	12.91	30.82	64.1	100
LiCl	(−8900)	−7585 ± 50	−8250	−9700 ± 50	−11480 ± 100
NaCl	915 ± 5	1690 ± 30	1600 ± 5	775 ± 25	−1450 ± 100
KCl	4075 ± 40	4625 ± 25	4495 ± 10	2960 ± 25	760 ± 50
RbCl	(4000)		4345	3670 ± 20	1275
CsCl	(4230)			3320	1855
NaBr	−40	680 ± 20	340 ± 10	−740 ± 20	−4000 ± 200
KBr	(4785)	5275 ± 20	4820 ± 15	3800 ± 15	685 ± 50
NaI	(−1820)	−955 ± 20	−1710 ± 10	−3275 ± 10	−7000 ± 100
KI	(4880)	5285 ± 25	4400 ± 100	3060 ± 10	175 ± 100
HCl	−17880	−17280 ± 150	−17000	−18400	−19700 ± 500

[a] Average deviations of experiments from the mean are given rather than the uncertainty of the determinations.

In this and the following tables a positive ΔH° will represent heat absorbed during solution. Heats of dilution were not measured in this research. The heats of dilution of several alkali halide salts in methyl alcohol have been measured.[10] Their values show that the correction to infinite dilution for the small samples used in this research is quite small in most cases. Apparent molal heat content values for salts in water–methanol solutions may be calculated by the Debye–Hückel limiting law. The dielectric constant and its temperature derivative for various water–methyl alcohol solutions was taken from the work of Åkerlöf.[11] The calculated apparent molal heat of dilution of a uni-univalent salt at 25° in pure methyl alcohol is $2900C^{1/2}$, where C is the concentration in moles per liter. The calculated heat of dilution of the average sample of about 0.0005 mole is 65 calories in absolute methyl alcohol. This Debye–Hückel heat of dilution becomes larger as one dissolves 0.0005 mole of salt in alcohol of increasing initial salt concentration. However, in the case of aqueous solutions the experimental heats of dilution of many salts go through a maximum and then change sign. This might well be the case for water–methyl alcohol solutions, because the average deviation of a number of successive integral heats of solution was not very great and certainly within experimental error. No correction was made for the heat of dilution of hydrogen chloride solutions.

Results. Heats of Solution at 25°

In Table II are the measured heats of solution in 0, 12.91, 30,82, 64.1 and 100.0 mole per cent. methyl alcohol. From two to five determinations were made on each salt, and the mean deviation is tabulated. The values in water in parentheses were taken from Bichowsky and Rossini[12] and corrected to 298.1°K. by partial molal heat capacity data.

All of the salts follow the same general curve, that is, they go through a maximum at low methyl alcohol concentrations, and evolve considerably more heat in methyl alcohol than in water.

In discussing the accuracy of the experimental results it might be said that the heats of solution are good to 100–150 calories in all but absolute methyl alcohol solution. The accuracy of any determination in this apparatus depended primarily on how nearly identical the heat leak for a heat of solution compared with that of calibration. It is apparent that this was closely approached for salts in pure water in which case one-minute heating periods were used for calibration. The time for solution of all the salts was very nearly the same for aqueous, 12.91, 30.82, and 64.1 mole per cent. methyl alcohol solutions. Therefore the same accuracy can be expected for these runs as in water. In absolute methyl alcohol lithium chloride, sodium bromide, sodium iodide, and potassium iodide dissolved at nearly the same rate as in water and the values are probably good to 200 calories. However it took ten to

---

[7] A. Lange and J. Monheim, *Z. physik. Chem.*, **A150**, 349 (1930).

[8] F. D. Rossini, *Bur. Standards J. Research*, **9**, 679 (1932).

[9] T. F. Young and P. Seligman, THIS JOURNAL, **60**, 2379 (1938).

[10] N. S. Jackson, A. E. C. Smith, O. Gatty and J. H. Wolfenden, *J. Chem. Soc.*, 1376 (1934).

[11] G. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

[12] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York 1936.

twenty minutes for the samples of sodium chloride, potassium chloride, and potassium bromide to dissolve in methyl alcohol and the resulting heat loss would give a very low heat of solution since one minute calibrations were used. This slow rate was observed despite the fact that only some 50 mg. of powdered sample was used for a liter of solvent and the solvent was well stirred. From the rate of solution of rubidium chloride and cesium chloride in absolute methyl alcohol the probable error is somewhat greater than 200 calories. The error in the values for hydrogen chloride is closer to 500 calories due to the greater heat effect.

