Computer-controlled potentiometric acid-base titrations*

By URS KELLER, JÜRG PADEL, HEINZ GAMSJÄGER, and PAUL W. SCHINDLER
Institut für anorganische Chemie der Universität Bern, Freiestraße 3, CH-3000 Bern (Switzerland)

Dedicated to Professor Rudolf Signer

Summary

A system has been developed for computer-controlled potentiometric acid-base titrations consisting of a HP 2114 B computer, a DM 2022 S digital voltmeter and further peripheral devices. Additions of acid and base were made with the aid of a coulometer. The actual concentrations of hydrogen ions were measured using a hydrogen electrode. The equipment is particularly suited for investigations of equilibria involving proton transfer reactions. Programs for titration control and real time evaluation of data are outlined and typical applications are briefly discussed.

Introduction

Apart from their wide analytical applications potentiometric acid-base titrations are frequently used in studies of equilibria involving proton transfer reactions. As far as aqueous systems are concerned the proton transfer is very fast. It is remarkably often experienced, however, that the electrode response is sluggish. Under unfavorable conditions, observation times of up to several hours are required until stable readings of potential are obtained. This is especially true for poorly buffered solutions and for heterogeneous systems. It has also been observed in the case of biopolymers, if the proton transfer gives rise to changes in conformation. In such cases the accomplishment of a complete titration curve exceeds by far the normal laboratory period. According to our experience it is difficult in the case of shift work to retain a constant standard of both precision and reliability. The availability of low cost laboratory computers offers an interesting opportunity for eliminating these problems.

On-line computers have already been used for automation of various analytical standard procedures[1]. The present report describes a system particularly suited for investigations of equilibria involving proton transfer reactions. Programs including titration control and real-time evaluation of the pertinent data are outlined. Typical applications and preliminary results are discussed.

Titration equipment

A block diagram of our titration equipment is shown in Fig. 1. The individual parts have the following functions:

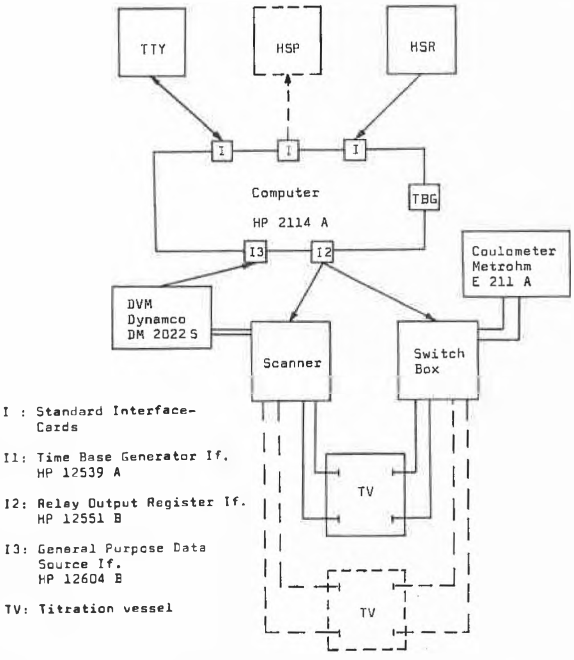

Figure 1. Block diagram of the titration equipment

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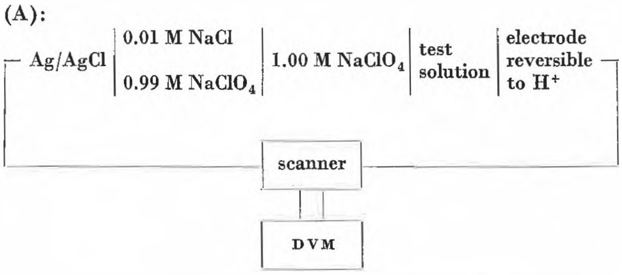
* Received December 22, 1972.

Titration vessel. Commercial titration vessels thermostated by a water jacket were used. In special cases, e.g. the presence of large amounts of OH^- or F^- respectively, the glass vessels were replaced by Teflon beakers.

Two pairs of electrodes namely *A* for e.m.f. measurements and *B* for coulometric generation of H^+/OH^- were inserted into the vessel. The electrode system for e.m.f. measurements is depicted by scheme (A).

