

Microscale Experiments in Chemistry – The Need of the New Millenium

4. Physical Chemistry Experiments on Microscale

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It is evident from the earlier articles in this series that considerable time and money can be saved if the academic laboratories are to adopt microscale techniques. In this context, however, the point regarding consumption of large quantities of chemicals appears irrelevant from the physical chemistry point of view. Most of the experiments are already being performed with instruments and require *per se* small amounts of chemicals. However, we felt that many of the traditional procedures should be reviewed and rewritten to bring about not only further reduction in chemicals, time and energy but also bring theory closer to the laboratories.

In the physical chemistry domain, the undergraduate syllabus includes experiments to demonstrate basic principles such as adsorption, partition coefficient, measurement of viscosity, stability constants of complexes, etc. It also includes experiments to illustrate the most important principle of 'chemical equilibrium'. The students are introduced to several instrumental methods such as spectrophotometers, potentiometers, pH meters and conductometers for quantitative estimations, rather than by the conventional pipette-burette titration.

One of the common experiments carried out in all the undergraduate laboratories is the determination of the stability constant of triiodide ion. The standard procedure prescribed requires that the distribution coefficient of iodine is first determined between carbon tetrachloride and water. This is used in the next step to estimate the concentration of iodine in aqueous layer containing KI. For this, about 50 ml of carbon tetrachloride (CCl_4) saturated with iodine (I_2) is to be equilibrated with



Part 1. Newer Ways of Teaching Laboratory Courses with New Apparatus, *Resonance*, Vol.5, No.10, p. 24, 2000.

Part 2. Experiments Which Bring Theory Closer to Laboratories, *Resonance*, Vol.5, No.12, p.6, 2000.

Part 3. Microscale Inorganic Qualitative Analysis and New Methods of Titrations for Introduction at All Levels in Chemistry Laboratories, *Resonance*, Vol.6, No.2, p.14, 2001.

200 ml of aqueous solution of KI. Iodine is then partitioned into the aqueous layer as KI_3 and as I_2 in carbon tetrachloride. After separation of the layers, iodine in each layer is estimated by titration. Taking into consideration the high cost of iodine, potassium iodide and CCl_4 , we thought of looking at this experiment specifically to reduce the required quantities to less than just a tenth of the prescribed volumes. The convention is to shake 250 ml of immiscible liquids in a separating funnel for about 20 minutes in order to attain equilibrium of the solute in the two phases. Simultaneously, the thermal equilibrium is to be maintained. With reduction in quantities, 'shaking' is replaced by 'agitation' by the Pasteur pipette. This can be easily done while keeping the container in the thermostat during this process. For effective agitation, the lower layer is taken into the Pasteur pipette. The pipette is withdrawn just about a centimeter above the upper layer and the liquid is injected through the upper layer by force using a rubber bulb. This is repeated a number of times to ensure thorough mixing of the two layers. We took aliquots at intervals of two minutes to find the partitioning and found that the time taken for equilibration of iodine in the two layers is reduced to just about 3 to 4 minutes. The separation of the two layers was done by Pasteur pipette. In the previous article, we described the use of Beral pipettes for carrying out the titrations on microscale. However, one of the limitations in the use of Beral pipettes became apparent when we tried to apply the same technique here. The number of drops for the same volume of water and any other volatile liquid are not the same. This is obvious since the drop size is determined by the surface tension of the liquid. To overcome this difficulty, a fixed volume (0.5ml) of CCl_4 is taken from the reaction flask using a measuring cylinder in a test tube and potassium iodide is added to it to extract the dissolved iodine. This is titrated against the standard thiosulphate solution by the new method. The experimental results are within the limits of errors as those obtained in the normal scale experiment. The cost effectiveness of this method would be evident if we compare the prices *vis-à-vis* the consumption of carbon tetrachloride, iodine and potas-



sium iodide and also elimination of apparatus such as separating funnels, burettes and pipettes.

