Thermometric Cyanide Titration of Silver, Nickel and Mercury

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Thermometric determination of the silver(I) or nickel(II) ions in aqueous solutions with potassium cyanide according to the method of David Hume yields results to a precision within 0.3 % and without any significant deviation from the results obtained by classical methods. Simultaneous determination is not possible. The rate of reaction of the formation of cyanide complexes of mercury is too low to give satisfactory results. The titrations were carried out with a motor-driven syringe burette and a strip chart recorder.

The principle of thermometric titration will be known for instance from the work of David Hume *et al.*¹ A survey of the work within this field up to 1959 has been given by Zenchelsky². The special case of cyanide reacting with silver, nickel, or mercury ions has been investigated by Mondain-Monval^{3,4}. These previous investigations have, however, been carried out with comparatively simple equipment, such as a Beckman thermometer for the temperature measurement and manual plotting of the titration curve. The purpose of the present work has been to make sure whether the processes mentioned can serve as the basis of a satisfactory quantitative determination of the metal ions, when modern automatic analytical equipment is used. The main advantage of this would be that the end point obtained on the recorder chart is always sharp and unambiguous, whereas the visual end point of the conventional cyanide titration (the dissolution of a small precipitate of silver halide) may be difficult — and in slurries or in strongly coloured solutions even impossible — to establish.

EXPERIMENTAL

Apparatus. The titration vessel was a Dewar flask 5" × 1 ½" i.d. fitted with a cork stopper to support the burette tip and the temperature sensing element. The flask was uncoated so that the reaction could be followed visually. The titrator was added from a motor driven syringe burette, Radiometer SBU1, at a rate of 0.75 ml per minute, total capacity 5 ml. The syringe was driven by its own motor, not coupled to the recorder

chart drive. The burette tip was bent upwards to prevent the concentrated titrator from falling out into the titrant before the piston was moved, and the solution stirred with an adjustable magnetic stirrer.

The temperature sensing element was a thermistor, Philips B8 320.05/1K1, and the recorder was a 2.5 mV, 1sec Honeywell 153XI8-VH-II-III-118-R; as to the circuitry, cf. Hume¹. The chart width corresponded to a little less than a tenth of one degree centigrade. The recorder chart speed was 8" per minute.

Reagents. The potassium cyanide was Merck (Darmstadt) 4965 96–98 % KCN, granular, free from sodium. All other reagents were Merck or Riedel-de-Haën reagent grade.

Calibration. The syringe burette was calibrated by a Volhard titration together with a thermometric titration of the same aliquot of hydrochloric acid solution. The syringe burette was charged with the acid and the Dewar flask with an excess of sodium hydroxide solution. A suitable amount of acid was run into the Dewar, and the temperature rise recorded. The chloride content of the Dewar and finally the strength of the hydrochloric acid were then determined by Volhard titrations. Comparison of the titrations with chart consumption during the addition of acid (the distance between the two break points on the temperature curve) showed that the burette discharge rate was (0.02361 ± 0.00004) ml per unit of chart consumption.

DETERMINATION OF SILVER

When potassium cyanide is added to a silver nitrate solution, a white precipitate of silver cyanide is formed; with an excess of cyanide it is dissolved again as dicyanoargentate(I) ions. According to Bjerrum's tables⁵ the solubility product of silver cyanide is 10^{-15} and the stability constant of the dicyanoargentate(I) ion is $10^{20.7}$; the conversion should therefore be complete at the equivalence points. The heats of reaction are, according to Landolt-Börnstein⁶ 27.8 kcal/mole for the formation of silver cyanide from the free ions in aqueous solution, and 6.5 kcal/mole for the dissolution to dicyanoargentate(I) ions. The thermometric titration curve does show two parts with different slopes, but the end point corresponding to silver cyanide is blurred, and there is no end point at all corresponding to total dissolution of the precipitate, this process apparently being too slow to follow the titration.

To overcome this difficulty, an amount of ammonia just sufficient to dissolve the silver oxide initially formed was added prior to the titration. The stability constant of silver diammino ion⁵ is $10^{7.2}$, and its heat of formation⁶ 13.4 kcal/mole. In the thermometric titration a precipitate of silver cyanide was still observed, but there was no corresponding break point on the curve. With the dissolution, however, a sharp break point corresponding to dicyanoargentate(I) ion formation was recorded, yielding both consistent and fairly accurate results. The addition of further amounts of ammonia was without perceptible influence.

The silver nitrate solution used in the experiments was prepared by weighing pure silver nitrate. The different samples were diluted to 40 ml before titration.

The potassium cyanide solution was standardized against the silver nitrate with an iodide indicator⁷. In such a solution cyanide ions will be oxidized slowly by the air to cyanate ions and thus the normality will decrease upon standing⁸. In order to compare the results from the thermometric and the conventional titrations it is therefore necessary to interpolate to the same date.

Table 1. Thermometric titration of silver nitrate with potassium cyanide to form dicyanoargentate(I) ions.