(A):



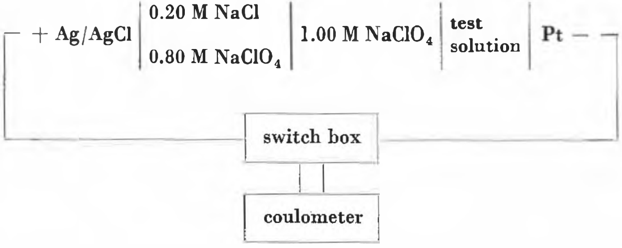
The test solutions were kept at a constant ClO_4^--molarity by adding $NaClO_4$ as an inert electrolyte. Under this condition the measured e.m.f. *E* is given by the equation

$$E = E^0 + k \log [H^+] + E_j, \qquad (1)$$
$$(k = RT \ln(10)/F).$$

E^0 denotes a constant to be determined with solutions of known hydrogen ion concentration. Regarding the comparatively low concentrations of the reacting species, the term E_j, which includes the liquid junction potentials and correcting terms for changes in activity coefficients, could generally be neglected.

The H^+/OH^- generating system is shown by scheme (B).

(B):



Hydrogen ions are produced by the following reactions

anode: $\frac{1}{2} H_2O \rightarrow e^- + H^+ + \frac{1}{4} O_2$
(cathode: $AgCl + e^- \rightarrow Ag + Cl^-$)

Reversing the sign of the current allows generation of OH^- ions.

The Ag/AgCl-electrodes and the connecting **Wilhelm**-type salt bridges, both being outside the titration vessel, were air-thermostated.

HSR: The high speed reader was used to read in the pertinent programs. (Generally these were absolute programs in Fortran II on paper tape.)

TTY: The teletype serves as a general input/output unit for data. Within the scope of our work the TTY was used to input starting conditions requested by the program. Similarly the data obtained are printed by the TTY. By a slight change of the program, the data can be punched on paper tape.

TBG: The time base generator effects waiting loops of definite length within the program.

Switch box: This serves as a link between coulometer and the H^+/OH^- generating cell (B). It operates in three different states to be called by the program.

State I: disconnection of coulometer and generating system,
State II: connection to produce H^+
State III: connection to produce OH^-
The connection time is controlled by the TBG.

DVM: The digital voltmeter indicates the prevailing e.m.f. This value is read into the memory of the computer by the program. Appropriate reading intervals are generated by the TBG.

Scanner: This connects the DVM with the sensing electrode (A) of the vessel chosen.

Evaluation

The evalutation of the titration curves obtained is based on **Gran**'s method[2]. Its application to the present work can be outlined as follows.

a) Titration of a strong acid

Let us start with a test solution of the composition

$$[H^+] = H_i\, M,$$
$$[Na^+] = (1.00 - H_i)\, M,$$
$$[ClO_4^-] = 1.00\, M,$$

which may also contain a small amount, *P*, of protolytic impurities (weak acids).

B is the concentration of the coulometrically generated base. The actual concentration of hydrogen ions is given by the equation

$$[H^+] = H_i - B + [OH^-]. \qquad (2)$$

Acid range: $[H^+] \gg [OH^-]$

Equations (2) simplifies to

$$[H^+] = H_i - B. \qquad (2a)$$

Equations (2a) and (1) result in

$$F_1 = 10^{E/k} = H_i \cdot 10^{E_0/k} - B \cdot 10^{E_0/k}. \qquad (3)$$

A plot of the experimental data F_1 against *B* (Fig. 2a) gives a straight line. The endpoint ($H_i = B$) of the titrations is defined by the intercept of F_1 with the *B*-axis ($F_1 = 0$).

The E^0-value of the cell (A) is obtained from the slope

$$\frac{dF_1}{dB} = -10^{E_0/k}.$$

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[1] F. B. **Stephens**, F. **Jakob**, L. P. **Rigdon**, and J. E. **Harrar**, *Anal. Chem. 42* (1970) 764; T. **Anfält**, and D. **Jagner**, *Anal. Chim. Acta 57* (1971) 177; D. **Jagner**, and K. **Arén**, *Anal. Chim. Acta 57* (1971) 185.

[2] G. **Gran**, *Analyst* 77 (1952) 661; W. **Stumm**, and J. J. **Morgan**, *Aquatic Chemistry*, Wiley/Interscience, New York 1970, p. 155.

