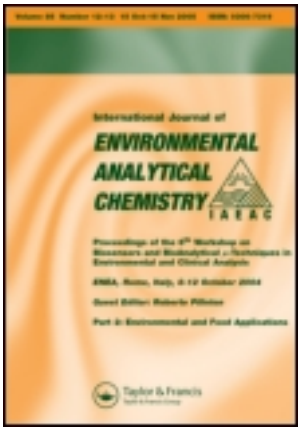

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

Determination of the rate of reaction between potassium iodide and potassium peroxodisulphate with the econoburette: a green chemistry and microscale titrations

Man Singh [a]

[a] Chemistry Research Laboratory, Deshbandhu College, University of Delhi, New Delhi, 110019, India

Available online: 22 Feb 2011

To cite this article: Man Singh (2011): Determination of the rate of reaction between potassium iodide and potassium peroxodisulphate with the econoburette: a green chemistry and microscale titrations, International Journal of Environmental Analytical Chemistry, 91:3, 272-279

To link to this article: http://dx.doi.org/10.1080/03067310903094537

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 3, 15 March 2011, 272–279

Taylor & Francis
Taylor & Francis Group

Determination of the rate of reaction between potassium iodide and potassium peroxodisulphate with the econoburette: a green chemistry and microscale titrations

Man Singh*

Chemistry Research Laboratory, Deshbandhu College, University of Delhi, New Delhi 110019, India

(*Received 14 March 2009; final version received 28 May 2009*)

Measurement for a rate of reaction for about 30 min at a 5 min interval between KI and $K_2S_2O_8$ aqueous solutions with conventional burette in industries and academics consumes about 3.375 g $K_2S_2O_8$/250 mL : 4.15 g KI/250 mL : 11.6 mL (CH_3COOH, glacial)/100 mL : 1 g starch/10 mL : 0.62 g $Na_2S_2O_3$ (sodium thiosulphate)/250 mL : 50 mL ice cold water. The number after the oblique in mL depicts an amount of aqueous solution where the amounts of chemicals in grams are dissolved. Similar determinations with econoburette reduced their amounts in 0.0675 g $K_2S_2O_8$/5 mL : 0.083 g KI/5 mL: 0.5 mL (CH_3COOH, glacial)/5 mL : 0.05 g starch/0.5 mL : 0.025 g $Na_2S_2O_3$/2 mL : 2.5 mL ice cold water. The reduction in amounts is about 50 times, and similarly the time and operational efforts are reduced in the same proportion. The econoburette is a 'green chemistry' instrument which performs valuable titration with microlitre of substances. The micro level amount of titer and titrant consumed less time in performing a volumetric tititration and also prevented much use of materials. In general, after titration a significant quantity of indicators, additives, titer and titrant are consumed and drained out in a sink with the possibility of causing pollution. The econoburette reduces such wastage of materials by up to 90%, with high accuracy in results. The rate constant $k = 0.0431\ sec^{-1}\ L^{-1}\ mol^{-1}$ remained fairly constant for successive measurements with time but with the conventional burette larger deviations were noted at 298.15 Kelvin temperature.

Keywords: potassium peroxodisulphate; potassium iodide; econoburette; titration; microlitre; titer; pollution

1. Introduction

Microscale, fast and multipurpose techniques for study of reactions are preferred over the conventional due to instrumental innovation around the globe. Currently, the resources such as electricity, water, solvents, space, chemicals are of great concern, their wise and smart use are the focus of current research [1–3]. Thus, nanotechnology and microscale chemistry have become the focal point of the environmental sciences in an attempt to prevent wastage of the natural resources [3–5] in chemistry experiments. This study deals with an econoburette that saves a large amount of materials and the human effort involved in determining rate constant of a reaction which occurred between potassium iodide and

*Email: mansingh50@hotmail.com

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903094537
http://www.informaworld.com

