

In conclusion, I wish to acknowledge my indebtedness to the Director of these Laboratories, Professor M. A. Rosanoff, under whose guidance the above study was carried out.

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NOTE.

On the "Color Demonstration of the Dissociating Action of Water" of Jones and Allen.—Jones and Allen¹ have published a well known lecture demonstration of the "dissociating action of water," which is repeated by Jones in his text-book, "The Elements of Physical Chemistry."² "A few drops of an alcoholic solution of phenolphthalein are placed in a glass cylinder, and diluted to, say, 50 cc. by the addition of alcohol. A few drops of an aqueous solution of ammonia are then added. A red color may appear where the aqueous ammonia first comes in contact with the alcoholic phenolphthalein but this will disappear instantly on shaking the cylinder. . . . Water is then gradually added to the cylinder, when the red color will appear, at first faint then stronger as the amount of water increases. When the red color has become intense, add a considerable volume of alcohol, and the entire color will disappear." This is given as a demonstration of the dissociating action of water, the explanation being that in the alcoholic solution the ammonia is so little dissociated that there are not enough hydroxyl ions present to color the phenolphthalein. Dilution with water dissociates the ammonia enough to give the red color to the indicator. The further addition of alcohol represses the dissociation and the solution again becomes colorless.

Recent light on the mechanism of the color change in indicators, and a comparison of the relative dissociating power of alcohol with its enormous decolorizing power on slightly alkaline phenolphthalein solutions made it seem highly improbable that the reason for the color change was the one assigned by Jones and Allen. This property of alcohol was noticed by the writer while measuring the dissociation constant of phenolphthalein.³ It was first remarked by Menshutkin⁴ and further observed quantitatively by McCoy.⁵

The effect of the alcohol in this respect is so great as to preclude the possibility of its being due, except in very small proportion, to the smaller dissociating power of the alcohol. Solutions of salts in alcohol show a degree of dissociation about one-third that in water.⁶ Mixtures of

¹ *Amer. Chem. J.*, **18**, 377 (1896).

² Third edition, 1907, p. 295.

³ *Z. Elektrochem.*, **14**, 352 (1908).

⁴ *Ber.*, **16**, 315 (1883).

⁵ *Amer. Chem. J.*, **31**, 503 (1904).

⁶ Jones, *Z. physik. Chem.*, **14**, 701 (1894).

alcohol and water as solvents show a decreased conductivity but the decrease is not great and even a large part of that is due to the increased viscosity.¹ Even if, say, twenty-five per cent. of alcohol repressed the dissociation of the ammonia to half its former value, the equilibrium equations involved show that we would expect the intensity of color of the indicator to be reduced one-half. As a matter of fact, under proper conditions this amount of alcohol is more than sufficient to decolorize the phenolphthalein completely.

How then is the great color change to be accounted for? All the recent work on indicators gives evidence that the color change is due not simply to a difference in color between the ion and undissociated molecule,² but rather to an equilibrium between two differently colored tautomeric forms, the amount of one varying according as the other is dissociated or not.³ In the double equilibrium $A \rightleftharpoons HB \rightleftharpoons H^+ + B^-$ if the first equilibrium is mostly in the direction of A and the dissociation constant of HB is small, then if H^+ is large the indicator exists mostly as A having one color, if small, mostly as B^- with a different color. Although the case with phenolphthalein is rather complicated,⁴ let us assume for simplicity that A represents the colorless part, and B^- the red ion. It is evident that the color could be diminished not only by increasing H^+ as Jones and Allen assume, but also by a combination of the alcohol with A. The solubility of phenolphthalein in alcohol renders this not improbable.

Now if the addition of alcohol changes considerably the concentration of the hydrogen ion, then the color change should be shown by other indicators besides phenolphthalein. If, however, the color of other indicators is not correspondingly altered, then the change in this case must be due to a combination of alcohol with the colorless form of the phenolphthalein.

Colorimetric measurements were made to compare phenolphthalein with other indicators in their behavior towards alcohol. To 15 cc. of a phenolphthalein solution partly dissociated with ammonia were added 2 cc. of neutral alcohol, and the change in color was noted, correcting for the dilution. The same procedure was carried out with litmus, paranitrophenol and rosolic acid. With litmus sodium light was used which gave the amount of blue in the presence of the red. With rosolic acid, green light gave the red in the presence of the yellow. The varying color was produced by ammonia or acetic acid as the case might be. The dissociation constant of acetic acid being nearly the same as that of am-

¹ Jones and Carroll, *Amer. Chem. J.*, **32**, 521 (1904).

² Ostwald, *Lehrb. d. allg. Chem.*, 2nd edit., Vol. I, p. 799.

³ Stieglitz, *J. Amer. Chem. Soc.*, **25**, 1112 (1903).

⁴ Acree, *Amer. Chem. J.*, **39**, 528 (1908).

monia, any decrease in dissociation due to the alcohol would be the same for both.

The results are given in the table. The figures for litmus are on the assumption that it is an acid.

Indicator.	Per cent. dissociation.		Decrease.
	Before adding alcohol.	After adding 13 per cent. alcohol.	
Phenolphthalein.....	67	30	37
Litmus.....	76	80	---4
“.....	42	45	---3
<i>p</i> -Nitrophenol.....	80	81	---1
“.....	12	16	---4
Rosolic acid.....	57	57	0

It will be seen that phenolphthalein is alone in its behavior with alcohol, the latter even producing a slight *increase* in dissociation with litmus and *p*-nitro phenol. It would seem, therefore, that the decrease in the dissociation of the ammonia plays but a very small part in the decolorization of phenolphthalein by alcohol, and that the "color demonstration" depends upon something quite different from that which its authors state.¹

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¹ This paper was submitted to Prof. Jones who very cordially urged its publication, saying that he also was of the opinion that the explanation offered by Mr. Allen and himself was not sufficient.