

THE POTENTIAL/pH DIAGRAM OF SILVER IN AQUEOUS AMMONIUM SALT SOLUTION*

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Abstract—The potential/pH diagram of silver in aqueous ammonium salt solution at 25°C has been calculated and verified experimentally.

Calculations were carried out on the basis of the standard potential of the silver/silver-ion couple, the dissociation constants of the silver mono- and di-ammonia complex, and the dissociation constant of the ammonium ion, the total silver and nitrogen content being kept constant. The calculated diagram was verified by measuring the potential of the silver electrode at pH values varying from 2 to 12.

The measured diagram agrees well with the calculated one; minor differences (up to 15 mV) occur only in the alkaline range.

The establishment of the potential is sufficiently rapid to record the entire diagram on a suitable pen-and-ink X/Y recorder within a few minutes. Accordingly, such a recording may serve well as a lecture demonstration on potential/pH diagrams.

Résumé—Le diagramme tension-pH de l'argent en solution ammoniacale aqueuse à 25°C a été calculé et vérifié expérimentalement.

Le calcul a été effectué à partir de la tension standard du couple Ag/Ag⁺ et des constantes de dissociation de l'ion ammonium et des complexes de l'argent avec une ou deux molécules d'ammoniac, les teneurs totales en argent et azote étant maintenues constantes. Le diagramme calculé a été vérifié en mesurant la tension de l'électrode d'argent à des valeurs du pH comprises entre 2 et 12.

Le diagramme mesuré est en bon accord avec le calcul; des différences relativement faibles (jusqu'à 15 mV) ont été observées seulement en milieu alcalin.

Zusammenfassung—Das spannungs-pH-Diagramm von Silber in wässriger Ammonsalzlösung bei 25°C. wurde errechnet und experimentell verifiziert.

Die Rechnung hatte die folgenden Werte als Grundlage: Das Normalpotential des Silber-Silberion-Paares, die Dissoziationskonstanten der mono- und di-Ammoniumkomplexe des Silbers die Dissoziationskonstante des Ammoniumions, wobei der Totalgehalt an Silber und Stickstoff konstant bleiben muss. Das gerechnete Diagramm wurde durch Potentialmessungen an der Silber-electrode bei pH 2 bis 12 kontrolliert.

Die Messwerte und das errechnete Diagramm stimmen gut überein; kleine Differenzen bis zu 15 mV ergaben sich nur im alkalischen Bereich.

Die Potentialeinstellung ist so rasch, dass das gesamte Diagramm sich in wenigen Minuten mittels eines X/Y-Schreibers direkt aufnehmen lässt. Demzufolge kann eine solche Aufnahme gut als Demonstration eines Spannungs-pH-Diagramms in der Vorlesung durchgeführt werden.

INTRODUCTION

POTENTIAL/pH diagrams owe their use to the clear mental picture one can build of possible reactions of a given Red/Ox system. Accordingly, they are used in many branches of chemistry,¹ analytical chemistry,² corrosion³ and geology.⁴

Many potential/pH diagrams have been calculated during the last decade⁵ from thermodynamic data. Experimental verification has been carried out in a number of cases,⁶ especially for elements that are of interest in view of corrosion.

Generally, verification by measuring equilibrium potentials meets with serious

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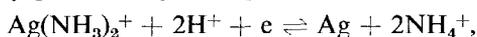
difficulties. These difficulties may be due to the slow establishment of various chemical equilibria pertaining to the given Red/Ox system. Especially when precipitates are present, it may take much time for equilibrium conditions to be attained.

Potential/pH diagrams being so instructive in teaching inorganic and electro-analytical chemistry, it was thought worth while to look for one of which the experimental verification could be easily carried out as a lecture demonstration. We examined the system consisting of a silver electrode in a concentrated solution of ammonium nitrate to which a small quantity of silver nitrate had been added, the pH being regulated by adding small quantities of concentrated solutions of sodium hydroxide or nitric acid. This system was chosen because (a) precipitation does not occur, (b) the silver electrode attains its equilibrium potential rapidly, (c) reliable equilibrium data are available.

QUALITATIVE DESCRIPTION OF THE POTENTIAL/pH DIAGRAM

At *low* pH values all silver present in solution occurs as "free" silver ions. The potential of the silver electrode is independent of pH.

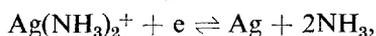
On *raising* the pH, precipitation does not occur but the silver in solution is gradually transformed into complex silver ammonia ions. The potential of the silver electrode is then mainly governed by the equilibrium



with

$$dE/dpH = -2 \times 0.059 \text{ V/pH (25}^\circ\text{C)}.$$

At *still higher* pH values the ammonium ions are gradually transformed into ammonia, and the silver in solution will be present as $\text{Ag}(\text{NH}_3)_2^+$ almost quantitatively. The potential-governing equilibrium may be written

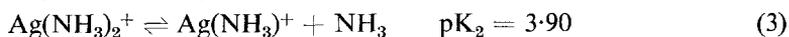


which is again independent of pH.