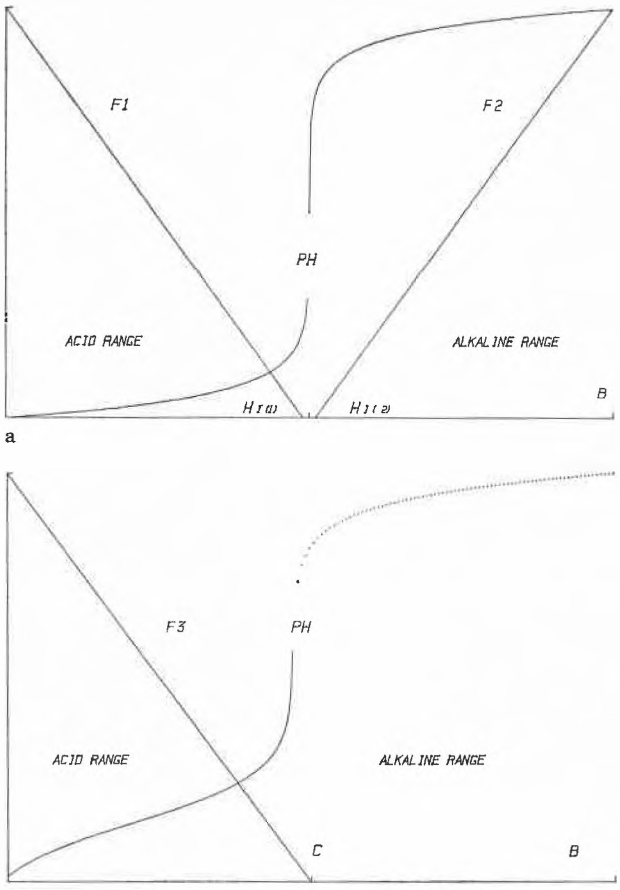

Figure 2

a) Titration of a strong acid presented by conventional titration curve and GRAN plot

b) Titration of a weak acid presented by conventional titration curve and GRAN plot

By GRAN's method the endpoint of the titration can be calculated from E-readings in sufficiently buffered solutions, which is a great advantage over the more conventional methods of endpoint determination. In practice it is sufficient to perform the titration until approximately 90% of the strong acid is neutralized. Under these conditions ($p\text{H} < 4$) the protolysis of the impurity P can safely be neglected.

Alkaline range: $[\text{H}^+] \ll [\text{OH}^-]$

Eq. (2) simplifies to

$$[\text{OH}^-] = B - H_i. \qquad (2\text{b})$$

In this case the e.m.f. measured is related to the OH⁻-concentration by

$$E \; = E^{0\prime} - k \log\,[\text{OH}^-], \qquad (4)$$

where $E^{0\prime} = E^0 + k \log Kw \quad (Kw = [\text{H}^+]\,[\text{OH}^-])$. (5)

Equations (2b) and (4) lead to

$$F_2 = 10^{-E/k} = B \cdot 10^{-E^{0\prime}/k} - H_i \cdot 10^{-E^{0\prime}/k}. \qquad (6)$$

Again a plot of F_2 against B (Fig. 2a) gives a straight line from which H_i and $E^{0\prime}$ can be calculated.

Empirically it is often found that H_i from the alkaline branch of the GRAN plot is slightly higher than H_i from the acid branch. This is easily understood since within the alkaline range ($p\text{H} > 10$), the protolytic impurity is completely deprotonated. Hence, P, the amount of hydrogen ions originating from the impurities is calculated by

$$P = H_{i\,(\text{alk})} - H_{i\,(\text{acid})}.$$

A sensitive test for the accuracy of a titration is the calculation of the pertinent Kw:

$$\log Kw = \frac{E^{0\prime} - E^0}{k}.$$

Literature data for Kw of the most common ionic media are available[3].

b) Titration of a weak acid HA

The general composition of the test solution is

$$[\text{HA}]_i \; = C\,M \quad (C \ll 1),$$
$$[\text{Na}^+] \; = 1.00 \text{ M},$$
$$[\text{ClO}_4^-] \; = 1.00 \text{ M}.$$

The acid constant of HA is defined by

$$Ka = \frac{[\text{H}^+]\,[\text{A}^-]}{[\text{HA}]}. \qquad (7)$$

Within the buffer range of the weak acid, the added base B generates an equivalent amount of A⁻ ions. Hence

$$[\text{A}^-] = B; \quad [\text{HA}] = \text{C} - B. \qquad (8)$$

From equations (1), (7), (8) one obtains

$$F_3 = B \cdot 10^{(E-E_0)/k} = Ka \cdot C - Ka \cdot B. \qquad (9)$$

A plot of F_3 against B gives a straight line (Fig. 2b). C can be calculated from the intercept

$$F_3 = 0: \quad C = B. \qquad (10)$$

Ka is obtained form the slope

$$\frac{dF_3}{dB} = -Ka. \qquad (11)$$

As can be seen from eq. (9) the calculation of Ka demands prior knowledge of E^0, thus requiring a preceding titration of strong acid. E^0 and Ka can be simultaneously obtained, however, from a titration of weak acid in the presence of approximately equivalent amounts of strong acid.