The recent trend in chemistry is to understand and explain the chemical and physical interactions on a molecular basis. In this direction, our attention is focused towards the reduction of size of the voltametric cells required in potentiometry. A typical concentration cell used in the estimation of Ag^+ ions can be used in several experiments like determination of stability constants of silver complexes, solubility products of silver salts, and halide estimations by argentometric titrations, etc. The main difficulty normally faced in assembling a cell, is the connectivity of the two half-cells. We used a 'U' shaped glass tube with 8 mm id (inner diameter) and 7 to 9 cm height and filled half of this with a warm solution of agar-agar gel containing requisite concentration of potassium nitrate to build a salt bridge. The glass tube may be replaced with polymer tubing. A small wooden plank with two holes is adequate to hold it vertically. The sleek assembly is very easy to construct, reduces the cost and also forms an unbreakable assembly. The upper unfilled part of the 'U' tube can be used as half-cells now. Building cells this way have many advantages as listed below:

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1. The continuity of the bridge is never broken. Besides being a

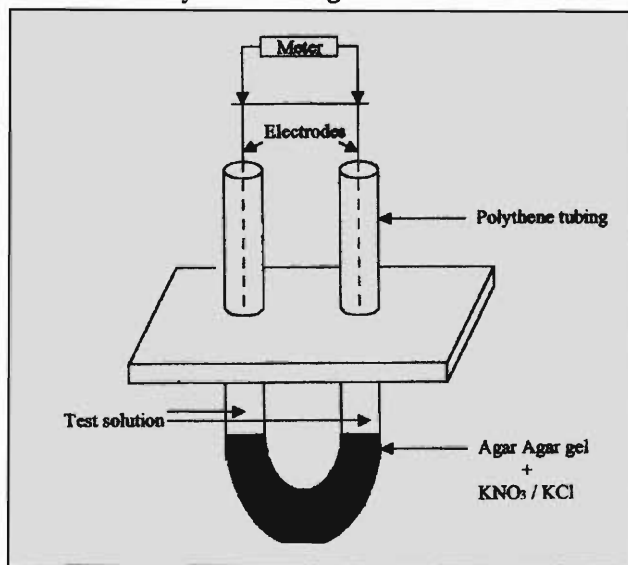


Figure 1. Cell assembly.

The volume of the electrolyte solutions required to construct the cells is just around 1 to 2 ml. This reduces the consumption of AgNO_3 substantially.

good conductor, the set agar-agar gel is quite stable, does not spill off and the assembly thus remains always clean.

2. The liquid at the top of each of the arms protects the bridge from drying. A small cotton plug on each end of the agar gel would guard it from any pricking by the electrode.

3. In each of the cell compartments, the solutions can be added or removed very easily with the Beral pipettes. Even cleaning the cell can be done very easily.

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5. Expensive metals in thin wire form are soldered to copper wire that is supported through an empty ballpoint pen refill. These are used as electrodes.

6. The same bridge could be used repeatedly with reproducible results. If needed, it could be refilled easily.

7. The e.m.f. generated in the cells is easily measurable on digital multimeters (which are accessible and available in the market).

The following experiments could be performed using this apparatus.

a. Halide estimation by potentiometric titration

A concentration cell is set up in this experiment. A silver electrode in about 0.5 ml of 0.1N or 0.01N silver nitrate solution serves as a reference, while the other half-cell contains silver electrode in the test halide solution measured by standardised Beral pipette. It is titrated against standard silver nitrate solution added through another standardised Beral pipette. Thus a microscale titration is performed with results of the same standard and accuracy as obtained by normal titrations.

b. Estimation of solubility product

The e.m.f. value upon addition of the first drop of silver nitrate



in the above titration could be used to estimate the solubility product of the particular silver halide formed.

c. Verification of Nernst's equation

Over a KNO_3 salt bridge, a concentration cell $\text{Ag}/\text{Ag}^+(c_1)//\text{KNO}_3//\text{Ag}^+(c_2)/\text{Ag}$ is formed. Keeping c_1 constant, c_2 is varied systematically by adding required quantity of distilled water. The linear variation of e.m.f. with $\log c_2$ can be shown graphically and c_1 can be determined from the intercept. The slope will be close to the anticipated value of 0.059.

d. Stability constant of $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{2-}$

Five different solutions of this complex are prepared with varying thiosulphate concentrations. A concentration cell is set up (*vide supra*) and the smallest concentration of c_2 of Ag^+ in the complex is estimated in an identical way. These values of c_2 are further used to determine the equilibrium constant as per the standard procedure.

e. Determination of pK_a of an acid

The utility of $\text{Ag}/\text{AgCl}/\text{Cl}^-$ reference electrode is explored in the potentiometric titration of acetic acid by NaOH . The pH at half neutralisation point is the pK_a of the acid. Hence standardization of the reference electrode is crucial. For this, a platinum electrode in 0.01M solution of potassium hydrogen phthalate saturated with quinhydrone forms one of the half-cells while $\text{Ag}/\text{AgCl}/\text{Cl}^-$ is the other half-cell. The salt bridge should now contain KCl instead of KNO_3 . We obtained absolutely reproducible and accurate values for $E_{\text{Ag}/\text{AgCl}/\text{Cl}^-}$ with this set-up. This electrode is easy to prepare, maintain and economical as well.