Discussion.—The heat of solution of sodium chloride at 20° in water–methyl alcohol solutions has been determined by Moss and Wolfenden[13] in a calorimeter described by Askew, Jackson, Gatty, and Wolfenden.[14] Moss and Wolfenden used data for the heat of solution in absolute methyl alcohol from a previous research.[15] In Fig. 2 the heat of solution of sodium chloride in water–methyl alcohol solutions is plotted from reference 11 (20°) and Table II (25°). The data are within experimental error at least as far as the 64.1 mole per cent. value obtained in this research, but deviate considerably toward the methyl alcohol axis. After considering the slow rate of solution of sodium chloride in methyl alcohol and the shape of the curves below 64 mole per cent., the value of $\Delta H^\circ_{298.1}$ for sodium chloride in absolute methanol was taken as -2000 calories. The solid line is the finally accepted curve for sodium chloride at 25°. The dotted line is the data of Moss and Wolfenden at 20°.

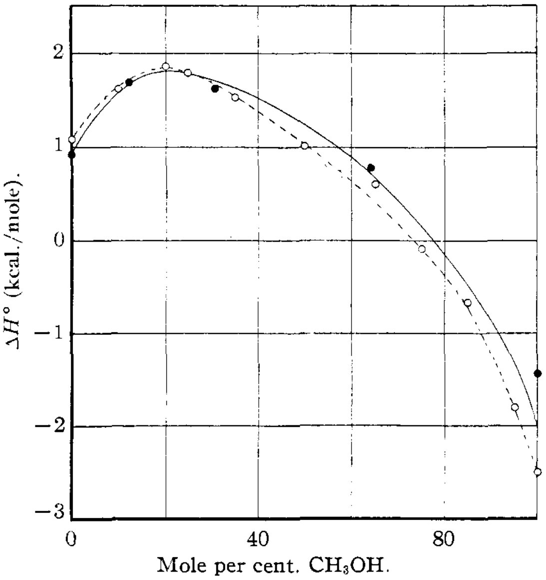


Fig. 2.—Heat of solution of sodium chloride in water–methyl alcohol solutions: ○, Moss and Wolfenden (20°); ●, This Research (25°).

Similar errors in the measurement of potassium chloride and potassium bromide in absolute methyl alcohol could be expected. Values of 1080 and 870 calories were chosen for potassium chloride and potassium bromide, respectively.

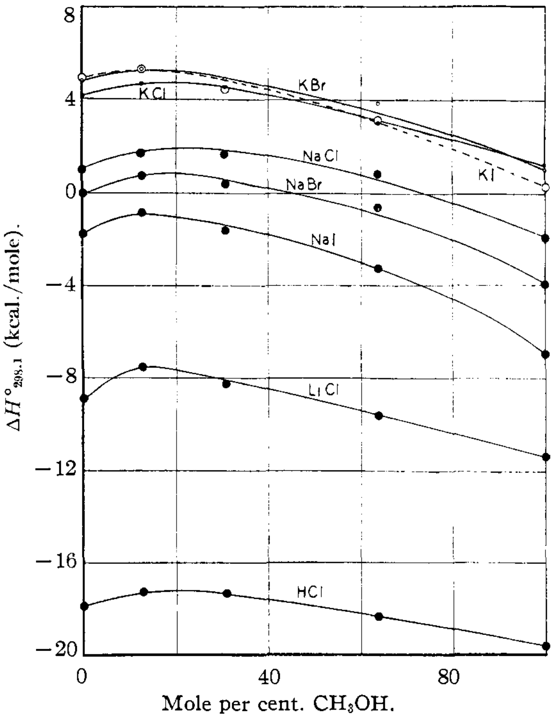


Fig. 3.—Heats of solution at infinite dilution at 298.1°K. in water–methyl alcohol solutions in kcal./mole.

In Fig. 3 is plotted all of Table II except the data for rubidium chloride and cesium chloride and the values for sodium chloride, potassium chloride and potassium bromide in absolute methyl alcohol. The values taken for the three latter salts are -2000, 1080 and 870, respectively. Rubidium chloride and cesium chloride were excluded to avoid crowding of the curves. Values from the smooth curves of Fig. 3 at intervals of 10% methyl alcohol by weight are given in Table III.

The author wishes to express his appreciation for the suggestions and advice given by Professor

---

[13] R. L. Moss and J. H. Wolfenden, *J. Chem. Soc.*, 118 (1939).

[14] F. A. Askew, N. S. Jackson, O. Gatty and J. H. Wolfenden, *ibid.*, 1362 (1934).

[15] F. A. Askew, E. Bullock, H. T. Smith, R. K. Tinkler, O. Gatty and J. H. Wolfenden, *ibid.*, 1368 (1934).