Day No.	AgNO ₃ taken mmoles	NH ₃ added	Number of chart units	Normality of KCN solution equiv./l	Deviation %
5	3.2108	yes	86.69	1.569	-0.3
	3.1146	yes	83.75	1.575	+0.2
	3.2798	yes	88.19	1.575	+0.2
	3.1146	yes	84.00	1.571	-0.1
				Mean: 1.573 ± 0.001	± 0.2
8	3.2140	no	~92	1.48	+0.7
	2.9590	no	~86	1.46	-0.7
				Mean: 1.47 ± 0.01	± 0.7
9	0.8003	yes	20.38	1.663	+0.6
	0.8099	yes	20.81	1.648	-0.6
				Mean: 1.656 ± 0.007	± 0.6
25	3.2429	yes	87.44	1.571	
32	3.3375	yes	90.88	1.555	+0.1
	3.2220	yes	87.69	1.556	+0.1
	3.2060	yes	87.88	1.545	-0.6
	3.1114	yes	85.13	1.548	-0.4
	3.1627	yes	86.00	1.558	+0.2
	3.3038	yes	89.38	1.565	+0.7
				Mean: 1.555 ± 0.003	± 0.5
40	3.2220	yes	88.69	1.539	-0.8
	3.2397	yes	88.75	1.546	-0.3
	3.2718	yes	88.38	1.563	+1.1
				Mean: 1.549 ± 0.007	± 1.0
51	3.2124	yes	88.00	1.546	

Normality of potassium cyanide solution on day No. 8:

As computed from the above data: 1.570 ± 0.005 equiv./l

As found by titration with iodine indicator: 1.575 ± 0.001 equiv./l

The results of the experiments are given in Table 1. It is seen that the reproducibility is fair except for silver concentrations smaller than 1 mmole in 40 ml, *i.e.* the concentration of the solution to be titrated should not be below 0.03 N. The normality of the cyanide solution on day No. 8 is found by interpolation of the results of thermometric titrations to be 1.570 ± 0.005 equiv./l and by titration with iodide indicator 1.575 ± 0.001 equiv./l. The disagreement between the two methods is thus less than 0.3 %.

DETERMINATION OF NICKEL

When potassium cyanide is added to a nickel sulfate solution, a precipitate of nickel cyanide is formed; with an excess of cyanide it is dissolved again as tetracyanonickelate(II) ions. According to Bjerrum's tables⁵ the solubility

product of nickelous tetracyanonickelate(II) is $10^{-8.77}$ and the stability constant of the tetracyanonickelate(II) ion is 10^{22} ; the conversion should thus be practically complete at the equivalence points. According to Landolt-Börnstein ⁶ the heat of formation of nickel cyanide from the free ions in aqueous solution is 31.6 kcal/mole. As in the case of the titration of silver, the thermometric titration curve showed no definite end point, the processes evidently being too slow to follow the titration. Calculation shows that this may well be due to the formation of basic precipitates instead of pure nickel cyanide.

It was first tried, as in the case of silver, to prevent the formation of any precipitate by adding ammonia prior to the titration. A rather concentrated ammonia solution, about 1 N, was required, however, and the thermometric titration curves continued to show fading end points, although the stability constant ⁵ of the nickelous hexammine complex is only $10^{8.31}$, so that total conversion to the cyanide complex was to be expected.

Next it was tried to add ammonium chloride prior to titration. Calculation shows that the ammonium ion should be able to prevent the formation of basic compounds while allowing nickelous tetracyanonickelate(II) precipitate. Experimentally both precipitation and redissolution were in fact observed; and the thermometric curve showed two break points, of which the end point corresponding to complete dissolution was sharp and reproducible. Sharp end points were also obtained, even if up to 3 moles of free ammonia per mole of nickel sulfate were present at the start of the titration. Mixed with 12 moles of ammonium chloride per mole of nickel sulfate this would give a pH of 8.5 at the end of the titration, and at that pH normal nickelous tetracyanonickelate(II) still precipitates.

The nickel sulfate solution used in the experiments was standardized by electrodeposition of the nickel ⁹. The sample volume at the start of the titration was 40 ml. The potassium cyanide solution was the same as that used for the silver determinations.

The results of the experiments are shown in Table 2. It is seen that the precision is better than 0.3 %, and that for nickel concentrations greater than 0.01 mole per liter the disagreement with the electrolytic determination is of the order of 0.3 %. This discrepancy may be due to impurities, *e.g.* zinc or alkali metals in the nickel sulfate used. In the titration of nickel solutions more dilute than 0.01 M larger negative errors occur.

SIMULTANEOUS DETERMINATION OF SILVER AND NICKEL

Solutions containing both silver nitrate and nickel sulfate were titrated with potassium cyanide. The thermometric curve showed only one break point, corresponding to the total complexation of both silver and nickel, so that the determination of each constituent was not possible.

DETERMINATION OF MERCURY

When potassium cyanide is added to a mercuric chloride solution a white precipitate of mercuric cyanide is formed; in excess cyanide it is dissolved again as tetracyanomercurate ions. The complexity constant of mercuric

Table 2. Thermometric titration of nickel sulfate with potassium cyanide to form tetracyanonickelate(II) ions.

