

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON EQUILIBRIUM DATA*

Recommended Procedure for Testing the
**POTENTIOMETRIC APPARATUS AND
TECHNIQUE FOR THE pH-METRIC
MEASUREMENT OF METAL-COMPLEX
EQUILIBRIUM CONSTANTS**

Prepared for publication by

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Recommended procedure for testing the potentiometric apparatus and technique for the pH-metric measurement of metal-complex equilibrium constants

The most widely used technique for the measurement of metal-complex stability constants is based on pH-metric titrations of a ligand in the absence and in the presence of metal ions. Collection and interpretation of experimental data is beset with difficulties and has frequently led to the calculation and publication of erroneous stability constants. This paper presents a recommended procedure for testing both the apparatus and technique, based on the measurement of the stability constants of proton and nickel(II) complexes of glycine. The technique has been extensively and independently tested in 9 laboratories, and recommended stability constants and standard deviations are given.

INTRODUCTION

The procedure described here is intended to be a supplement to 'Guidelines for the Determination of Stability Constants' by Nancollas and Tomson¹, and to be of particular help to those new to the measurement of formation constants or designing new apparatus for their measurement. For fuller definitions of the terms used when referring to formation constants, and the presentation of formation constant data, see the introduction to the most recent supplement to 'The Stability Constants of Metal-Ion Complexes'².

The equilibrium constant, K , for the formation of a metal-ligand complex, ML , (where $K = a_{ML}/a_M \cdot a_L$) is a very useful thermodynamic quantity since it is related directly to the Gibbs standard free energy change of complex formation, ΔG^\ominus :

$$\Delta G^\ominus = -RT \ln K.$$

This, in turn, contains contributions from the standard enthalpy (ΔH^\ominus) and entropy (ΔS^\ominus) changes accompanying complex formation:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus.$$

At constant pressure K is therefore temperature dependent by the relationship:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\ominus}{RT^2}$$

assuming that both ΔH^\ominus and ΔS^\ominus are temperature independent over the temperature range used. Because of these logarithmic relationships, and the fact that formation constants are usually numerically large, they are frequently expressed in a logarithmic form, generally as $\log_{10} K$. Several terms are often used synonymously with 'equilibrium constant', e.g. 'stability constant' and 'formation constant'. The term 'instability constant' is frequently used. It refers to the dissociation reaction and is the reciprocal of the stability constant. It is often expressed as pK rather than $\log_{10} K$ values. Its use is to be avoided where possible to avoid confusion.

The 'overall' formation constant of a complex, $M_p H_q L_r$ (generally expressed as a β -value) refers to the formation of that complex from the participating species, i.e. to the reaction:



'Stepwise constants' refer to any designated step in the complex formation, e.g. K_{MHL}^{ML} refers to the reaction: $ML + H = MHL$. For a fuller description of the symbols used see the introduction to the compilation of stability constants given in reference 2.

To have a rigorous thermodynamic meaning equilibrium constants (β_T) should be expressed in terms of the activities of the component ions or complexes at equilibrium. This is impractical and for convenience and reproducibility concentrations are generally used

where, for a particular species, i , $a_i = [c_i] \cdot \gamma_i$. This gives a stoichiometric constant, β_S . Hence, for reaction (1):

$$\beta_{T(pqr)} = \beta_{S(pqr)} \frac{\gamma_{pqr}}{\gamma_M \cdot \gamma_H \cdot \gamma_L} \quad \text{and} \quad \log \beta_T = \log \beta_S + \log(\gamma_{pqr} / \gamma_M \cdot \gamma_H \cdot \gamma_L).$$

Hence, provided activities are maintained constant by working in a medium of constant ionic strength, $\log \beta_T$ will differ from $\log \beta_S$ by a constant amount, and values for β_S measured under identical conditions may be regarded as directly comparable. This assumption assumes that the concentrations of the reacting species are low compared to that of the ionic medium and that the ions are not of abnormal size or charge. Quantities of material of all components of the equilibrium mixture should therefore be measured in concentrations and not activities, including the free hydrogen ion concentration (pH). This is done by calibrating the electrode system used in terms of hydrogen ion concentrations using a strong acid such as perchloric acid and assuming it to be fully ionized. This can be achieved by direct titration of a dilute solution of perchloric acid using the same ionic background as the equilibria under study³, or by calibrating recognised buffer solutions (again of the same ionic strength) in terms of concentrations, and using these to calibrate the electrodes⁴.