potassium peroxodisulphate. There are several types of microburettes which are used in biosciences [6,7] but these are not feasible with the chemical sciences. Their capacity is too small to be sufficient for routine titrations for volumetric estimation. In general, for ordinary titrations the capacity of a burette is 50 mL with a zero mark at the top. For titration purpose a 100 or 150 mL conical flask containing the titrand is used. Hence for use the burette is filled up to the zero mark where it holds the 50 mL solution and 10 mL of titrand is used for titration. The indicator which assists detection of an end point of a chemical reaction during the titration is taken in the same proportion, and after titration the whole material is just drained out in the sink. A single user generally repeats a titration at least three times to record three concordant readings and each set of solution is discarded, which results in a wastage of chemicals and solutions. If there are 'n' number of users in the class, the wastage of the solution would be '3 × n' times of the single user but the econoburette saves more than 90% of the solution as compared to the 50 mL burette. Additionally, it reduces the operational steps, saving time for the users. For example, for successfully running the reaction between the KI and $K_2S_2O_8$, the solutions of glacial CH_3COOH, starch, $Na_2S_2O_3$ and ice cold water were required. Instead of taking them in conical or round bottom flasks, these were taken in the limbs of the econoburette, which reduces the operational steps and enhances accuracy in the results. The solutions are not exposed to the environment and no fractions of the solutions escape. As compared to the usual burette [8,9], the econoburette is simple to handle which allows 0.01 mL solutions to be released for titration.

2. Experimental

The KI, $K_2S_2O_8$, $Na_2S_2O_3$ and CH_3COOH (AR BDH, India) were used for solution preparations w/v, with Millipore water. Both the burettes were carefully cleaned and dried in the usual manner. The NaOH and HCl (AR, BDH, India) were used and the NaOH was standardised with standard oxalic acid (AR, BDH, India). Further, a standard NaOH solution was used to standardise the HCl solution. The econoburette was calibrated with MSME Testing Centre, Government of India, New Delhi, with calibration no. M/0408/1097.

2.1 *Calculation*

The liberated Iodine (I_2) from a reaction of the KI and $K_2S_2O_8$ reactants in acidic medium due to CH_3COOH was titrated with $Na_2S_2O_3$, the reaction is as shown:

$$S_2O_8^{2-} + 2I^- + 2H^+ = 2SO_7^{2-} + H_2O + I_2 \quad (1)$$

The k is calculated with Equation (2), given below:

$$k = \frac{1}{t}\frac{V_t}{V_0(V_0 - V_t)} \quad (2)$$

The k is a rate constant, t time is in sec, the V_0 is an initial volume in mL and the V_t is at time t, of the $Na_2S_2O_3$ solution. Such measurements are well established and could be consulted elsewhere [8] but their measurements with microscale technique is unique and is a step forward in saving resources in chemistry experiments and helpful to the users.

The amounts used for particular solution preparation are given in Table 1, along with details of a saving of materials with the econoburette as compared to the usual burette.

2.2 *Instruments*

2.2.1 *Description*

A sketch diagram of the econoburette is found in Figure 1 along with vertical dimensions in millimetres. It is made up of borosil glass material (Borosil Glass Pvt. Ltd, India). The econoburette was developed by the author and can be procured from Chemistry Research Laboratory, Deshbandhu College, University of Delhi, New Delhi, India. It is under an Indian patent process, with the Government of India, New Delhi for patenting purposes. The L1, L2, L3, L4 and L5 marked in the sketch diagram in Figure 1 are limbs, and each is of 10 mL capacity, except for L5. The limbs L1, L2, L3, L4 and L5 are fitted with valves S1, S2, S3, S4 and S5, respectively. The S5 is a stopper and releases the reaction mixture after titration. The L5 opens to a common bulb B of 25 mL capacity marked in the sketch diagram (Figure 1). The L5 end remains open for pressure control. The limbs are graduated in 0.01 mL with simple etching technique with hydrofluoric acid (HF) assisted with wax. The upper ends of the limbs are fitted with standard joints with movable stopper arrangements and the lower ends are fitted with the air and liquid proof rotating Teflon stoppers which open to a common bulb B. Alternatively the limbs can be made from 10 mL pipette. The L1, L2, L3, L4 and L5 limbs open to bulb B which is connected to stopper S5. The lower end of the stopper S5 opens to a tapered tube. The titrant and titer solutions are taken in limbs L1 and L2 respectively and aqueous starch solution as indicator in the L3. The L4 is an optional limb for any other additive required for titration if need arises for oxidation and reduction purposes. The econoburette is vertically mounted on a stainless steel stand with an ordinary burette clamp. The reproducibility in vertical position is assisted by a spirit leveller. The L4 limb can be used for any additional liquid solution which assists the completion of the reaction or the control of the pH of the titration mixture in bulb B.

The stirring of the reaction mixture in bulb B is made with a glass rod of 1.5 mm inner diameter and 320 mm length. The rod was not fused with the L5 but was movable and inserted through an opening of L5 to bulb B. There is a remarkable difference in the costs incurred with, on the one hand, the econoburette, and on the other hand, the ordinary burette, in performing a similar titration experiment.

