NOTES

A Convenient Form of Gas Combustion Pipet.—The following type of gas combustion pipet has been found convenient and possesses several advantages. There is absolutely no danger of leakage, the time necessary for a combustion is materially shortened, and the pipet is adaptable to various volumes of gas over a wide range. The apparatus is illustrated in the accompanying diagram. The main portion of the pipet consists of a piece of straight tubing of from 1 to 2 cm. diameter, and a length of 50 to 75 cm. A platinum wire having a diameter of about 0.15 mm. is sealed in at each end and runs axially through the tube. As in the ordinary form of pipet, the upper end is connected to a capillary tube and the lower end to a mercury reservoir. To prevent excessive heating due to the narrowness of the tube, the whole length is surrounded by an oil jacket having a diameter about 1 cm. greater than that of the tube.

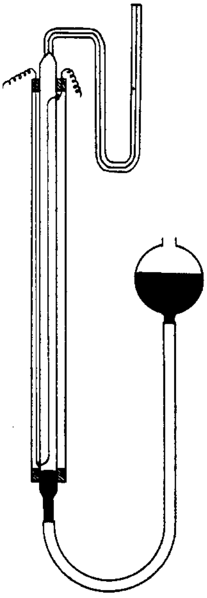

Fig. 1.

The pipet is extremely robust and no possibility of leakage exists. If desired it can also be used as an explosion pipet. On account of the axial situation of the filament the time necessary for a combustion is shortened to about two minutes. One great advantage of this form of pipet is its adaptability to different volumes of gas. For very small samples only a short length of the filament is exposed above the surface of the mercury. If the apparatus is used with 110 volts and an external resistance, the raising or lowering of the mercury level has practically no effect on the temperature of the wire. A similar type of pipet with a total volume of about 6 cc. has been found convenient with a "semi-micro" apparatus of the Ambler[1] type.

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The Temperature Coefficient of the Dielectric Constant of Water.—For the theoretical calculation of activity coefficients of strong electrolytes the dielectric constant of the medium, and not the less certain dD/dT, comes into question. The D of the pure solvent has in general been used, the justification of which is shown by Debye and Pauling.[1] Of

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[1] H. R. Ambler, *Analyst*, **54**, 517 (1929).

[1] Debye and Pauling, This Journal, **47**, 2129 (1925).

much greater importance in the theoretical treatment of integral heats of dilution is an exact knowledge of $\mathrm{d}D/\mathrm{d}T$. The more exact development of the fundamental theory of Debye and Hückel[2] by Gronwall, LaMer and Sandved[3] and the application of their calculations to the theoretical integral heats of dilution by Lange and Meixner[4] give $V_c = -\frac{N}{n}\sum_{j=1}^{s} n_j \frac{z_j\epsilon}{Da_j}\left[\psi_j - \frac{z_j\epsilon}{Da_j}\right]\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right]$ ergs per mole of salt. The integral heat of dilution is equal to the ionic electrical potential energy at the concentration c less that at infinite dilution multiplied by the factor $\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right]$, which is characteristic of the solvent alone. The numerical value of this factor is greatly influenced by small changes in $\mathrm{d}D/\mathrm{d}T$. The previous measurements of D and $\mathrm{d}D/\mathrm{d}T$ by Drude[5] and Kockel[6] show relatively large differences, as a result of which the theoretical V_c values at 25° show an uncertainty of approximately ±35%. Until now the value -0.337 for $\mathrm{d}D/\mathrm{d}T$ at 25° derived from the Drude interpolation formula $D = 88.23 - 0.4044t + 0.00135t^2$ has seemed most probable, as numerous measurements of the heats of dilution of 1–1 type salts in the concentration range $10^{-1} - 10^{-4}$ M made in this Laboratory show, within the limits of the experimental error, a proportionality of V_c with $\sqrt{c}$ below 0.0025 M and permit a rather certain extrapolation to $c = 0$, from which values of the initial slopes (A) are obtained ($V_c = A\sqrt{c}$) ranging from 290 to 430, that is, corresponding to "a" values of 1.25 to 5 Å.