In the second part of the experiment, instead of potassium hydrogen phthalate, measured amount of acetic acid solution is taken up in the half-cell. It is saturated with quinhydrone and then titrated with standard solution of NaOH using Beral pipettes. A titration curve is constructed using the e.m.f. values measured. From the e.m.f. at half neutralization point, the pK_a



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value is obtained. The cleaning and refilling of the reference electrode is very easy and inexpensive. The repeated cleaning also ensures high reproducibility. Further, the half-cell can be filled or emptied very easily by Beral pipettes. Many acid-base titrations can be performed with such a set-up. Measurement of pH of many acidic solutions could be a logical extension of this experiment.

One more modification of the set-up is the use of digital millivoltmeter to measure the potential difference. Basic requirement of a potentiometer is that the instrument should draw a minimum current for an accurate measurement of the e.m.f.. Since the current drawn in these digital instruments is negligibly small, they can easily replace the traditional potentiometers in the laboratories. Cost of a typical classical potentiometric assembly is around Rs. 5000 as against that of a digital multimeter, which is just Rs. 400. Besides, the digital multimeters are very rugged, can save a lot of space and are maintenance free.

In the next experiment, we scaled down the chemicals used in the photometric titration to estimate Cu^{2+} using a UV-visible spectrophotometer. In the conventional method of EDTA titration of a buffered cupric solution, the absorbance of the solution being titrated is measured at each interval. The solution from the titration vessel is frequently transferred to and from the photometric cuvette and the vessel. We took about 0.25 ml of the buffered Cu^{2+} solution in the cuvette. The part of the cuvette above the solution level is covered with an opaque paper. With this arrangement, the Beer-Lambert Law is still valid, since the path length of the incident light is the same. Thus the volume required to conduct the experiments is reduced substantially. The titration is carried out on a microscale quantity in the cuvette itself by adding the titrant with the help of a Beral pipette. The volume of each drop from Beral pipette is about 0.03 to 0.04 ml making it possible to take several readings using the free space of 0.5 ml in the cuvettes. The results obtained are as accurate as the ones obtained by the method prescribed in the standard textbooks.



In yet another experiment, photometric determination of two ions, cobalt and nickel, is attempted by this technique. The volumes of metal salt solutions required in this new method are very small. The results are very satisfactory.

Our aim in all these attempts is to obtain the same results using small quantities of the chemicals as one would get in the conventional experiments. The time of operation is reduced considerably. Transportation of the assembly is easy and so also the multiplication of the units.

Acknowledgement

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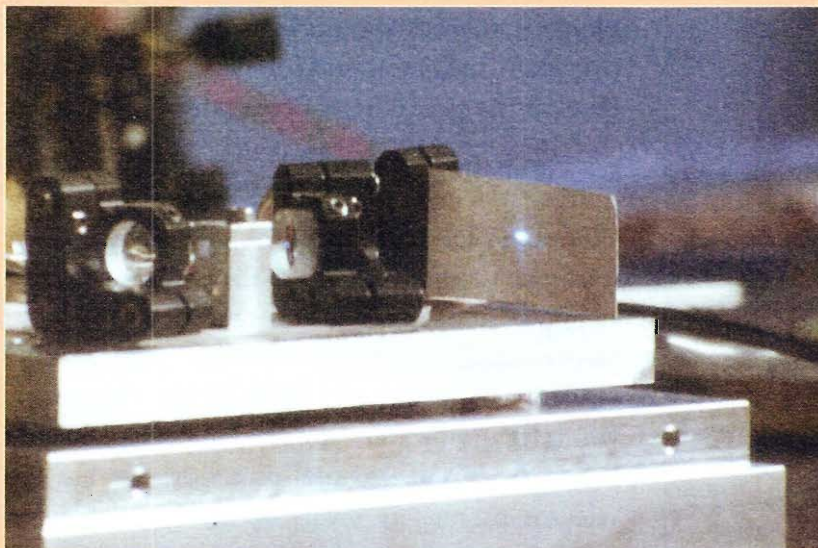
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The photograph shows blue light from a frequency doubled diode laser. The diode laser output is at 800 nm (Infrared) which is frequency doubled using a nonlinear crystal to 400 nm (blue). This technology has extended the use of diode lasers for spectroscopy in the visible and ultraviolet regions. (See Article-in-a-Box for applications in laser cooling.)

