NOTES

A Greaseless Magnetic Valve for High Vacuum Systems

By Don L. Armstrong

Although high vacuum technique has become highly developed in recent years, there is yet need for an easily constructed valve which avoids the presence of any substance other than glass and which may be heated without injury. Several mechanically or magnetically operated valves have been described in the literature,[1-12] but each fails to meet one or more of the above requirements. It is believed that the valve described in Fig. 1 satisfies all of these conditions.

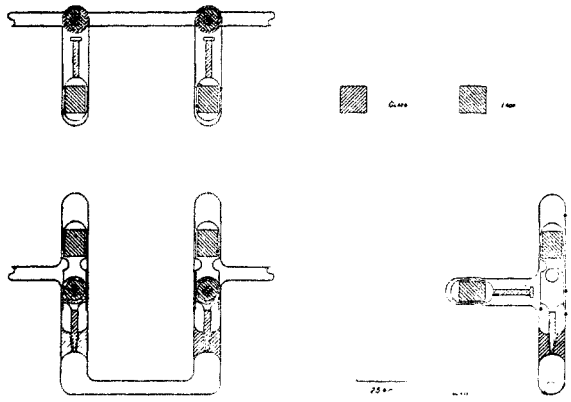

Fig. 1.

The valve is opened by placing a solenoid around one of the vertical tubes containing a valve stem within which is sealed a small piece of iron rod. While the valve stem is thus raised, another solenoid is placed about the corresponding horizontal tube holding the valve support, and the latter is moved toward the stem. The current through both solenoids is now shut off. This allows the valve stem to drop so that the support collar engages the support. This process is repeated with the other half of the valve. While the valve is open, it may be heated by a flame to assist the passage of difficultly volatile materials.

The valve seats are formed with the aid of a carbon rod, accurately tapered at an angle of 7° to the axis of the rod. The valve-plugs are made by drawing out the ends of solid rods to nearly the same taper, and grinding them into the seats to produce a high polish. The grinding is done before the excess length of rod is cut off.

The valve described here was able to maintain a pressure of 900 mm. on one side and a vacuum on the other with less than 0.05 cc. (gas at S.C.) leakage in ten minutes. Such performance could be obtained only when the valve seat and valve-plug were perfectly clean. Sutton and Mayer[11] made a much more modest claim for a one-way valve of related design. The difference is probably due to the double-plug arrangement of the two-way valve here described.

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The Synthesis of 6-Diethylamino-1-aminohexane[1]

By David S. Breslow and Charles R. Hauser

In connection with another problem a relatively large amount of 6-diethylamino-1-aminohexane was needed. This diamine has previously been synthesized apparently only from ϵ-benzoylaminoamyl chloride, which itself is rather difficult to prepare, in a yield of only 9%.[2] We have prepared the diamine from hexamethylene bromide and diethylamine using the Gabriel synthesis and from ϵ-bromocaproic acid by the following series of reactions.

$$\mathrm{Br(CH_2)_5COOH} \xrightarrow[NH_3]{SOCl_2} \underset{(64\%)}{\mathrm{Br(CH_2)_5CONH_2}} \xrightarrow{SOCl_2}$$

$$\underset{(76\%)}{\mathrm{Br(CH_2)_5CN}} \xrightarrow{(C_2H_5)_2NH} \underset{(90\%)}{(C_2H_5)_2N(CH_2)_5CN} \xrightarrow{[H]} \underset{(70\%)}{(C_2H_5)_2N(CH_2)_6NH_2}$$

The yield (45%) by the Gabriel method is satisfactory but we prefer the latter method, since the reactions are readily carried out and the yields (given in parentheses) are satisfactory. We have made no attempt to obtain optimum yields. The ϵ-bromocaproic acid is readily prepared from cyclohexanone by oxidation with potassium persulfate followed by hydrolysis of the resulting lactone with hydrogen bromide.[3]

(1) The work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Duke University.
(2) Magidson and Grigorowsky, *Ber.*, **69B**, 402 (1936).
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The method should be applicable to the preparation of other 6-dialkylamino-1-aminohexanes.

Procedure.—Crude ϵ-bromocaproic acid[3] (165 g., 0.85 mole) was heated on a steam-bath for one hour with 100 ml. of thionyl chloride. The excess thionyl chloride was removed under reduced pressure and the residue was added drop by drop to 1 liter of concentrated ammonium hydroxide with vigorous stirring, keeping the temperature below 10°. The solid amide was filtered, washed with ice-water and air dried; yield, 104 g. (64%).

The crude amide was heated on a steam-bath for two hours with 100 ml. of thionyl chloride, a vigorous reaction ensuing. The excess thionyl chloride was removed under reduced pressure and the residue distilled through a 15-cm. Vigreux column. ϵ-Bromocapronitrile was obtained as a pale yellow liquid, b. p. 115–117° at 6 mm., yield, 72.5 g. (76%).