2.3 *Titration expenditure with the usual burette*

The amounts incurred with a use of 50 mL burette for two repetitions of volumetric titrations by a single student for a reaction between the KI and $K_2S_2O_8$ are 3.375 g $K_2S_2O_8$/250 mL, 4.15 g KI/250 mL, 11.6 mL CH_3COOH/100 mL as titre, and 0.62 g $Na_2S_2O_3$/250 mL as titrant, 1 g starch/10 mL as indicator and the 50 mL ice cold water to arrest the reaction in bulb B. The amounts of these materials for 40 students are 40 times the above-mentioned amounts. Then after titration the waste from bulb B is discharged to the sink and drained out to the land. Thus, there is huge wastage of chemicals, human effort, electricity and laboratory infrastructure.

Similar cost estimation for a standard HCl versus NaOH titration is made using one molar (1M) HCl and NaOH solutions. Each student had filled up the 50 mL burette to the zero level at the top with 1M NaOH where a total solution which was used is

Table 1. Amounts (g) of chemicals used with both the usual and econoburette for titrations of $K_2S_2O_8$ *vs.* KI reaction and NaOH *vs.* HCl. The numbers in oblique denote mL of the solution to dissolve amounts of the chemicals written before oblique in g.

$K_2S_2O_8$	KI	$Na_2S_2O_3$	CH_3COOH glacial	Starch
With usual burette amounts				
3.375 g/250 mL	4.15 g/250 mL	0.62 g/250 mL	11.6 mL/100 mL	1/100 mL
$10^1 \times 3^2 \times 40^3 = 1200$ mL	$10 \times 3 \times 40 = 1200$ mL	$10 \times 3 \times 40 = 1200$ mL	$10 \times 3 \times 40 = 1200$ mL	$3 \times 3 \times 40 = 360$ mL
16.2 g	19.92 g	2.976 g	139.2 mL	3.6 g
With econoburette				
0.0675 g	0.083 g	0.025 g	0.5 g	0.005/5 mL
$1^4 \times 3 \times 40 = 120$ mL	$1 \times 3 \times 40 = 120$ mL	$1 \times 3 \times 40 = 120$ mL	$1 \times 3 \times 40 = 120$ mL	$1 \times 3 \times 40 = 120$ mL
1.62 g	1.992 g	0.2976 g	13.92 g	0.12 g
Saving				
14.58 g	17.928 g	2.6784 g	125.28 g	3.48 g
% saving				
90	90	90	90	98

NaOH *vs.* HCl

NaOH	HCl	Phenolphthalein
With usual burette		
$10 \times 3040 = 1.2$ L	$10 \times 3040 = 1.2$ L	$2 \times 3 \times 40 = 0.240$ L
48 g	100, 12 N	
With econoburette		
0.12 L	0.12 L	$0.05 \times 3 \times 40 = 0.006$ L
4.8	10, 12 N	
Save		
43.2 g	90	0.234 L
% saving		
90	90	97.5

Notes: L = Litre, N = Normality.
Superscripts 1 and 4 denote 10 mL and 1 mL used with usual and econoburette respectively, the superscripts 2 and 3 denote, the 3 concordant readings and 40 students, respectively.

