are in agreement with the results of Harned and Murphy, and Larsson and Adell.

4. The classical dissociation constant of acetic acid is found to increase slightly between 25 and 35°.

PHILADELPHIA, PA. RECEIVED AUGUST 14, 1934

NOTES

A Quantitative Addition Tube

BY JOSEPH GREENSPAN

It is often necessary to add quantitatively a definite weighed amount of solid through a narrow opening, *e. g.*, the neck of a volumetric flask, bottle or separatory funnel in a brief interval of time. We have found the glass tube illustrated in the figure useful for this purpose. The required amount of material is weighed out directly in the tube, and the latter, held by the central rod, is set in position through the opening. Upon depressing the rod, the stopper opens and the major portion of the solid drops into the lower container. Any solid clinging to the walls is then washed down with a solvent, at the same time inclining either addition tube or receiver to prevent splashing or dusting.

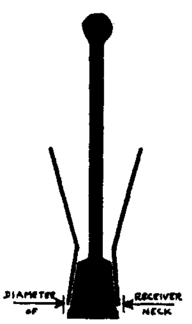

Fig. 1.

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RECEIVED JUNE 19, 1934

The "Dead-Space" Correction in Gas Reaction Rate Measurements

BY AUGUSTINE O. ALLEN

In the course of some kinetic studies on the decomposition of acetaldehyde–azomethane mixtures, a formula was derived for the effect on the measured pressure of the "dead-space," or part of the reaction system external to the high temperature bath which surrounds the main portion of reactant. Later this formula was found not to be needed in this particular research; its applicability, however, is fairly general, so it may be worth separate presentation.

In many gas reactions the pressure increases as the reaction occurs, so that gas will be continually expanding from the hot part of the system into the "dead-space;" an accurate correction must take account of this effect, as well as of the initial distribution of reactant between the two zones. The problem is to determine for any reaction the actual partial pressure of reactant in the reaction as a function of the measured pressure, and also the ratio of the pressure measured at the end of the reaction to the initial pressure. It is assumed that no back-diffusion occurs from the dead space; this must be true as long as the reaction is proceeding at any appreciable rate.

Let N be the total number of moles in the hot part of the system, R of these being moles of reactant. Let the ratio of the number of moles produced by the reaction to the number consumed be q. Now let dx moles react. The total increase in the number of moles is $(q-1)\mathrm{d}x$. This increase distributes itself between the hot and cold parts of the system in accordance with the gas laws; the amount dN remaining in the hot part is obviously

$$(q - 1)\mathrm{d}x \frac{V_h}{V_h + \frac{T_h}{T_c} V_c} = (q - 1)\mathrm{d}x \frac{1}{a}$$

where the subscripts refer to the hot and cold parts of the system, and T and V are, respectively, absolute temperature and volume. We thus have

$$\mathrm{d}x = a\mathrm{d}N/(q - 1) \qquad (1)$$

This expansion of the gas causes a loss of reactant from the hot part, given by $R/N[(q - 1)\mathrm{d}x - \mathrm{d}N]$. Thus the total change in number of moles of reactant in the hot part is

$$\mathrm{d}R = -\mathrm{d}x - \frac{R}{N}[(q - 1)\mathrm{d}x - \mathrm{d}N] \qquad (2)$$

Substituting for dx from (1), we find

$$\frac{\mathrm{d}R}{\mathrm{d}N} + \frac{(a - 1)}{N} R = -\frac{a}{q - 1} \qquad (3)$$

This differential equation is readily solved, the constant of integration being obtained from the condition that at the start of the reaction $N = R = N_0$. We find

$$R = \frac{q}{q - 1} \frac{N_0^a}{N^{a-1}} - \frac{N}{q - 1} \qquad (4)$$

For the ratio between final and initial pressure, we set $R = 0$ in (4) and find

$$N_{\text{final}}/N_0 = q^{1/a} \qquad (5)$$

Neglecting the dead-space effect is equivalent to setting $a = 1$ in the above formulas; this may lead to considerable error if the dead-space is appreciable. For the case where the reaction results in a decrease of pressure, reactant will diffuse in from the dead-space, and the appropriate modifications of the above derivation give

$$R = N(1 + s) - N_0 s \qquad (6)$$

and

$$N_{\text{final}}/N_0 = s/(1 + s) \qquad (7)$$

where

$$s = aq/1 - q$$

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Received July 7, 1934

The Preparation of Perrhenic Acid

By J. T. Dobbins and J. K. Colehour

In connection with an investigation which was being carried out in this Laboratory, it became necessary to prepare some perrhenic acid. The usual method for preparing this acid consists of the decomposition of potassium perrhenate into potassium oxide, rhenium dioxide and rhenium by heating it in an atmosphere of hydrogen. The resulting residue is leached with water to dissolve the potassium oxide. Then the rhenium dioxide and rhenium are heated in an atmosphere of oxygen and are converted into perrhenic anhydride which is volatilized and absorbed in water to form the perrhenic acid.

As the sublimation of the anhydride gave considerable trouble, some modification of the method by which this difficulty might be avoided was sought. The fact that rhenium dioxide is oxidized by hydrogen peroxide suggested the following method. The residue of rhenium dioxide and rhenium, obtained as above, is placed in a combined flask and reflux condenser, a small quantity of water added and treated with 30% hydrogen peroxide. As the reaction is very vigorous at first, the hydrogen peroxide must be added in small portions. After the reaction slows down, the flask is heated gently until the solution becomes colorless and then refluxed vigorously for thirty minutes. Invariably, a small white precipitate appears in the solution, due possibly to occlusion of potassium oxide in the residue.

To prevent the volatilization of perrhenic acid, the solution is concentrated either in the air or over concentrated sulfuric acid. The evaporation is allowed to continue until the solution becomes a pale yellow viscous liquid.

To remove any potassium perrhenate the viscous liquid is taken up in 95% alcohol and filtered. The alcoholic solution is evaporated to remove the alcohol and diluted with water to the desired concentration.

The method is easily carried out and gives a better yield than the one now used.

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Received July 27, 1934

[Contribution from the Department of Chemistry, University of Notre Dame]

Organic Reactions with Boron Fluoride. VII. The Rearrangement of Isopropyl Salicylate and the Condensation of Propylene with Salicylic Acid

By W. J. Croxall, F. J. Sowa and J. A. Nieuwland

The condensation of propylene with phenol in the presence of boron fluoride[1] has been found to yield alkyl substituted phenols and phenyl ethers. The purpose of this work was to investigate the influence of a carboxyl group in a phenolic compound on the course of condensation of propylene in the presence of boron fluoride, and for this purpose salicylic acid was used. The rearrangement of isopropyl salicylate was also investigated to show the course of the condensation of propylene with salicylic acid.

The rearrangement of isopropyl phenyl and cresyl ethers[2,3] and the allyl ethers of salicylic acid[4] have been studied. The use of boron fluoride as a catalyst for the condensation of olefins with fatty acids, aromatic acids, benzene and various substituted benzenes will soon be published.[5]

The action of propylene on salicylic acid in the presence of boron fluoride may be represented as taking place through a series of condensations and subsequent rearrangements. For example, pro-

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(1) Sowa, Hinton and Nieuwland, This Journal, **54**, 3694 (1932).

(2) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933).

(3) Niederl and Natelson, *ibid.*, **53**, 1928 (1931).

(4) Claisen, *Ann.*, **418**, 69–120 (1919).

(5) Sowa and Nieuwland, unpublished work, University of Notre Dame, Notre Dame, Indiana.