CALCULATIONS

(a) Basic equilibria and assumptions

The following equilibria* and constants are taken into account:



Four simplifying assumptions are made in our calculations:

(1) For practical reasons, the total silver content and the total nitrogen content† of the solution are taken as constant:

$$[\text{Ag}^+] + [\text{Ag}(\text{NH}_3)^+] + [\text{Ag}(\text{NH}_3)_2^+] = C_1 \quad (5)$$

$$[\text{NH}_3] + [\text{NH}_4^+] + [\text{Ag}(\text{NH}_3)^+] + 2[\text{Ag}(\text{NH}_3)_2^+] = C_2 \quad (6)$$

* The equilibria previously used in the qualitative description of the potential/pH diagram are not independent. They are related to the basic equilibria (2), (3) and (4).

† Except, of course, for the nitrogen added as NO_3^- during acidification of the solution with nitric acid.

(2) We assume that the total silver content is much smaller than the total nitrogen content. Only a negligible quantity of ammonia will then be involved in the complex formation. Consequently, equation (6) reduces to

$$[\text{NH}_3] + [\text{NH}_4^+] = C_2. \quad (7)$$

(3) Dilution effects as a result of the addition of base or acid are not taken into account. This assumption is allowable, provided that the base or acid is sufficiently concentrated (see also experimental procedure).

(4) Activities are assumed to be identical with concentrations.

(b) *Calculation of potential/pH curve*

The potential of the silver electrode at a given pH is calculated as follows. At the given pH, the ratio $[\text{NH}_3]/[\text{NH}_4^+]$ is calculated from the relationship

$$\text{pK} = \text{pH} + \text{pNH}_3 - \text{pNH}_4. \quad (8)$$

From this ratio together with the known sum, equation (7), of $[\text{NH}_3]$ and $[\text{NH}_4^+]$ the concentration of NH_3 is found as a preliminary result.

Introduction of the known NH_3 concentration into the relationship

$$\text{pK}_1 = \text{pAg} + \text{pNH}_3 - \text{pAg}(\text{NH}_3) \quad (9)$$

yields the ratio $[\text{Ag}(\text{NH}_3)^+]/[\text{Ag}^+]$. Knowledge of this ratio enables us to substitute $[\text{Ag}(\text{NH}_3)^+]$ by $[\text{Ag}^+]$ in equation (5).

Substitution of the *di*-complex concentration by $[\text{Ag}^+]$ in equation (5) is carried out in a similar way. The ratio $[\text{Ag}(\text{NH}_3)_2^+]/[\text{Ag}(\text{NH}_3)^+]$ is computed from

$$\text{pK}_2 = \text{pAg}(\text{NH}_3) + \text{pNH}_3 - \text{pAg}(\text{NH}_3)_2 \quad (10)$$

at the known NH_3 concentration. The concentration of $\text{Ag}(\text{NH}_3)_2^+$ can then be expressed in that of $\text{Ag}(\text{NH}_3)^+$ which, in turn, can be expressed in that of Ag^+ .

Finally, the concentration of free Ag^+ ions is calculated from equation (5) and is introduced in the Nernst equation,

$$E = E^\circ - 0.05915 \text{ pAg}, (25^\circ\text{C}) \quad (11)$$

from which E follows immediately.

The foregoing calculation of E has been carried out for $C_1 = 10^{-3} \text{ M}$ and $C_2 = 10^{-1} \text{ M}$ at a number of pH values (varying from 2 to 12). The result is shown in Fig. 1, in which the solid curve represents the calculated potential as a function of pH. The small insert in Fig. 1 indicates that the entire curve lies within the stability range of water. One may show that at pH values smaller than 6.53 (dotted line *a*) more than 50 per cent of the silver present in solution occurs as free Ag^+ ions, whereas at pH values exceeding 6.75 (dotted line *b*) more than 50 per cent of it is involved in the *di*-complex formation. Dotted line *c* (drawn at $\text{pH} = \text{pK}$) separates the regions of predominance of NH_3 and of NH_4^+ .