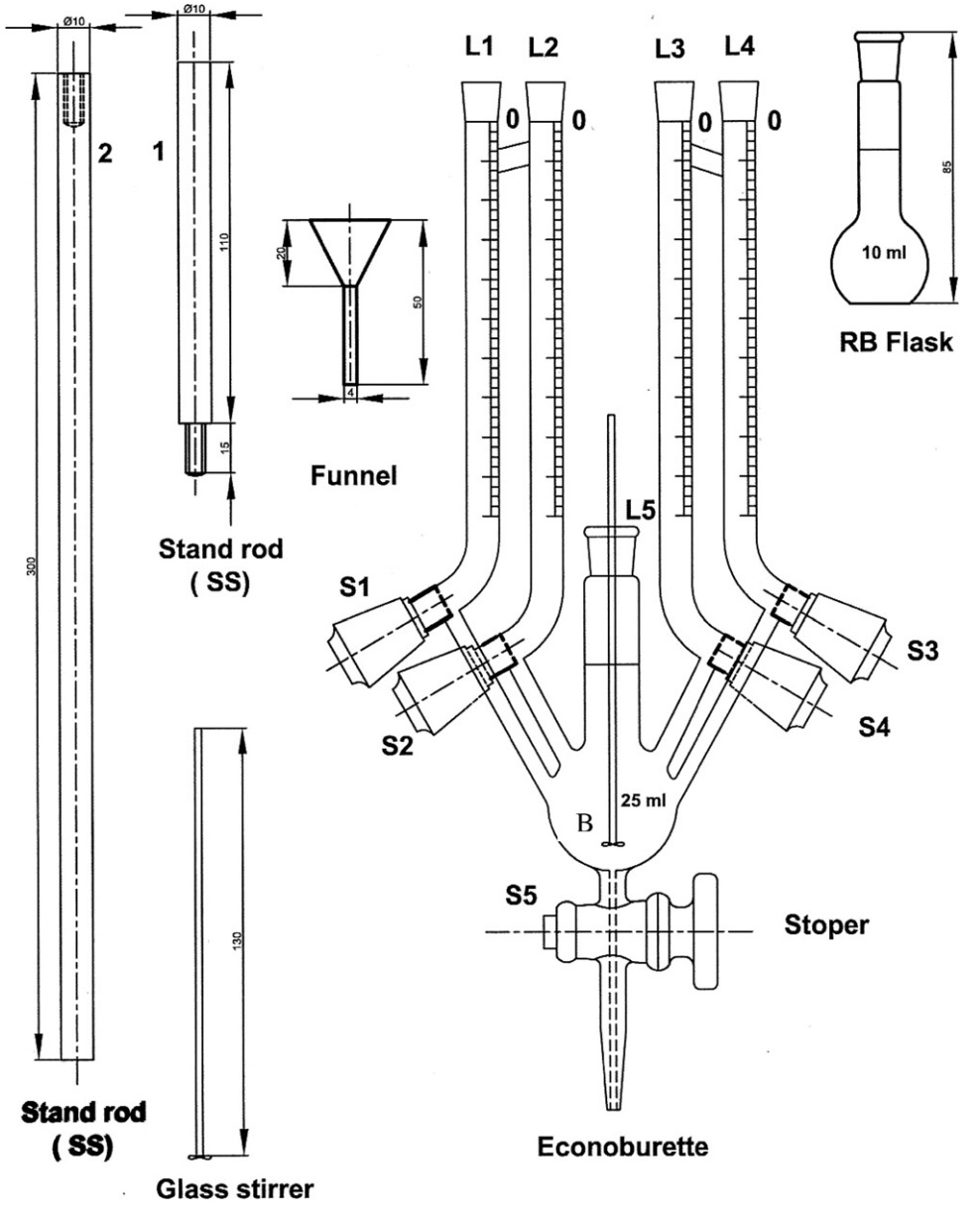

Figure 1. Sketch diagram of the semimicro volumetric kit: Stopcock model.

$40 \times 50 = 2000$ mL (2 L) NaOH. Each student used 10 mL 1 M HCl in a conical flask for each titration against 1M NaOH with the usual burette, and three concordant readings were collected and a total $10 \times 3 \times 40 = 1.2$ L HCl was used. The 1.2 L of the 1 M HCl needs 100 mL of 12 M HCl and similarly an amount for the 1M NaOH for the 40 students is $10 \times 3 \times 40 = 1.2$ L which requires 48 g NaOH. Thus, the 40 students filled the 50 mL burette with the 1 M NaOH, and an instructor needs to prepare about 2 L of 1 M NaOH with 80 g NaOH.

This is a special sheer along with additional effort to deal with larger amounts of the reactants because larger solutions require much time for titration. Along with acid and NaOH, the distilled water was prepared with distillation plant of 2000 Watt heating element. It required about an hour for distilling a litre of water. The electric element in an hour consumes about 20 units of electricity and each unit costs Rs. 4/- only. The total distilled water which was used for acid-base titration is $1.2\,L + 2\,L = 3.2\,L$. It costs $3.2 \times 20 \times 4 =$ Rs. 254/- only or approximately US$ 5.50.