TABLE III

HEATS OF SOLUTION AT INFINITE DILUTION AT 298.1°K. FROM SMOOTH CURVES, CAL./MOLE OF SOLUTE

Wt. % CH_3OH	Mole % CH_3OH	$-\Delta H^\circ$ HCl	$-\Delta H^\circ$ LiCl	ΔH° NaCl	ΔH° KCl	ΔH° KI	$-\Delta H^\circ$ NaI	ΔH° KBr	ΔH° NaBr	ΔH° RbCl	ΔH° CsCl
0	0.00	17880	8900	920	4120	4870	1820	4780	−30	4000	4240
10	5.88	17550	8000	1400	4410	5200	1250	5050	450	4170	4400
20	12.32	17320	7600	1680	4610	5300	1000	5230	650	4290	4450
30	19.41	17200	7800	1750	4620	5200	1150	5150	660	4340	4420
40	27.25	17240	8050	1720	4540	5000	1400	4950	550	4350	4340
50	36.08	17440	8400	1590	4280	4620	1750	4550	300	4290	4160
60	45.74	17740	8800	1375	3870	4100	2150	4070	−40	4150	3920
70	56.73	18030	9350	1030	3400	3470	2800	3530	−600	3910	3600
80	69.41	18500	9950	500	2790	2700	3750	2820	−1320	3450	3150
90	83.50	19030	10650	−350	2060	1700	5050	2020	−2400	2630	2580
100	100.0	19700	11500	−2000	1080	175	7000	870	−4000	1280	1850

K. S. Pitzer. The difficult task of constructing the thermopile was carried out by Mr. G. F. Nelson and Mr. P. Fabricius.

Summary

The heats of solution at infinite dilution of the chlorides of lithium, sodium, potassium, rubidium, cesium and sodium bromide, potassium bromide, sodium iodide, potassium iodide and hydrogen chloride were determined in water–methyl alcohol solutions at 298.1°K. All of the compounds exhibited an appreciable maximum heat absorbed at around 15 mole per cent. methyl alcohol, and all of them evolved more heat upon solution in absolute methyl alcohol than in water.

BERKELEY, CALIFORNIA RECEIVED APRIL 2, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, AND THE DEPARTMENT OF SURGERY, CORNELL UNIVERSITY MEDICAL COLLEGE]

Oxidation–Reduction Potentials Measured with the Dropping Mercury Electrode. III. Polarographic Study of Quinhydrone in Buffered and Unbuffered Solutions[1]

BY OTTO H. MÜLLER[2]

In the first paper of this series,[3] it has been shown that a slowly dropping mercury electrode can function as a reliable indicator electrode for oxidation–reduction potentials. Under certain well defined conditions, this dropping mercury electrode was used in the presence of quinhydrone to determine the *p*H of solutions which were well buffered between *p*H 2 and *p*H 8. Even poorly buffered solutions were studied with this electrode and the *p*H values thus found agreed well with results obtained in different ways by others.

The latter investigations were carried out in potassium acid phthalate solutions which were diluted to different degrees. In spite of the fact that all were saturated with quinhydrone, the potentials were poorly poised in the more dilute solutions of potassium acid phthalate. One could notice marked oscillations of the galvanometer with each growing drop of mercury; also changes in the balancing e. m. f. produced relatively small changes in current. This is in contrast to well-buffered, well-poised systems, where oscillations of the galvanometer from its zero position during the growth of the mercury drops are negligible, and where slight changes in the balancing e. m. f. throw the galvanometer off scale. It seemed of interest to investigate this action of buffers further, using a polarograph for the automatic plotting of current–voltage curves.[4,5,6]

These experiments have brought out many peculiarities of polarographic curves which have hitherto not been observed. They also give new information about the processes at electrode–

---

[1] Presented in part before the Division of Physical and Inorganic Chemistry at the Ninety-sixth meeting of the American Chemical Society held at Milwaukee, Wisconsin, September 5–9, 1938. This work was supported at Stanford University by a fellowship from the Upjohn Company and at Cornell University Medical College by a grant from the John and Mary B. Markle Foundation.

[2] Present address: Cornell University Medical College, New York City.

[3] O. H. Müller and J. P. Baumberger, *Trans. Electrochem. Soc.*, **71**, 169 (1937).

[4] J. Heyrovský and M. Shikata, *Rec. trav. chim.*, **44**, 496 (1925).

[5] J. Heyrovský, in W. Böttger, "Physikalische Methoden der analytischen Chemie," Akademische Verlagsgesellschaft, Leipzig, Vol. II, 1936, and Vol. III, 1939.

[6] I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).