VII.—On some Lecture Experiments illustrating Properties of Saline Solutions.—By Prof. J. G. MacGregor, *Dalhousie College, Halifax, N. S.*

[*Received May 1st, 1891.*]

(1.) In a paper printed in the last volume of this Institute's Proceedings,* I pointed out that, according to Kohlrausch's observations, sufficiently dilute solutions of sodium hydroxide have volumes which are less than the volumes which their solvent water would have in the free state, one gramme of a solution containing about six per cent. of the hydroxide, having a volume 0.0045 cu. cm. less than the water it contains. Several other substances are known which exhibit the phenomenon of contraction on solution, in a similarly marked manner, but none which exhibit it to such an extent. This hydroxide, therefore, affords the best means of exhibiting the phenomenon of contraction by a lecture experiment.

The simplest mode of conducting the experiment is to pass the powdered caustic soda, little by little, down a glass tube forming a prolongation of the neck of a large bottle, the bottle and part of the tube having been first filled with distilled (or, indeed, undistilled) water. The substance is quickly dissolved by the water, the strong solution thus formed sinks and mixes with the water below, and the change of volume of the liquid is indicated by the change of height of the column of liquid in the tube. In order that the experiment may be made quickly, the powder must not be allowed to form a cake in the tube where it meets the water. To avoid this, a tube of about seven or eight mm. diameter must be used. It should be several inches in length, and should have the upper end opened out to a funnel shape, to facilitate the introduction of the powder. The tube being necessarily of large bore, the bottle must also be large, so that a small change of

* Proc. and Trans. N. S. Inst. Nat. Sci., Vol. VII. (1889), p. 368.

volume may be indicated by a comparatively large elevation or depression in the tube. The hydroxide should be in the form of a powder, not only that its solution may be accomplished quickly, but also because the solution formed must be dilute in order to secure a depression of the liquid in the tube. If it be not powdered, the substance falls to the bottom and forms a strong solution there, which only gradually diffuses into the water above. Even with a fine powder, however, a comparatively strong solution is formed at the bottom. Hence I have found it advisable to catch the powder in a wire gauze cage, attached by sealing-wax to the inner end of the rubber stopper which carries the tube, and to hasten the mixture of the strong solution, formed in the tube and cage, with the water, by diverting the downward currents of the strong solution towards the sides of the bottle by means of a plate of glass hanging horizontally below the cage. If a wide-mouthed bottle be used, a stirrer may be introduced through the stopper, but leakage is thereby rendered more probable. The full amount of the contraction indicated by Kohlrausch's observations cannot, of course, be shown. For (1), the powdered caustic soda already contains a considerable quantity of water; (2), the solution of the substance is attended by a development of heat involving a rise of the liquid in the tube; (3), the powder carries air with it into the water, which must increase the volume whether it dissolves or remains suspended; for in the latter case, if a quick effect is desired, there is not sufficient time for it to escape up the tube; and (4), whatever precautions may be taken to secure a uniform solution throughout the bottle, it cannot be at all completely secured in the time at disposal. But notwithstanding these difficulties, the experiment is a very striking one, especially if projected by a lantern on a screen. As the powdered caustic soda is passed down the tube, little by little, the liquid is seen to dissolve it without any increase in bulk, and if the substance does not already contain too much water, with an actual diminution in bulk, the level of the liquid sinking in the tube. If the powder be added in large quantity, there is a sudden rise of liquid in the tube, followed by a gradual shrinkage, which continues until the level of the liquid is lower than at the outset. The amount of the depression of the liquid in the tube is sometimes small, depending apparently upon the amount of water which the powdered caustic soda has already absorbed. The substance should not be too finely powdered, as in that case it is likely both to have taken up a considerable quantity of water and to carry down with it a considerable quantity of air. The experiment requires only a few minutes to perform.