The procedure outlined below involves the titration of nickel-glycine mixtures in an ionic background of NaCl such that the total ionic strength is 1.0 mol dm^{-3} . This system has been studied with great care by a number of different research laboratories active in the field of stability constant measurement⁵, and has been used subsequently by other laboratories as a check of apparatus and technique. As a result it is possible to quote very reliable stability constants for the complex species present, and to give these constants reliable standard deviations. It should be noted that the Cl^- ion can form complexes with many metal ions and care should be exercised when selecting the ionic background for a particular study. Over the pH range 2.5 to 9 glycine forms two protonated species, $[\text{H}_2\text{L}]^+$ and $[\text{HL}]$ and, with nickel, three metal complexes, $[\text{NiL}]^+$, $[\text{NiL}_2]$ and $[\text{NiL}_3]^-$. At high pH hydroxy species are almost certainly formed, but these are insignificant below pH 9 and protonated complexes are insignificant above pH 2.5. Hence, over the intermediate pH range, the only complex species that need to be considered are $[\text{H}_2\text{L}]$, $[\text{HL}]$, $[\text{NiL}]$, $[\text{NiL}_2]$ and $[\text{NiL}_3]$ (charges being omitted for simplicity). By following this procedure, and the computation method recommended, new-comers to the field of the pH-metric measurement of stability constants should be able to check their technique and apparatus. In addition the reliable stability constants reported provide good values for testing new or simplified methods of calculation using the original experimental data which are included in the original publication⁵. Copies of the data may be obtained from the authors of this recommended procedure.

THE NICKEL-GLYCINE PROJECT

Seven laboratories participated in this project⁵. The general experimental conditions to be used were agreed by all participants with the objective of obtaining an assessment of the variables that influence the measurement of stability constants. The conditions were as follows: temperature: 25°C , ionic strength: $I=1.00 \text{ mol dm}^{-3}$ (NaCl) and variable concentrations of both nickel ion and glycine with a maximum concentration of either reagent of 0.1 mol dm^{-3} .

The other experimental conditions (such as the choice of type of electrodes, methods for calibrating the electrodes, checking the liquid junction potentials, purity of reagents,

Table 1: Stability Constants Determined by Participating Laboratories.
(sigma = standard deviation)

Laboratory	$\log\beta_{\text{HL}}$	$\log\beta_{\text{H}_2\text{L}}$	$\log\beta_{\text{NiL}}$	$\log\beta_{\text{NiL}_2}$	$\log\beta_{\text{NiL}_3}$	pK_w
1	9.629	12.036	5.80	10.588	14.308	13.68
2	9.67	12.14	5.53	10.26	13.59	-
3	9.654	12.067	5.625	10.356	13.75	13.704
4	9.656	12.076	5.625	10.398	13.911	13.68
5	9.652	12.109	5.60	10.325	13.65	13.67
6	9.659	12.071	5.625	10.381	13.805	13.73
7	-	-	5.66	10.43	14.08	-
a) mean	9.653	12.083	5.638	10.391	13.922	13.693
sigma	0.011	0.031	0.071	0.089	0.191	0.02
b) mean	9.6552	12.081	5.627	10.378	13.879	13.685
sigma	0.0031	0.0149	0.017	0.033	0.132	0.012
R	0.0406	0.1038	0.27	0.328	0.558	0.06

Table 2

	A		B		C	
	mean	sigma	mean	sigma	mean	sigma
$\log\beta_{\text{HL}}$	9.655	0.003	9.654	0.003	9.651	0.012
$\log\beta_{\text{H}_2\text{L}}$	12.080	0.019	12.074	0.003	12.071	0.026
$\log\beta_{\text{NiL}}$	5.619	0.012	5.631	0.010	5.615	0.035
$\log\beta_{\text{NiL}_2}$	10.365	0.032	10.399	0.010	10.363	0.062
$\log\beta_{\text{NiL}_3}$	13.779	0.18	13.907	0.023	13.93 ^a	0.34 ^a

a. Non-normal population of titrations.

determination of the concentration of reagents, titration procedure and methods of calculation) were left to the discretion of individual researchers, who employed the procedures and apparatus normally used in their own laboratories.

Values of the stability constants obtained are given in Tables 1 and 2.

The following is a summary of the procedures which were used. This serves to define the experimental conditions under which the mean values of the stability constants were determined.

