Classroom

In this section of *Resonance*, we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. “Classroom” is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

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Volume Effects in Potentiometric Titrations

Chemical titration is one of the important methods in chemical analysis. The titration can be non-instrumental or instrumental. In the present day trend of automation, instrumental methods are preferred. In the undergraduate and postgraduate courses important instrumental methods employed are potentiometric and conductometric titrations. Usually changes near the equivalence point are used for identifying the end point and they need to be sharp for better utility.

Conductivity measurements near the equivalence point have no significance in conductometric titrations; the equivalence point is determined by the steady changes before and after the end point. Further, the accuracy of the conductometric method is compromised by the necessity to have the titrant to be ten or more times concentrated than the titrand so that the steady changes before and after the equivalence point can be linearized. On the other hand, potentiometric titrations are more precise and accurate. The effects of concentration of the solutions to be titrated become less and less steep as the concentration goes down with the corresponding less sharp first derivative peak (*Figure* 1). It is usually thought that there is no significant effect of the titrated volume at an indicated concentration level. The

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The purpose of this article is to emphasize the effect of titrated volume in potentiometric titrations.

Figure 2 shows two pairs of experimental potentiometric titration curves where 0.1M of acetic acid and 0.1M of malonic acid are
titrated with approximately 0.1M NaOH taking two different volumes (2.5 ml and 25 ml). The first derivative data is plotted in conventional manner versus the volume of the titrant. It is clear that the potentiometric signal is sharper in a smaller volume. Further, for the dibasic acid much better defined first stoichiometric end point is obtained with smaller volume. It is evident that smaller volume endpoints are much more sharply defined.

Figure 3 indicates calculated potentiometric titration curves by titration of strong base by a strong acid at 0.1M concentration level and several titrated volumes. The increments in volumes of the titrant were taken proportional to the titrated volume, e.g., 2.50 ml with an increment of 0.010 ml (3a); 5.00 ml with 0.02 ml (3b); 10.0 ml with 0.04 ml (3c); 25 ml with 0.10 ml (3d) and 50.0 ml with 0.2 ml (3e). With such proportional increments the same percentage of neutralization was achieved at each titrant addition, with equal changes. This volume effect is universal and can be observed in any potentiometric titration. The only practical difficulty in dealing with smaller volume is the tendency to add relatively high volume increment of the titrant, which leads to the incremental ratio of $\Delta E/\Delta V$ to be lower than the true $dE/dV$. 
Let us consider the following arguments: An addition of 0.010 ml of 0.10 M HCl to 1.0 ml of water causes a theoretical pH change of 4.0 units, from 7.0 to 3.0, which corresponds to a $\Delta \text{pH}/\Delta V$ of 400. If this volume of acid were added to 10.0 mL of water, the pH change would be 3.0 units, which corresponds to a $\Delta \text{pH}/\Delta V$ of 300. It can also be argued that a proportional increment, 0.10 ml of acid in 10 ml of water, would cause the same 4.0 pH change as observed for 0.010 ml in 1.0 ml of water, which does not appear to be advantageous at all. But the calculated $\Delta \text{pH}/\Delta V$ for these conditions is only 40 instead of 400 as achieved for 1.0 ml of water.

In practice the advantage of dealing with smaller volumes is closely related to the precision of the micro burette as compared with the macro type. Many modern micro burettes can deliver smaller volumes with a precision comparable with that of macro burettes, which deliver higher volumes. In view of the trend for adopting microanalysis in recent days and the increasing cost of chemicals it is useful for the teachers as well as students to know this effect of titrated volume in potentiometric titrations.

Suggested Reading


The grand aim of all science is to cover the greatest number of empirical facts by logical deduction from the smallest number of hypotheses or axioms.

– Sir Humphrey Davy