EXPERIMENTAL TECHNIQUE

The cell (filled with a solution 0.1 M in ammonium nitrate and 0.001 M in silver nitrate) contains the following components (see also Fig. 2): silver electrode, glass electrode ("Radiometer" type G 202B with negligible salt error), one end of a salt

bridge and inlet tubes (from burettes filled with 5 N NaOH and 8 N HNO₃ respectively), all these components being mounted in a rubber stopper at the top of the cell. The mountings should be gas-tight to prevent loss of NH₃ to the atmosphere (see also results). The salt bridge (filled with a solution of 1.75 M KNO₃ and 0.25 M NaNO₃ in agar) keeps the silver solution separated from the saturated calomel electrode, thus preventing contamination of the silver solution with chloride. Stirring is magnetic. The cell is kept at constant temperature (25°C ± 0.2).

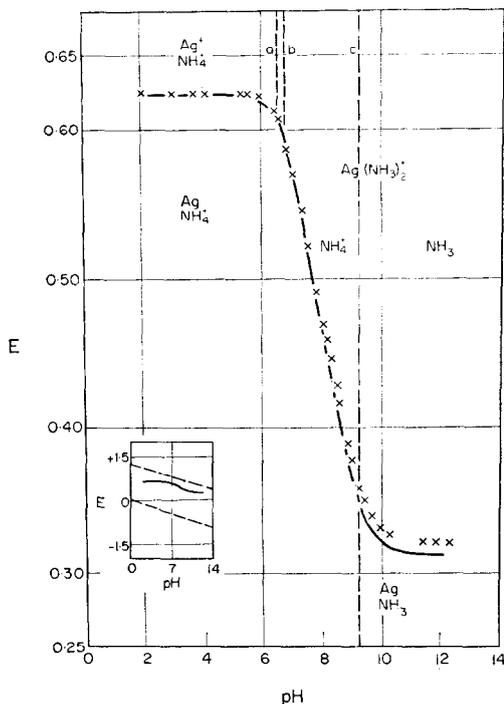


FIG. 1. Potential/pH diagram of silver in aqueous ammonium salt solution. Solid curve represents calculated diagram; points of measured diagram are indicated with *x*. Dotted lines: see text. Inset shows position of curve with relation to the stability region of water.

When a "manually" determined diagram is aimed at, the pH of the solution is varied at will by adding small quantities of base or acid from the burettes. Readings of potential and pH are taken from a "Radiometer" type 22 pH-meter, set for millivolt measurements, and from a similar one, set for pH measurements, respectively.

In case automatic recording of the diagram is desired, the output of the former pH-meter is led (after adequate attenuation) to the Y channel of a Leeds and Northrup G-type *Speedomax* X/Y recorder, whereas the output of the latter feeds the X channel. Smooth recording is obtained by applying capillary inlet tubes which ensure a regular flow of base or acid.

Measurements are carried out as follows. To begin with, the solution is acidified to pH 2 with the aid of some nitric acid. Working manually, small quantities of base are then added successively and a reading of both potential and pH is taken after each

addition. When pH 12 has been reached the addition of base is stopped and acid is allowed to enter the cell. Readings are now taken from pH 12 to pH 2. With automatic recording, the base and acid, respectively, are allowed to flow into the cell at a moderate rate. Recording may be finished within five or ten minutes.

RESULTS

A series of readings of potential at varying pH is shown in Fig. 1. Only readings at increasing pH have been shown. Readings at decreasing pH appeared in good agreement as can be seen from the "to and fro" recording shown in Fig. 3.

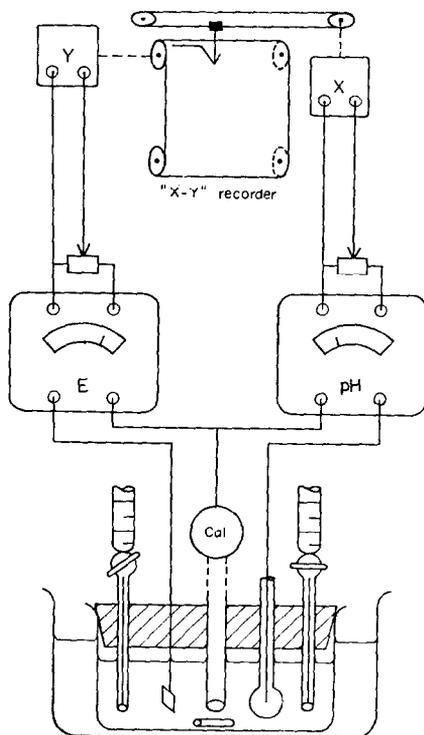


FIG. 2. Experimental technique (schematic) for either manual or automatic measurement of potential/pH diagram.

Preliminary measurements on an *open* cell yielded somewhat unsatisfactory results. In the alkaline range, the potential of the silver electrode showed a tendency to increase with time after addition of a given quantity of base or acid. Obviously, loss of NH_3^* from the solution to the atmosphere shifted the dissociation equilibria in favour of free silver ions, thus giving rise to an increasing potential of the silver electrode.