Reagents All authors used doubly distilled deionised water while other reagents were handled in the different ways described below:

SODIUM CHLORIDE. Analytical grade salt was used either: a) as supplied commercially, b) after drying at 300–350°C, or c) after purification by treating a saturated salt solution with HCl gas, followed by heating in an oven up to 400°C.

HYDROCHLORIC ACID was obtained by dilution of analytical grade hydrochloric acid in the form of the aqueous azeotropic mixture. The acid was standardised against either: a) a solution of NaOH of known concentration, b) KHCO_3 , c) Ti_2CO_3 , d) borax or e) THAM (tris(hydroxymethyl)aminomethane).

SODIUM HYDROXIDE. Dilution of analytical grade solution, or of a concentrated solution obtained by treating the reagent with an equal weight of water. The alkali was standardised against either: a) solutions of known concentration of hydrochloric acid, b) oxalic acid, c) $\text{KH}(\text{IO}_3)_2$ or d) potassium hydrogen phthalate.

NICKEL CHLORIDE. Some workers used analytical grade $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. Others prepared the salt in their laboratory by dissolving either nickel metal (99.999% pure) or nickel bicarbonate in hydrochloric acid solution. The concentration of the stock solution was determined by either: a) complexometric titration, b) electrodeposition or c) gravimetry as oxinate.

GLYCINE. A commercial product was used in all cases. One group checked the composition of the reagent by elemental analysis. In some cases the product was recrystallised from water or aqueous methanol (1:1 v/v) and dried in an oven at 104°C or at $25\text{--}30^\circ\text{C}$ under vacuum. The purity of the raw or recrystallised material was checked by titration.

Methods of titration The titrations were performed by either: a) the alkalimetric method, in which solutions containing mixtures of reagents were titrated with a sodium hydroxide solution or b) mixing solutions containing various proportions of reagents, and in the case of complex formation, titrating solutions containing a) a predetermined concentration of the nickel ion, b) a predetermined concentration of glycine.

Methods of measurement The glass electrodes used were of various types:

Russel pH Ltd., Beckman N.40493, Orion 91-01, Metrohm EA 109T, Ingold 201-NS, Radiometer G 2025 B, Beckman 39099E-3. and as reference electrodes Ag/AgCl electrodes prepared in the laboratory or calomel electrodes of the following types: Radiometer K401, Ingold 330NS, Ingold 303-90SN, Metrohm EA 414. The salt bridge (Wilhelm bridge or porous septum) was filled with $1.0 \text{ mol dm}^{-3} \text{ NaCl}$. During the measurements an inert gas (N_2), pre-conditioned by being bubbled through a solution of $1 \text{ mol dm}^{-3} \text{ NaCl}$, was bubbled through the active solution.

Piston burettes were generally used to provide additions of the titrant solution: Radiometer ABU-12, Metrohm E415-5, or Micrometer Institute microsyringes. The potential was measured with a notable variety of devices: Radiometer pHM4, pHM64, pHM52; Metrohm E383, Orion 701 digital voltmeter, Solatron LM1867 digital voltmeter with Analog Devices impedance converter 311K, and Power-supply Contant OA/O. In one case the measurements were conducted by a completely automatic set-up in which the additions of titrant and reading of the potential in conditions of equilibrium were controlled by a Hewlett-Packard HP9810A computer.

Calibration of the glass electrodes in terms of hydrogen ion concentration was performed by means of a titration of hydrochloric acid with sodium hydroxide. The experimental data ranged over pH values between 1.6 and 11.2. Corrections for the effects of junction potential changes, E_j , were included in the calibration procedure in the region of low pH which is useful for the determination of protonation constants. Some of the researchers calibrated the electrodes using an acid medium to determine the values of E_j and E_o , and used a basic medium to determine $\text{p}K_w$. In some cases the acid solution obtained after the calibration titration was used as the starting solution for the determination of either protonation or complexation constants; the appropriate quantities of reagent were added to the starting solution and a second titration was then performed. In one case the response of the glass electrode was checked against a hydrogen electrode.