2.3.1 *Savings of materials with the econoburette*

For three concordant readings the titration of 1M HCl versus 1 M NaOH, the 120 mL 1M HCl and 120 mL I M NaOH solutions were used with the econoburette which utilised 10 mL of the 12 M HCl and 4.8 g NaOH. Therefore, the econoburette saved 90% cost of the titration and time of the users as compared with the conventional burette. Similarly the titrations with the econoburette for estimation of rate constant k of a reaction between the KI and $K_2S_2O_8$ reduce their amounts to 0.0675 g $K_2S_2O_8$/5 mL, 0.083 g KI/5 mL, 0.5 mL CH_3COOH/5 mL, 0.025 g $Na_2S_2O_3$ 2 mL^{-1}, 0.05 g starch/0.5 mL, 2.5 mL ice cold water. Thus, the reduction in the amounts of the chemicals and solvents is more than 90%, which makes the experiment considerably ecofriendly and 'green chemistry', less time consuming and occupies the laboratory infrastructure for shorter times.

2.4 *Titration with the econoburette*

As is shown in Figure 1, the limbs between S1 and L1, S2 and L2, S3 and L3, S4 and L4, S5 and bulb B with stoppers S1, S2, S3, S4, and S5 have capacity to hold 10 mL solution and bulb B holds 25 mL. The 1 M HCl was taken in the L1, 1 M NaOH in L2 and phenolphthalein as an indicator in the L3. The limbs are graduated in 0.01 Ml. Initially the 1 mL of the HCl was taken from limb L1 to a bulb B by opening S1 and the 0.1 mL phenolphthalein was taken from limb L3 to B and stirred with a glass stirrer (Figure 1). Then the 0.01 mM NaOH was added from L2 to B to titrate the I M HCl and the addition was continued till a pink colour was noted that indicates a complete neutralisation of an acid by the base. After each addition of 0.01 mM NaOH, the mixture was properly mixed with the stirrer. The titration procedure was repeated till three concordant readings were obtained and then the neutralised mixture was removed from B through S5.

For the titrations with the econoburette for k estimation of a reaction between the KI and $K_2S_2O_8$, the reaction mixture (RM) was prepared by mixing 5 mL solution each of 0.0675 g $K_2S_2O_8$/5 mL, 0.083 g KI/5 mL and 0.5 ml CH_3COOH/5 mL solutions. The 0.025 g $Na_2S_2O_3$/2 mL was used as titrant, the 0.05 g starch/0.5 mL as indicator and 3 mL ice cold water was used to arrest a reaction. The 20 mL stock solution of each chemical substance was prepared with their above-mentioned ratios of w/v. Thus, the 10 mL of a RM of the $K_2S_2O_8 + KI + CH_3COOH$ was taken in the L1, the $Na_2S_2O_3$ in the L2 and the starch solution as indicator in the L3. The ice cold water was taken L4 to arrests the reaction at low temperature. First, the ice cold water was taken from L4 to bulb B, by opening valve S4. Secondly, 1 mL of the RM was taken from L1 to B by opening S1 and the 0.1 mL starch was taken from L3 to B. These contents in B were stirred smoothly with a glass rod and no I_2 was allowed to escape. Then the 0.01 mL $Na_2S_2O_3$ was added from L2 to B to titrate the RM and the additions were continued until a violet colour was noted on completion of a reaction between the $K_2S_2O_8$ and KI. This operation is repeated

for three concordant readings and after each titration the RM was removed from the B valve S5.

2.5 *Washing bulb B and valve S5*

When the titrant and titrand were allowed to bulb B, for a reaction, in general, a small volume of them stick to an inner wall of B. This is removed by washing bulb B with Millipore water after each titration. For washing, the S1, S2, S3 and S4 were tightened and about 2 mL water was poured from the top of the L5, which removed both the titrant and titrand, and were drained out through the S5.

2.6 *Accuracy in measurements*

An ordinary burette measures volume of a liquid with 0.1 mL accuracy but with an econoburette the accuracy in volume measurement is 0.01 mL. This accuracy in volume ensured high accuracy in titration results because the measured volumes are directly used in the $N_{NaOH}V_{NaOH} = N_{HCl}V_{HCl}$ and Equation (2). Also an inner radius of a usual burette tube is about 7 mm which permits an escape of the solution due to evaporation because a larger surface remains in contact with the air. This radius of the econoburette is 2 mm only and does not allow much surface of a solution to be in contact with the air. It further improved accuracy in results with the econoburette in comparison to a usual burette. Hence a better accuracy in k values with the econoburette is obtained.