Day No.	Normality of KCN solution equiv./l	Conc. of NH ₃ moles/l	Conc. of NH ₄ Cl moles/l	NiSO ₄ taken mmoles	NiSO ₄ found mmoles	Deviation %
1	1.575	0.1	0.5	1.594	1.593	— 0.1
				1.589	1.596	+ 0.4
				1.593	1.607	+ 0.9
				1.593	1.600	+ 0.4
				1.596	1.599	+ 0.2
				1.756	1.756	0.0
				1.593	1.596	+ 0.2
				1.594	1.596	+ 0.1
				1.598	1.604	+ 0.4
				1.549	1.560	+ 0.7
		Mean:	+ 0.3			
2	1.574	0.005	0.5	1.623	1.636	+ 0.8
			1.662	1.669	+ 0.4	
4	1.573			1.570	1.574	+ 0.3
				1.573	1.575	+ 0.1
					Mean:	+ 0.4
4	1.573	0	0.5	0.385	0.383	— 0.5
				0.386	0.384	— 0.5
				0.172	0.165	— 4.1
				0.080	0.073	— 8.8
8	1.570	0	0	1.546	1.573	+ 1.7
				1.448	1.499	+ 3.5
4	1.573	0	0.5	1.568	1.566	— 0.1
				1.565	1.572	+ 0.5
33	1.553			1.567	1.574	+ 0.5
				1.516	1.524	+ 0.5
				1.644	1.644	0.0
				1.513	1.519	+ 0.4
				1.553	1.558	+ 0.3
				1.425	1.425	0.0
				1.432	1.434	+ 0.1
				1.633	1.643	+ 0.6
				Mean:	+ 0.3	

Concentration of NiSO₄ solution, determined by electroprecipitation:

$$0.07726 \pm 0.00003 \text{ mmoles/g}$$

chloride is $10^{13.22}$ and that of the tetrachloromercurate ion is $10^{15.22}$; but the complexity constants of mercuric cyanide and of the tetracyanomercuate ion are $10^{34.70}$ and $10^{41.52}$, respectively (all constants taken from Bjerrum's tables ⁵). The conversion should therefore be complete at the equivalence points. The heat of reaction ⁶ by the conversion of mercuric chloride in solution to a mercuric cyanide precipitate is 33.2 kcal per mole, and by the subsequent dissolution process 12.4 kcal per mole. Correspondingly, the thermometric

titration curve has two parts with different slope; but in this case the break point corresponding to maximum precipitation is sharp and reproducible, whereas the dissolution process is slow and yields a smooth curve with no break points at all. This applies whether a solution of pure mercuric chloride in water is titrated, or a solution of mercuric chloride in excess potassium chloride, *i.e.* the tetrachloromercurate ion is titrated. Some experiments with potassium tetraiodomercurate were also carried out, but no precipitates were formed from these solutions and there were no break points at all on the corresponding thermometric curves. This does not necessarily mean that a conversion does not occur, for the complexity constant ⁵ of the tetraiodomercurate ion is only $10^{30.2}$, and a decolorizing of the solution is observed upon the addition of potassium cyanide; but the conversion is too slow for the titration procedure.

In order to find out whether the exchange of other ligands than halogens for cyanide would proceed more expediently, a solution of mercuric oxide in as small excess of nitric acid as possible was titrated with potassium cyanide. Again no precipitate was formed, but nevertheless the titration curve showed the same appearance as in the titration of mercuric chloride. Because of the unfeasibility of titrating with cyanide into an acid solution these experiments were not pursued; but they seem to indicate that the slow conversion to tetracyanomercurate ion is not due to a slow dissociation of the mercuric halide complexes, but rather to a slow uptake of the last two cyanide groups.

The mercuric chloride solution used in the experiments was standardized by the weighing out of pure mercuric chloride. The potassium cyanide solution was the same as that used for the silver and nickel determinations.

The results of the titrations of mercuric chloride are given in Table 3. It is seen that the precision is but mediocre, and that on an average the results are more than 1 % high.

CONCLUSIONS

The experiments have shown that it is possible to determine silver and nickel by thermometric titration with potassium cyanide with a precision of ± 0.3 % and without significant deviation from the results obtained by

Table 3. Thermometric titration of mercuric chloride with potassium cyanide to form a precipitate of mercuric tetracyanomercurate.

Day No.	Normality of KCN solution equiv./l	HgCl ₂ taken mmoles	HgCl ₂ found mmoles	Deviation %
29	1.556	1.680	1.694	+ 0.8
		1.647	1.660	+ 0.8
		1.576	1.609	+ 2.1
40	1.548	2.404	2.430	+ 1.1
		2.405	2.449	+ 1.8
		1.900	1.910	+ 0.5
				Mean: + 1.2

Concentration of HgCl₂ solution, by weighing: 0.08031 moles/l.

classical methods. Thermometrical titration of mercury with potassium cyanide does not give satisfactory results.

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