Methods of calculation The Gran method was used by all workers to determine the end-point in the acid-base titrations, and to find the quantity of excess acid present in the solutions of reagents. In two cases the constants were estimated using graphical methods involving normalised curves, followed by successive numerical approximations. In the other cases the calculation was carried out by means of a computer program. The most commonly used programs were SCOGS⁶ and MINIQUAD⁷. The programs PSEUDOPLOT⁸ and COMPLIT^{9,10} were sometimes used to obtain species distribution plots, and the program ACBA¹¹ was employed

to determine protonation constants with simultaneous optimisation of the ligand concentration. New, up-to-date versions of these programs are now available, e.g. SUPERQUAD¹², ACBA¹³ and ESAB¹⁴. The strategies employed in the calculations were: 1) separate refinement of the protonation constants, which were then given fixed values in the calculation of the complexation constants; 2) simultaneous refinement of both the protonation and complexation constants; 3) separate refinement of the data from each titration; 4) comparison of the results of the calculations based on data with and without the points for which the pH was greater than 9.

The values reported by each laboratory are given in Table 1. The means and standard deviations were calculated from these values a) by considering all the data and b) by excluding the maximum and minimum values. The range R is the difference between the maximum and minimum values of each constant.

A more rigorous statistical analysis of the data reported by different laboratories was undertaken^{15,16} in order to establish criteria on which to base a choice of the best strategy to be used for stability constant calculations. For reasons of compatibility between the experimental methodologies and calculation procedures, only the data presented by the laboratories marked 3, 4, 5 and 6 in Table 1 could be considered together. The statistical analysis has shown that the variability in stability constant values between titrations was in all cases greater than the uncertainty indicated by the calculations on data from single titrations. It is therefore considered that it is more correct in principle to evaluate an equilibrium constant with data from an individual titration, and to express the final result as the mean of the values obtained from all the titrations.

Some mean values derived from the data from laboratories 3, 4, 5 and 6 are given in Table 2. The means calculated from the data in Table 1(a) are given in the columns under A, whilst under B are the weighted grand averages of the mean values reported by each laboratory, and under C are the values obtained from the means of the values calculated from single titration data. When one compares the values given in Tables 1 and 2, one may observe that, while the stability constant values are in good agreement with one another, the values of standard deviation vary significantly depending on the type of evaluation used. One may also observe in Table 2 that in general the largest estimates of the standard deviation are those under C, in which each titration curve was considered individually.

RECOMMENDED PROCEDURE

Reagents Solutions of known titre of HCl, NaOH, NiCl₂ and glycine. NaCl as background electrolyte. Pure inert gas (N₂). The reagents should be analytically pure. The glycine may be purified by recrystallisation from water/methanol, 1:1 v/v.

Apparatus A couple consisting of glass and reference electrodes. Cell thermostatted at 25 ± 1°C. A high impedance voltmeter with a reproducibility of ± 0.1 mV. Piston burette or microsyringe depending on the concentration of the titrant solution.

Measurement procedure The solutions to be prepared by mixing together solutions of the reagents, and to be brought to ionic strength of 1 mol dm⁻³ with NaCl. The electrodes to be calibrated by means of titrations of HCl solutions of known titre with solutions of NaOH. The titre of the HCl solutions to lie between 5 × 10⁻³ and 1.5 × 10⁻² mol dm⁻³. For the solutions used in the stability constant determination the concentrations of glycine (C_{gly}) and of the nickel ion (C_{Ni}) must be known. The total concentration of dissociated or dissociable hydrogen ions must also be known; when NiCl₂ is present the value of C_H should take into account the excess hydrogen ions added with each aliquot of the mother solution of NiCl₂.

Determination of protonation constants. It is advisable to prepare at least two series of three glycine solutions from different mother solutions of the reagents. The glycine concentration should lie in the range between ca. 3×10^{-3} and ca. 10^{-2} mol dm⁻³ and the equivalent concentrations of HCl should be approximately equal. The titrations with NaOH should cover a range of pH from ca. 2 to ca. 10.5 or 11.

Determination of complexation constants. Groups of titrations may be performed using the same mother solutions for each group. In each group there is to be a different ratio of glycine to nickel ion, such as $C_{Ni}:C_{gly} = 1:1, 1:2, 1:3$ or $1:4$, and the glycine concentration is to be varied in each group in such a way that the sum $C_{Ni} + C_{gly}$ does not exceed 10^{-2} mol dm⁻³. The titrations should not be taken above a pH of ca. 9 to 9.5 in order to avoid the formation of hydrolysed species or precipitates.