The evaluation is then performed by iteration. (In the following description small corrections originating from P are omitted.)

After addition of base, the charge condition requires

$$[\mathrm{H^+}] = H_i - B + [\mathrm{A^-}] + [\mathrm{OH^-}]. \qquad (12)$$

In the case of weak acids of medium strength ($pKa \leqslant 7$) the $\mathrm{OH^-}$ concentration is negligible within the buffer range of HA. Hence

$$[\mathrm{H^+}] = H_i - B + [\mathrm{A^-}]. \qquad (12\,\mathrm{a})$$

The calculation starts by splitting the titration curve into two parts.

The first part (corresponding predominantly to the neutralization of the strong acid) is used to estimate preliminary values of H_i and E^0, taking $[\mathrm{A^-}] = 0$ as a first approximation. From the second part, values for C and Ka are then approximated. With these parameters better values for $[\mathrm{A^-}]$ are accessible

$$[\mathrm{A^-}] = \frac{Ka\,(C - [\mathrm{A^-}])}{[\mathrm{H^+}]}.$$

This in turn leads to improved values for H_i and E^0. The iteration usually converges after about ten cycles. (In the case of very weak acids [$pKa > 7$] no iteration is necessary since the titration curve is clearly separated in two parts.)

Programs and applications

A survey of the programs developed is given in Table 1.

TITR is the general control program for coulometric addition of both acid and base and subsequent e.m.f. measurement (Fig. 3). This addition of reagents requires a logical step. In conventional potentiometric titrations it is the laboratory worker who decides from his e.m.f. readings whether the potential is already constant. In the program TITR this decision is made by two stability criteria based on $(n+1)$ e.m.f. measurements:

$$1.\ |E_{n+1} - E_n| \leqslant |\delta E|.$$

$$2.\ \left| E_{n+1} - \frac{\overset{n+1}{\Sigma}E}{n+1} \right| \leqslant |\delta E|.$$

The appropriate value of $|\delta E|$ is read in at the beginning of the titration. In the course of most titrations, a range of low buffer capacity is passed and in such regions the stability criteria will never be fulfilled. To avoid inconveniently long titrations, the period for e.m.f. reading after the addition of reagent must be limited. Further addition of acid/base is then performed regardless of the unstable potentials. These essential parts of TITR are included in all subsequent programs.

Table 1. Outline of programs

TITR:	General control program for optional and/or alternative addition of acid/base with simultaneous e.m.f. measurement.
System:	Any kind of protolyte solution.
Input:	Time intervals for acidising/alkalising steps; frequency of e.m.f. readings; stability criteria; maximum time interval for e.m.f. observation.
Output:	E, time required to obtain stable e.m.f.
TITAU:	Control and evaluation program for titration of strong acid.
System:	Inert salt solution with small amount H_i of strong acid contaminated with protolytic impurity P.
Input:	TITR + number of alkalising steps, current, temperature, volume of test solution.
Output:	H_i, E^0, Kw, P.
TITAS:	Modified version of TITAU; real time evaluation of e.m.f. data with subsequent adjusting of the time intervals for alkalising steps.
System:	see TITAU.
Input:	see TITAU.
Output:	see TITAU.
TITIT:	Control and evaluation program for titration of weak acid ($pKa < 7$).
System:	Inert salt solution with small amounts of weak acid (C), strong acid (H_i) and protolytic impurity P.
Input:	TITAU + Kw, P, Ka (P), *even* number of alkalising steps.
Output:	E^0, H_i, C, log Ka
TWEST:	Control and evaluation program for titration of very weak acid ($pKa > 7$).
System:	see TITIT: ($pKa > 7$).
Input:	TITAU + Kw, P, Ka (P), number of alkalising steps, range of E-values for evaluation of H_i, E^0, C and Ka.
Output:	E^0, H_i, C, Ka.