The ϵ-bromocapronitrile (0.41 mole) was stirred and heated under reflux for eighteen hours with 87.5 g. (1.2 moles) of diethylamine. The reaction mixture was cooled, 100 ml. of ether was added and the diethylamine hydrobromide filtered off. The precipitate was washed thoroughly with ether, the combined ether solutions distilled and the residue distilled through a 15-cm. Vigreux column. The ϵ-diethylaminocapronitrile was obtained as a colorless liquid, b. p. 102–102.5° at 4 mm.; yield, 62 g. (90%). The picrate melted at 62–62.5°; a mixed melting point with the picrate of the aminonitrile prepared by another method[2] was the same.

ϵ-Diethylaminocapronitrile was reduced with Raney nickel in the usual manner in 70% yield. The 6-diethylamino-1-aminohexane boiled at 103–105° at 10 mm. and formed a chloraurate salt melting at 118–120° (reported,[2] 120–122°).

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The Partial Specific Volumes of Zein and Gliadin

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In order to evaluate molecular weight and shape from sedimentation and diffusion data it is necessary to know rather accurately the partial specific volume of the solute in the solvent used. In the case of the prolamines the usual solvent is aqueous alcohol, the optimum concentration being about 70% alcohol in the case of zein and somewhat lower in the case of gliadin. To the authors' knowledge no experimental values of the partial specific volumes of any of the prolamines in aqueous alcohol have been reported. This is largely due to the difficulty in making sufficiently accurate measurements of partial specific volumes in mixed volatile solvents. For example, an error of only 0.03% in solvent composition in the case of a measurement on a 1% protein solution in 70% alcohol will cause an error of 1% in the measured partial specific volume. It is very difficult if not impossible to control the alcohol composition to the necessary accuracy in the usual pycnometric method.

Krejci and Svedberg[1] have reported a partial specific volume for gliadin in dilute hydrochloric acid of about 0.72, the value varying somewhat with concentration. In the absence of any experimental value for zein, values anywhere from 0.71 to 0.75 have been assumed by various investigators.

To eliminate these uncertainties the authors have evolved a dilatometric technique which is especially applicable to the prolamines. This technique reduces evaporation errors to a minimum and appears capable of a high degree of reproducibility. The results show that the partial specific volumes of zein and gliadin are far from being the same, as sometimes assumed.

Experimental

Apparatus.—A Pyrex dilatometer was constructed from a bulb of approximately 100 ml. capacity and a capillary of 1 ml. capacity with 0.01-ml. graduations. The top of the capillary was enlarged and fitted with a glass stopper to minimize solvent evaporation. For equilibration the bulb and stem of the dilatometer were immersed in a water-bath at 25.00 ± 0.01°. The capillary stem was calibrated by filling the dilatometer to the lowest mark on the stem, equilibrating at 25° and noting the increase in volume on the addition of weighed amounts of mercury or lead shot.

Materials Examined.—"Standard Zein" is a commercial product[2] containing about 0.4% ash and a small amount of insoluble organic matter. "Washed Zein" is commercial zein which has been washed exhaustively with water at 0°. "Fractionated Zein" is commercial zein from which the most and least soluble components have been removed by alcohol–water fractionation. "Laboratory Zein"[3] was prepared in this Laboratory from white corn at 0°. The gliadin sample had been dialyzed against 70% alcohol and precipitated in acetone, and contained only about 0.2% ash.[4]

Method.—The powdered sample (of known moisture content) is compressed into small rod-shaped pellets which will readily slide down the dilatometer capillary. The dilatometer bulb and lower part of the stem are filled with solvent, equilibrated at 25°, and the meniscus estimated to 0.001 ml. The dilatometer bulb is then cooled[5] to −5°, and a weighed portion of the pellets added. The dilatometer is twirled to facilitate solution of the pellets, allowed to stand with occasional shaking until the pellets are completely dissolved (usually twelve to twenty-four hours), and the solution thoroughly mixed and re-equilibrated at 25°. The increase in volume is read and the volume increment per gram of (anhydrous) protein ($\Delta V/\Delta g$) is calculated as follows:

$$\frac{\Delta V}{\Delta g} = \frac{\Delta v - (\bar{V}_w)(\alpha)(W)}{W(1 - \alpha)}$$

where Δv is the observed increase in volume, $\bar{V}_w$ is the partial specific volume of H_2O in the solvent, W is the weight and α the moisture content of the sample. In general the pellets were added in increments of about 0.7 to 1.0 g. The dependence of the volume increment on the protein concentration was investigated by starting with a protein solution of given concentration rather than the pure solvent. No hysteresis effects after cooling the dilatometer to −5° and warming to 25° have been noted.

Discussion

The experimental results are presented in the table. The increment quotient ($\Delta V/\Delta g$) actually

(1) L. Krejci and T. Svedberg, THIS JOURNAL, 57, 946 (1935).

(2) Supplied by the Corn Products Refining Company, Argo, Illinois.

(3) This preparation was made by C. C. Jensen and C. R. Harmison.

(4) The authors are indebted to Dr. H. B. Vickery of the Connecticut Agricultural Experiment Station for this gliadin sample.

(5) This step serves the double purpose of emptying the capillary by contraction of the solvent and of minimizing evaporation during the addition of the sample.