3. Results and discussion

Statistical analysis of the data of the amounts of the chimericals and saving with the econoburette as compared to the usual burette is given in Table 1. Initially, the solutions were prepared in g/mL ratios given in Table 1. Secondly, the solutions used for three concordant readings by a class of 40 students are also given in Table 1. The differences in amounts with both the burettes are calculated for a net saving of the chemicals and then the saving is converted to a percentage. More than 90% saving is noted by titrating with an econoburette. If expenditure incurred in washing of individual glassware with the usual burette and the econoburette is also compared, then this saving is further enhanced. This is because in the case of the usual burette the individual tools such as pipette, beakers, burette, flask funnel, etc. are washed with chromic acid and distilled water. But in the case of the econoburette, the use of the pipette and Erlenmeyer flask, commonly known as a conical flask, is done away with. So there is also further saving of washing reagents such as chromic acid and water. Both the starch and phenolphthalein as indicators are saved more than 98%. About eight readings of the V_t at intervals of 5 min were taken and the $0.0431\,\mathrm{sec}^{-1}\,\mathrm{L}^{-1}\,\mathrm{mol}^{-1}$ value of k is with $\pm 0.0007\,\mathrm{sec}^{-1}\,\mathrm{L}^{-1}\,\mathrm{mol}^{-1}$ deviation in each set of readings. But for the measurements with the conventional burette, the $\pm 0.0013\,\mathrm{sec}^{-1}\,\mathrm{L}^{-1}\,\mathrm{mol}^{-1}$ deviation is found. The error in results with the econoburette is 1.62% against 3.02% with the conventional burette. Thus, the econoburette is a simple device to save the materials and time of the experimenters for volumetric analysis. With conventional burettes, large quantities of the chemicals and time were wasted but a huge saving has made the econoburette a ‘green chemistry’ and microscale instrument. Also if it is put in practice at a mass level, it would save the environment from being

polluted. The fabrication, handling and operation of the econoburette are simple, and it is an effective tool for industries and educational institutions alike. A comparative study about the chemicals utilised with both the burettes demonstrates, too, many benefits of the econoburette. For preparation of larger amounts of the solutions, the higher amount of water is needed and the titration with larger amounts conducted with the usual burette ultimately makes for huge wastage and poses a pollution menace. The econoburette has saved about 98% amounts of the indicators (Table 1) as compared to the usual burette.

3.1 *Versatility of the econoburette*

The econoburette is highly significant for pharmaceutical and soil chemistry for checking the pH or acid or base contents in the respective samples. As compared to usual burette, it is an integrated and handy unit and needs 1 to 4 mL sample so is it an asset to check acid or base contents in several biofluids and biochemical samples. The econoburette gives a quick and authentic determination of the acid and bases contents in several materials such as facial creams, anti-wrinkle creams, sol gels, inks, dyes, food items, textile, soaps and detergents, paper and pulps, etc. [10]. The acidity and basicity checking of the materials such as milk products, syrups, tablets, emulsions, nano-emulsions, shampoos, pesticides, insecticides and polymer products is essential. The econoburette with minimum infrastructure and time produces accurate results in many fields such as protein solutions and aqueous titration for phase formation. The econoburette is fitted on joining the SS rods 1 and 2 together through inbuilt nut bolt arrangement (Figure 1) in a very small space. The work with the econoburette is being continued and will soon be communicated with new information on titration technology.

Acknowledgement

The author thanks Dr A.P. Raste, Principal, Deshbandhu College, DU, New Delhi, for infrastructural support.

References

[1] F.J. Millero, J. Phys. Chem. **74**, 356 (1970).
[2] M. Mozel and A. Ben-Naim, J. Phys. Chem. **92**, 1359 (1990).
[3] M. Singh, J. Biochem. Biophys. Methods **67**, 151 (2006).
[4] M. Singh, J. Ind. Chem. Soc. **78**, 397 (2001).
[5] M. Singh and A. Kumar, J. Soln. Chem. **35**, 587 (2006).
[6] M. Singh, J. Instr. Exp. Techn. **48**, 270 (2005).
[7] M. Singh, J. Chem. Thermo **39**, 240 (2006).
[8] B.D. Khosla, V.C. Garg, and A. Gulati Sr, *Physical Chemistry*, 11th ed. (R. Chand & Co, New Delhi, India, 2002), pp. 141–145.
[9] L. Rosenfeld, *Four Centuries of Clinical Chemistry* (CRC Press, Boca Raton, FL, USA, 1999), p. 72.
[10] Sci-Tech Encyclopedia, McGraw-Hill Encyclopedia of Science and Technology (Maidenhead, UK, 2005).