(2.) The working hypothesis which I use when thinking of the phenomena of solution, has led me to the conclusion that elevation of the temperature of a solution will have, if not identically, at any rate in a general way, the same effect on its selective absorption of light, and therefore on its colour, as increase in its concentration. All the experimental evidence of which I can find any record bears out this conclusion. But, whether it holds generally or not, it may be shown, by a striking lecture experiment, to hold in the case of two salts, the chlorides of cobalt ($CoCl_2$) and iron ($FeCl_6$). To do so, make a trough, for projection with a lantern, having thin glass sides, about the size of a lantern-slide, the glass sides being one or two mm. from one another. It may readily be made by cutting a U-shaped piece from a sheet of india rubber, and cementing the glass plates to its opposite sides. Half fill the trough with a saturated solution of either salt, and fill up with a weak solution. If cobalt chloride have been used, the solution in the lower part of the trough will at ordinary temperatures be of a purplish blue, that in the upper part red; and it will be obvious that increase of the concentration of this salt involves increase of blueness in the transmitted light. If, now, a Bunsen flame be played carefully over one side of the trough, the solutions rapidly rise in temperature, and both are seen to increase in blueness, the saturated solution becoming deep blue and the weak solution purplish red. If the iron chloride have been used, the solution in the lower part of the trough, before heating, is seen to be of a deep orange color, that in the upper part yellow; and it is obvious that increase in the concentration of this salt involves increase in redness. If, now, the flame be applied as before, the yellow solution is at once seen to become orange and the orange solution red. Owing to the narrowness of the trough and the thinness of its glass sides, sufficient heating to produce a marked change of colour occupies only half a minute or so. The same trough may of course be used to project the absorption spectra of these solutions on the screen. If the slit be covered half by the one solution and half by the other, both absorption spectra may be seen at once, side by side, and the gradual variation of the spectra may be watched as the trough is gradually heated.

As a means of showing the variation of the colour or absorption spectrum of a solution with concentration, the above experiment has an obvious defect, viz., that the thickness of the layer of the strong and weak solutions being equal, the numbers of the salt molecules through which any ray of light passes are very different in the two cases. It should therefore be supplemented by showing also the colour or the spectrum obtained when the light is passed through a wide trough of the dilute solution, the ratio of the widths of the troughs being the reciprocal of the ratio of the percentages of salt in the two solutions.

(3.) Dr. W. W. J. Nicol's observation* that anhydrous sodium sulphate will dissolve in a supersaturated solution of that salt may readily be shown as a lecture experiment by projection. For that purpose place a test tube containing the solution, in a trough with glass sides full of water, and focus it on the screen. Then, let the anhydrous salt in the form of a fine powder, fall upon the surface of the solution. By taking a pinch of the powder between the thumb and forefinger (both being quite dry), it may be made to fall as a shower of fine particles. These pass into the solution and are seen to move slowly across the screen through the solution, dissolving as they go, in some cases disappearing, and often changing the concentration of the part of the solution through which they have passed, so as to produce obvious refraction effects. Finally, to show that the solution was supersaturated, add a few crystals of the hydrated salt and crystallization at once occurs. The anhydrous salt

* Phil. Mag., Ser. 5, Vol. xix (1885) p. 453.

must be added as a shower of fine powder, as larger pieces may by taking up water and forming crystals of the hydrated salt before they can dissolve, give rise to a general crystallization of the solution.

(4.) The peculiarity of the solubility in water of such substances as anilin, carbolic acid, etc., observed by Alexejew,* may readily be shown on the screen, by using carbolic acid, whose critical temperature (the temperature above which it and water are mutually infinitely soluble) is about 69° C. For this purpose, pour some of the acid into a long test-tube, of about 12 or 15 mm. diameter, and add water. The water will lie in a layer above the acid. Support the test-tube by a clip grasping it at the top, and focus on the screen. The line of demarcation between the two liquids will be evident. Now mix the liquids by stirring, and the whole becomes cloudy. Let the tube stand, and the liquid separates again into two layers, having different depths from those they had before, both being now solutions. As this process requires considerable time, the stirring may have been done beforehand. Next surround the test-tube by a beaker of boiling water, passing it upwards from below, and stir the liquids with a hot glass rod. A slight cloudiness appears, but the liquid quickly clears and is seen to have become homogenous throughout, the line of demarcation having disappeared. If now the beaker of hot water be removed, and one of cold water be substituted for it, the liquid becomes cloudy, a strong solution separating out everywhere, and the little spherical masses of strong solution sinking and coalescing as they sink, to form larger spheres. After a time the liquid is seen to have again become separated into two layers. If the necessary time is not available, the separation into layers may be obtained very quickly by removing the beaker of cold water and again applying the hot bath, which, raising the temperature, stops the separating out of the strong solution and re-dissolves it in the surrounding weaker solution, thus producing a comparatively strong solution in the lower part of the tube and a comparatively weak one in the upper part. The experiment requires but a few minutes and is both striking and instructive.

* Wied. Ann. Bd. XXVIII. (1886), p. 305.