It is seen from Fig. 1 that the measured diagram agrees fairly well with the calculated one. Minor departures (up to 15 mV) from the calculated diagram in the alkaline range may be due to identification of activities with concentrations.

Automatic recording of the diagram may be attractive as a lecture demonstration on potential/pH diagrams.

* partial pressure of NH_3 at pH 11, under conditions prevailing here, is *ca.* 3 cm of Hg.

The present diagram being established we hope to investigate some of its kinetic⁸ aspects by means of relaxation methods developed in our laboratory.^{9,10}

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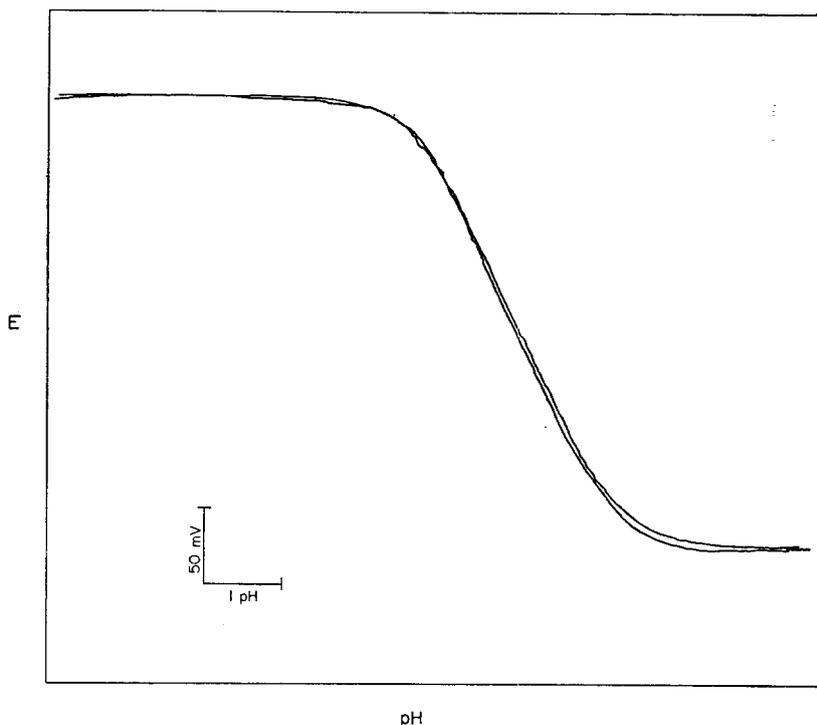


FIG. 3. Recording on X/Y recorder of potential/pH diagram of silver in aqueous ammonium salt solution. pH has been varied from 2 to 12 and back. The curves are practically indistinguishable.

DISCUSSION

G. VALENSI. Je félicite les auteurs pour l'élégance de leur technique et la concordance remarquable entre les résultats expérimentaux et les données théoriques d'équilibre. Pour multiplier de tels recouplements, ne serait-il pas intéressant de faire varier expérimentalement la tension (au lieu du pH), en disposant dans les burettes une solution oxydante et une solution réductrice convenables (exemple: quinone-hydroquinone)? Bien entendu, la complexité du système total pourrait alors être responsable de complications parasites. Toutefois, ayant déjà essayé cette méthode pour le diagramme du soufre, je pense que c'est une question de tâtonnement dans le choix des réactifs.

J. H. SLUYTERS and M. D. WIJNEN to G. VALENSI (partially communicated): The addition of oxidizing or reducing reagents to the present system (where *only* the Ox component Ag^+ is in solution) would have the effect of changing the silver content of the solution. It would not yield an appreciable pH response since only a small quantity of total nitrogen is involved in the pH dependent complex formation.

On the other hand, addition of oxidants or reductants to a Red/Ox system the components of which are *all* in solution and in which, moreover, hydrogen ions are involved (example: quinone-hydroquinone) would yield a pH response. It is questionable, however, whether the potential/pH relation so obtained represents a potential/pH diagram in the usual conception.

L. A. VAN ALMKERK: Avez-vous déjà étudié des autres systèmes que le système Ag-NH₃, et quels sont les résultats que vous avez obtenus avec ces systèmes?

J. SMITTENBERG to L. A. VAN ALMKERK: We started with systems in which hydroxide precipitation occurred, but could not obtain satisfactory results, mainly since most hydroxides start to precipitate in some colloidal or other non-stable state. Therefore we looked for a system without precipitation in a large pH range. In this respect, the silver-aqueous ammonium salt system appeared the very thing we wanted and no other systems have been investigated as yet.

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