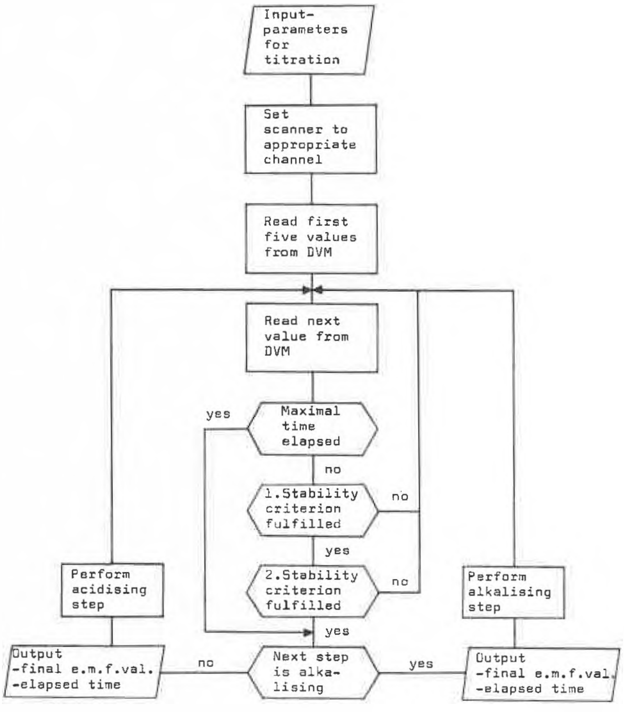

Figure 3. Simplified flow chart of TITR

Table 2. Survey of data

1. Problem:	Kw in 1 M $NaClO_4$ (25°)
Program:	TITAU, TITAS
Result:	log $Kw = - 13.77$ (± 0.01)[a]
Literature data[3]:	log $Kw = - 13.77$, 1 M $NaClO_4$ (25°)
2. Problem:	Ka of $CH_3{-}COOH$ in 1 M $NaClO_4$ (25°)
Program:	TITIT
Result:	log $Ka = - 4.58_2$ ($\pm 0.00_7$)[b]
Literature data[3]:	log $Ka = - 4.55$ to -4.61, 1 M $NaClO_4$ (20°) log $Ka = - 4.30$, 1 M $NaClO_4$ (30°)
3. Problem:	Ka of $CH_2Cl{-}CH_2{-}COOH$ in 1 M $NaClO_4$ (25°)
Program:	TITIT
Result:	log $Ka = - 3.96_1$ ($\pm$ 0.01_2)[b]
Literature data[4]:	log $Ka = - 3.99_6$, $I = 0.01$ to 0.5 (25°) log $Ka = - 4.09_7$, $I = 0$ (18°)
4. Problem:	Ka of H_4SiO_4 in 1 M $NaClO_4$ (25°)
Program:	TWEST
Result:	log $Ka = - 9.47_1$ (± 0.004)[a]
Literature data[3]:	log $Ka = - 9.46$, 0.5 M $NaClO_4$ (25°) log $Ka = - 9.43$, 3 M $NaClO_4$ (25°)

[a] Determined by P. SANTSCHI
[b] Determined by K. SINGH

TITAU is a control and evaluation program for titrations of strong acids. The program demands the input of both number and time of the alkalising steps to be performed. As a result, H_i, Kw, E^0 and P are obtained. For statistical reasons an equipartition of data pairs in the acid and alkaline range is desirable. TITAU is therefore only convenient in cases where H_i is approximately known. For systems with completely unknown H_i a modified version of TITAU, TITAS, was developped. Let us assume that n data pairs are required; from the first two points of the acid branch, H_i is approximated in real time. Subsequently the appropriate length of the following alkalising steps is evaluated in such a way that $n/2$ points fall on both the acid and alkaline branch.

TITIT is a control and evaluation program for the titration of weak acid ($pKa < 7$) in the presence of strong acid. The parameters of interest, H_i, E^0, C and Ka are calculated by iteration as shown in the previous section. The simpler version TWEST applies for very weak acids ($pKa > 7$).

First results obtained with our equipment are summarized in Table 2. The examples were partially chosen to test programs and equipment. Since both accuracy and precision of the log Ka-values obtained is satisfactory it can be expected that the method developed is also adaptable to more complicated systems such as those mentioned in the first section.

Dr. OTTAWAY was kind enough to revise the English of the text. This work was financially supported by the Swiss National Foundation (Project No. 2.404.70).

Addendum: After completion of this manuscript a paper by S. GOBOM and J. KOVACS, *Chem. Scripta 2* [1972] 103, appeared. This deals with the on-line application of a digital computer in studies of complex formation. The titration system is very similar to that described in the present article.

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[3] L. G. SILLÉN, and A. E. MARTELL, *Stability Constants*, Special Publication 17, The Chemical Society, London 1964; *Stability Constants*, Special Publication 25, The Chemical Society, London 1971.

[4] G. KORTÜM, W. VOGEL, and K. ANDRUSSOV, *Dissociation Constants of Organic Acids in Aqueous Solutions*, Butterworths, London 1961