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.

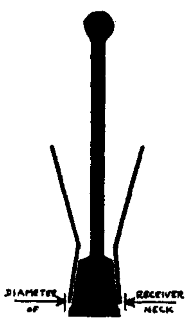

Fig. 1.

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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

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

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