Within the past few months three new series of measurements of D for water have appeared.[7] For comparison of the various measurements, the accompanying table is given, and the various measurements are, for the sake of brevity, denoted by Drude (graphic) I, Drude (interpolated) II, Kockel III, Cuthertson and Maass IV, Drake, Pierce, and Dow V,

		12.5°			25°			40°	
	D	$\frac{\mathrm{d}D}{\mathrm{d}T}$	$1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}$	D	$\frac{\mathrm{d}D}{\mathrm{d}T}$	$1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}$	D	$\frac{\mathrm{d}D}{\mathrm{d}T}$	$1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}$
I	82.77	−0.368	−0.269	78.26	−0.349	−0.329	73.18	−0.330	−0.411
II	83.39	− .371	− .269	78.96	− .337	− .272	74.21	− .296	− .248
III	82.81	− .404	− .393	77.84	− .385	− .474	72.24	− .349	− .512
IV	79.42	− .368	− .323	75.40	− .289	− .142	71.48	− .248	− .086
V	83.29	− .393	− .427	78.57	− .362	− .374	73.41	− .326	− .390
VI	83.16	− .379	− .376	78.54	− .361	− .371	73.28	− .341	− .457

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[2] Debye and Hückel, *Physik. Z.*, **24**, 193 (1923).

[3] Gronwall, LaMer and Sandved, *ibid.*, **29**, 358 (1928).

[4] Lange and Meixner, *ibid.*, **30**, 670 (1929).

[5] Drude, *Wied. Ann.*, **59**, 48 (1896).

[6] Kockel, *Ann. Physik.* **77**, 430 (1925).

[7] Cuthbertson and Maass, THIS JOURNAL, **52**, 483 (1930); Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930); Wyman, *ibid.*, **35**, 623 (1930).

Wyman VI. It is readily seen that the theoretically important factor $\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right]$ is extraordinarily sensitive to small differences in $\mathrm{d}D/\mathrm{d}T$. The good agreement of V and VI at 25° is fortuitous, as is seen from an examination of the various factors at other temperatures. III and IV must be regarded as incorrect not only because of poor agreement with the other measurements but also in view of the improbable value given for $\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right]$, a value not easily reconciled with the experimental measurements of V_c. It would seem that the exact values of $\mathrm{d}D/\mathrm{d}T$ lie between those of measurements I, II and V, VI; at any rate it cannot be said, unfortunately, that we have obtained more probable values of these theoretically important factors in spite of the several comprehensive series of newer measurements. For a comparison of measured and calculated integral heats of dilution it is necessary that $\mathrm{d}D/\mathrm{d}T$ be known with an accuracy of ±0.5%, an accuracy which has probably not yet been reached in these difficult measurements.[8]

CONTRIBUTION FROM THE
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Inorganic Lubricants. II. Phosphoric Acid Mixtures.—The use of moistened phosphorus pentoxide, boiled orthophosphoric acid and similar materials as inorganic lubricants on glass stopcocks and ground connecting tubes has been more or less common practice[1] wherever organic lubricants must be avoided. Such materials, however, have the disadvantage of being markedly hygroscopic in moist air, and eventually become thin, watery and of lower lubricating value.

Stephens' recently described phosphoric acid mixture[2] is a lubricant of superior physical properties, but this product also is freely hygroscopic in air of moderate humidity.

Phosphoric acid mixtures containing chiefly metaphosphoric acid, on the other hand, are not markedly hygroscopic in air of even as high humidity as 80%, except after exposure of weeks or months, and then only slightly. The following procedure yields a satisfactory lubricant of this nature.

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[8] A more detailed discussion of these various series of dielectric constant measurements will be included in a paper to be read at the Heidelberg meeting of the Bunsen Society, May 29–31. The paper will be published in *Z. Elektrochem.*, **36**, (1930).

[1] See, for example, Baxter and Chapin, *Proc. Am. Acad. Arts Sci.*, **46**, 239 (1910); Richards and Krepelka, THIS JOURNAL, **42**, 2226 (1920).

[2] Stephens, *ibid.*, **52**, 635 (1930).