

dependent of the pressure. The results of two typical tests made by connecting manometers to both sides of the diaphragm, are given in the tables labelled Test 1 and Test 2.

Neither of the diaphragms used was excessively thin. The one used in Test 2 was capable of withstanding an outward pressure of at least 60 cm. No special care was taken in this test to have the manometer tubes or mercury scrupulously clean nor to check the cathetometer used. However, it is readily seen to be very easy to make diaphragms of this type which are sensitive to at least 0.2–0.3 mm. Furthermore, we have used diaphragms which had been "clicked" probably hundreds of times with no damaging results to them. We have used these devices at temperatures from 20–360° and have observed no change in their behavior within this temperature range.

Although the blowing of the diaphragms is a more or less "cut and try" process, several satisfactory pieces can be turned out within an hour or so after a little practice. It is possible to sort out the satisfactory pieces very easily—merely by exerting pressure in the blowing tube. The setting up of the satisfactory pieces is all simple glass blowing.

#### Summary

1. An accurate, and easily made all-glass device for measuring the pressure of corrosive gases has been described.
2. Tests showing the accuracy attainable with the device have been presented.

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[CONTRIBUTION FROM THE COLORADO SCHOOL OF MINES]

### DIPHENYLAMINE INDICATOR IN THE VOLUMETRIC DETERMINATION OF IRON

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The excellent method developed by J. Knop<sup>1</sup> using diphenylamine as an internal indicator in dichromate titrations of iron, makes one wonder why it is that this was not thought of before. The writer suggests an application of the same principle to iron titrations with potassium permanganate. The advantage in the use of diphenylamine over the use of permanganate alone is in the fact that titrations may be made in the presence of mercurous chloride, the end-point being sharp and permanent, furthermore, the blue color or violet, as the case may be, is more pronounced than the pink of permanganate alone. Hydrochloric acid does not interfere in concentrations ordinarily present. The use of stannous chloride for reducing iron has advantages over zinc, and this procedure for reduction

<sup>1</sup> Knop, *THIS JOURNAL*, **46**, 263 (1924).

of iron may be used in connection with permanganate titrations, with diphenylamine indicator. The phosphoric-sulfuric acid mixture (15 cc. of each increased to 100 cc. with water) was used by the writer, as is suggested by Knop, to repress the yellow color of (ferric iron) chloride. The indicator proved successful with both dichromate and permanganate titrations of iron in the writer's class in quantitative analysis of over eighty students. The results shown in Table I are his own.

The delicacy of the reaction depends on a judicious use of the indicator in permanganate titrations. The quantity of the indicator should not exceed 0.4 cc. Larger amounts of indicator require a larger amount of permanganate to obtain a blue color; the diphenylamine itself is responsible for a yellowish-green color being produced before the end-point is reached. Best results are obtained by 0.2 cc. of the indicator, made according to Knop's directions (1 g. of salt per 100 cc. of concd. sulfuric acid) in solutions of iron in volumes of 100 to 250 cc.

Diphenylamine indicator may be used in the standardization of potassium dichromate by means of standard ferrous sulfate solution, since titrations may be made with either reagent without destroying the qualities of the indicator, the blue color disappearing with an excess of ferrous salt, but being restored by an excess of dichromate.

In Table I are given the cubic centimeters of diphenylamine indicator and the volume of the solution at the beginning of the titration; 0.1 *N* reagents were used in all cases, and 10-15 cc. of phosphoric-sulfuric acid solution was used in each analysis.

TABLE I

|                      | A                 | B   | C                 | D                 | E                 | F                 | G                 |
|----------------------|-------------------|---|-------------------|-------------------|-------------------|-------------------|-------------------|
| Indicator used, cc.  | none              | 0.2   | 0.2               | 0.2               | 0.4               | 1.0               | 2.0               |
| Volume of soln., cc. | 120               | 120   | 120               | 220               | 220               | 220               | 220               |
| Iron present         | KMnO <sub>4</sub> | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> | KMnO <sub>4</sub> | KMnO <sub>4</sub> | KMnO <sub>4</sub> | KMnO <sub>4</sub> | KMnO <sub>4</sub> |
| G.                   | Cc.               | Cc.   | Cc.               | Cc.               | Cc.               | Cc.               | Cc.               |
| 0.04467              | 8                 | 8   | 8.1               | 8.0               | 8.3               | 11.0              | 13.0              |
| .08934               | ...               | ..  | 16.1              | 16.0              | 16.4              | 19.8              | 22.4              |
| .13401               | ...               | ..  | 24.05             | 24.0              | 24.4              | 28.4              | 32.0              |
| .17868               | ...               | ..  | 31.9              | 31.95             | 32.4              | 36.9              | ...               |
| .22335               | 39.95             | 40.0  | 39.85             | 39.9              | 40.35             | 45.3              | ...               |

A study of the results obtained shows remarkable agreement between potassium permanganate used alone compared with potassium dichromate and potassium permanganate containing 0.2 cc. of diphenylamine indicator. A comparison of C and D shows that an increase in the volume of solution from 120 cc. to 220 cc. makes practically no difference in the titrations. The increase of diphenylamine reagent, however, does make a decided difference, as is shown in F and G. Under Column E the first result was apparently influenced by the increased indicator. In the additional increments of iron the results show titrations of 8.1, 8.0, 8.0, 7.95 cc. per 0.04467 g. of iron. It is evident that 0.2 cc. of the indicator gives

very satisfactory results with volumes up to 250 cc. With more dilute solutions the end-point is a violet in place of a deep blue obtained in a volume of about 150 cc. Dilution of over 300 cc. is not to be recommended. Over 0.4 cc. of indicator should not be used. In using 0.4 cc. of reagent the solution acquires a greenish hue with the addition of permanganate. This is very predominant with larger amounts of indicator and is evidently due to the action of permanganate on the indicator rather than to the iron in the solution. The green produced by adding an excess of diphenylamine to the blue solution of a completed titration bears out this conclusion.

### Summary

Diphenylamine indicator, shown by Knop to be valuable in titration of iron by potassium dichromate, may also be applied in potassium permanganate titrations of iron. The presence of hydrochloric acid, stannic chloride and mercurous chloride do not interfere, thus enabling potassium permanganate titrations to be made where formerly they were not possible.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
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## THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. II

BY EDGAR R. SMITH AND DUNCAN A. MACINNES

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This article describes a test of a simplification of the moving-boundary method for determining transference numbers. The method depends upon measuring, with a silver coulometer, the number of coulombs that pass through the circuit during the time it takes a single-boundary to sweep through a known volume.

The transference number  $T$  obtained by the single-boundary method is given by the equation

$$T = \frac{VF}{\phi Q} \quad (1)$$

in which  $V$  is the volume passed through by the boundary,  $\phi$  is the volume of the solution which contains one equivalent,  $F$  is 96,500 coulombs, and  $Q$  is the number of coulombs passed during the measurement. The derivation of this equation is very simple. If  $F$  coulombs were passed, the single boundary would sweep through a volume of  $T\phi$ , and for a different number of coulombs,  $Q$ , the volume traversed will be  $V = T\phi Q/F$  which is Equation 1.

It has been shown theoretically<sup>1</sup> that if a boundary is to move at its

<sup>1</sup> Kohlrausch, *Ann. Physik*, **62**, 209 (1897). Masson, *Z. physik. Chem.*, **29**, 501 (1899). Denison, *ibid.*, **44**, 581 (1903). Miller, *ibid.*, **69**, 436 (1909).