The electrodes should be calibrated both before and after each of the titrations which are to be used for the stability constant determinations. The calibration should employ relationship (1).

$$E = E_o - a \text{ pH} + E_j \quad (1)$$

$a = 59.162$ mV at 25°C, $E_j = K [H]$, with $K = \text{ca. } 67 \pm 6$ mV mol⁻¹. The liquid junction potential depends on the hydrogen ion concentration, and E_o' is assumed to include a term relating to the activity coefficient, which is assumed to be constant. The calibration procedure ensures that the electrode responds linearly in hydrogen ion concentration, i.e. $\text{pH} = p[H]$. The value of E_o' is derived from data between pH 2 and 3.5. The liquid junction potential can be obtained by titration of solutions of HCl with an initial pH of ca. 1.5 to 2; it is then revealed as a deviation from linearity of the observed potential as a function of pH, i.e. equation (1) does not apply with $E_j = 0$. The electrode response in the alkaline region (pH 9) can be checked by calculating the value of pK_w and assuming a slope of 59.162 mV at 25°C as in the acid region.

Methods of calculation The experimental data may be subjected to a preliminary examination by graphical methods to determine the mean degree of formation both for protonation (\bar{p}) and complexation (\bar{n}). A plot of the values of \bar{p} as a function of pH, and of \bar{n} as a function of pH serves to evaluate the agreement between data taken from different titrations and to ascertain whether the range of concentrations examined is adequate for the species formed in the system being considered. Approximate values of the equilibrium constants may be derived from the curves of \bar{p} as a function of pH or of \bar{n} as a function of pH; these values may be used as the initial values in the subsequent numerical refinement. The refinement is to be conducted using the method of least squares, and computer programs such as SCOGS⁶, MINIQUAD⁷ or one of the more recent versions¹¹.

The following strategies should be followed in the calculation:

- 1) Evaluation of the protonation constants first, followed by the evaluation of the formation constants of the complexes.
- 2) Simultaneous evaluation of the protonation and complexation constants.

It is furthermore necessary to compare the results obtained by:

- 1) treating the data from each titration curve separately
- 2) treating all the experimental data together.

It should be noted that, at 25°C, an error of 0.01 log units corresponds to 0.59 mV.

Hence errors are generally higher than the precision of a pH meter (0.1 mV), indicating that there are unidentified but real sources of 'noise' somewhere in the procedure.

Users of this recommended procedure should expect to calculate values for the stability constants from individual titrations within the following ranges. These have been estimated using data from Table 2, column C, and deviations of 2 sigma (i.e. 97% confidence level):

$$\begin{aligned} \log \beta_{\text{HL}} &= 9.63 - 9.67 & \log \beta_{\text{H}_2\text{L}} &= 12.02 - 12.12 \\ \log \beta_{\text{NiL}} &= 5.54 - 5.63 & \log \beta_{\text{NiL}_2} &= 10.24 - 10.48 \end{aligned}$$

The stability constant represented by $\log \beta_{\text{NiL}_3}$ does not belong to a normal population of titrations and cannot therefore be given reliable statistical limits. However users should obtain a value in the region of 13.9.

The value for pK_w should be between 13.64 and 13.74.

TESTING OF THE PROCEDURE

This procedure has been followed by Zuberbuhler and Kaden (Basel) in order to test a new computer-based method of calculating stability constants (TITFIT)¹⁷. It has also been tested in Leeds¹⁸, using the experimental conditions specified and a Radiometer PIM 64 pH meter with a combined glass/saturated calomel electrode (Russel pH) calibrated in terms of hydrogen ion concentrations using HClO_4 . NaOH (0.25 to 0.37 mol dm^{-3}) was dispensed manually from a calibrated 0.25 cm^3 Hamilton 'Gastight' syringe using the Hamilton auto-dispenser (P-600). BDH 'AnalaR' $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was used without further purification with the nickel content determined by EDTA titration. The pH range studied was 2.2 - 11.0 but only values below 9.2 were used to calculate nickel complex stability constants. Calculations used the SUPERQUAD computer program¹².

In these two studies the following results were obtained at 25.0°C and $I = 1.00$ mol dm^{-3} (NaCl).

	Basel	Leeds
$\log \beta_{\text{HL}}$	9.63	9.64
$\log \beta_{\text{H}_2\text{L}}$	12.08	12.06
$\log \beta_{\text{NiL}}$	5.58	5.63
$\log \beta_{\text{NiL}_2}$	10.30	10.44
$\log \beta_{\text{NiL}_3}$	13.75	13.96
pK_w	13.69	13.69

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