solution would be expected to show only half the original color. In point of fact such dilution actually increases the color in a material degree owing to the dissociation of solute molecules which accompanies the dilution. The effect of similar dilution with alcohol is even more marked. The color differences of such solutions become greatly accentuated on standing. The color of the undiluted aqueous solution decreases at a relatively rapid rate, owing to further progressive association of solute molecules. The corresponding alteration in the dilute aqueous solution is much less and the dilute alcoholic solution gives but little indication of physical instability. The phenomenon appears suitable for classroom demonstration.

Table I gives the spectrophotometric measurements obtained in such tests. The values recorded are the extinction coefficients measured at the absorption maxima of the respective solutions in a 1cm. layer. In the aqueous solutions the maximum absorption was found at 542 mμ and in the aqueous alcoholic solution at 548 mμ. The original aqueous solution was prepared by saturating distilled water with phenolate at room temperature.

TABLE I

EXTINCTION COEFFICIENTS AT ABSORPTION MAXIMA

	Original aqueous soln.	Original soln. diluted with an equal volume of water	Original soln. diluted with an equal volume of alcohol
Immediate absorption	0.54	0.69	0.88
After 1 day	.34	.63	.875
After 6 days	.16	.41	.85

CONTRIBUTION FROM THE
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Determination of Excess of Alkali in Hypochlorite Solutions.—The procedure is based upon the removal of the hypochlorite by means of a reducing agent, giving removable and non-interfering compounds. The hypochlorites are removed as indicated in the equation $2Ni(OH)_2 + NaOCl + H_2O = NaCl + 2Ni(OH)_3$. The change in condition from nickelous to nickelic is indicated by the change in color from light green to black. Inasmuch as both nickel hydroxides are insoluble in water, they can be completely removed before titrating.

Ferrous, manganous and cobaltous hydroxides react in like manner. Nickelous hydroxide, however, was found to be best for the purpose, due to its stability and insolubility.

The presence of ammonium salts vitiates this method.

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Procedure

The nickelous hydroxide is employed in the form of a suspension in water, 0.0050 g. in 1 cc., prepared by precipitation from a soluble nickelous salt with excess of sodium hydroxide. The precipitate must be washed free from all the excess of sodium hydroxide; it is then stirred with distilled water. This mixture will keep indefinitely. The mixture is well shaken and then added in excess to the hypochlorite solution. This is heated, just under its boiling point, for about ten minutes, and then filtered. While filtering, a portion of the filtrate can be tested for unconverted hypochlorite by adding a few drops of the nickelous hydroxide suspension to it and heating for one minute. A darkening of the precipitate indicates the presence of hypochlorites. Should this occur, the entire filtrate must be retreated with nickelous hydroxide. The filtrate is now ready for titration with hydrochloric acid.

The error of the determination was found to be ± 0.06 cc. when the alkali was sodium hydroxide in a 1 N solution. For determining calcium hydroxide it was found that this method could not be used, since the calcium hydroxide was partially removed from the solution by adsorption into the gelatinous nickel hydroxide.

The simplicity and accuracy of this method are of practical interest and value, and commend themselves to all analysts.

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The Thermodynamics of Non-Isothermal Systems.—In a recent article Eastman[1] has discussed the application of thermodynamics to non-isothermal systems and especially to the Soret effect, in an interesting manner. It will be difficult to add anything of practical significance to Eastman's paper since his conclusion that in general these effects can only be determined empirically is undoubtedly correct. It seems necessary, however, to urge a different viewpoint from that of his paper in certain particulars. In the first place, his statement of the condition for equilibrium $\Sigma\delta S = 0$ is incomplete. Gibbs[2] has stated the conditions for equilibrium upon which the laws of thermodynamics are based in two ways which are equivalent: (a) in an *isolated system* at constant energy the entropy shall be a maximum, or (b) in an *isolated system* at constant entropy the energy shall be a minimum.

These conditions are stated mathematically as $(\delta S)_E \leqq 0$, $(\delta E)_S \geqq 0$.

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[1] Eastman, THIS JOURNAL, 48, 1482 (1926).

[2] Gibbs, "Scientific Papers," Longmans, Green and Co., New York, 1906, vol. 1, p. 56.