in this paper, but the complicated and laborious study of the medium effect of glycine has just been begun experimentally.

2. It has been demonstrated that the use of silver–silver chloride electrodes or amalgam electrodes leads to identical results in the measurements with alkaline glycine solutions.

3. In the absence of any information concerning the medium effect of glycine, we have drawn, by analogy, upon our study of this subject with acetic and formic acids, and have calculated the activity coefficients of the 0.1 molal amphanion and amphcation in sodium chloride solutions. The logarithms of the activity coefficients are linear functions of the ionic strength, which is in accord with theory.

4. By an exact thermodynamic method which eliminates the use of liquid junctions and which takes into account certain medium effects heretofore neglected, we have shown that the acid and base constants of an ampholyte may be evaluated. Further, in the case of glycine, the first steps toward an experimental solution have been made, and preliminary values of the important constants determined.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A MANOMETER FOR THE MEASUREMENT OF SMALL PRESSURE DIFFERENTIALS AT HIGH PRESSURES[1]

BY JAMES H. BOYD, JR.[2]

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Introduction

In an investigation of the viscosity of compressed gases by the author a new instrument was developed[3] for the measurement of the small pressure differentials which existed between the two ends of a capillary tube through which flowed compressed gas. It relies on electrical means for determining the pressure differential but requires no calibration and does not demand the use of clean mercury to gain accurate results. This manometer is primarily a laboratory precision instrument though by suitable calibration it may be used as a high pressure flowmeter.

The only other instrument for this use at high pressures described in the literature and known to the author is that used by Wildhagen.[4] It

[1] This article is based on a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Science from the Massachusetts Institute of Technology.

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[3] J. H. Boyd, Jr., *Phys. Rev.*, **35**, 1284 (1930).

[4] Wildhagen, *Z. angew. Math. Mech.*, **3**, 181 (1923).

consisted in principle of a mercury-filled differential steel manometer in one arm of which was a fine platinum resistance wire coaxial with the tube. On applying a pressure differential to the manometer the mercury rose in the arm containing the wire and decreased the electrical resistance of a circuit of which the previously calibrated platinum wire formed the major resistance. In such an instrument errors due to the contamination of the mercury might well prove serious and such fouling is difficult to avoid in practice. Were the mercury contaminated it would adhere to the wire on receding after making an observation and subsequent lesser differential readings would be in error owing to the change in the apparent resistance of the exposed wire.

The New Manometer.—The new differential manometer does not require any calibration and the use of clean mercury is not imperative though ordinary precautions taken to avoid undue contamination are desirable. Essentially, the instrument consists of a mercury reservoir of relatively large diameter (8.9 cm.) beneath whose mercury surface projects the lower end of a riser well of relatively small bore (8 mm.) in which runs a movable screw rod enabling the completion of an electrical circuit through the mercury. The whole is suitably enclosed to permit the use of high pressures. The level of the mercury in the riser well is determined by trial by moving the contact or screw rod so as to make and then break the circuit as indicated by a galvanometer. When this has been done the relative position of the screw rod is determined by measuring the distance to the top of the rod from a fixed reference plane by means of a micrometer depth gage. The difference of such readings when the upstream and downstream pressures are equal and when they are unequal, as is the case for gas flow, is the observed pressure differential. The true differential is obtained on correcting for the drop in level in the reservoir corresponding to the elevation in the riser well, for the buoyant effect of the displaced gas and for the temperature variation of the mercury density. If desired further corrections for the capillarity and compressibility of the mercury may be applied. Calculation showed that pressures up to 3000 lbs. per sq. in. and fluctuations in the room temperature did not affect appreciably the instrument readings.

The construction of the manometer is shown diagrammatically in Fig. 1, which is approximately to scale. A set screw in one of the guide blocks and a stop pin not shown in the drawing allow locking the depth gage in a fixed position. The instrument was designed to give a factor of safety of five based on the ultimate tensile strength of the steel for a working pressure of 5000 lb. per sq. in. at room temperature. The maximum pressure actually used was 3000 lb. per sq. in.

Four auxiliary valves are necessary in the operation of the instrument. Two valves, one in each connection line, permit isolation of the manom-

eter from the rest of the system. A third valve in a by-pass line allows equalization of pressures in the instrument, while the fourth serves as a pressure relief for the mercury reservoir. In addition a mercury trap in the downstream connecting line between the valve and the manometer is desirable to prevent accidental flooding of the rest of the apparatus with mercury.

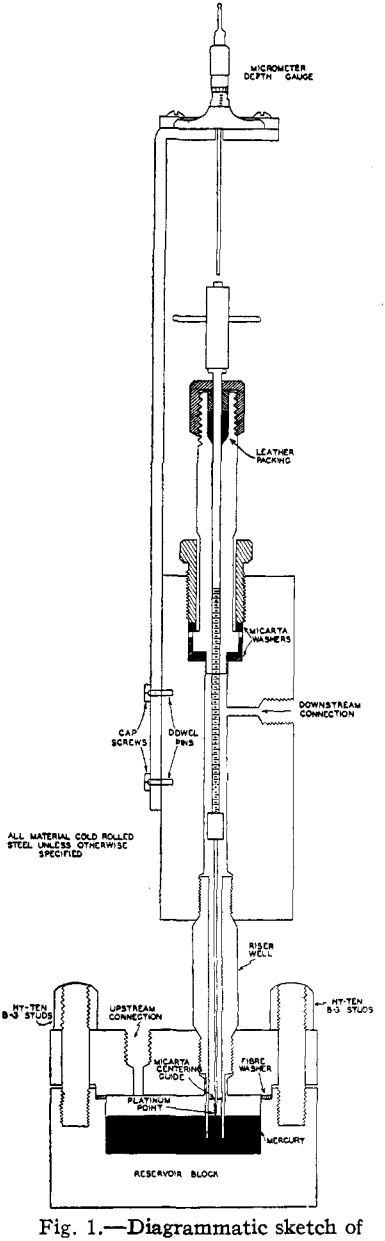

Fig. 1.—Diagrammatic sketch of high pressure manometer.

Operation of the Manometer.—The operation of the instrument is quite simple. It is brought under pressure with only the downstream valve open to allow gas to flow down the riser well and under the mercury seal, thus substantially equalizing the pressure in the system. Complete equalization of pressure results on opening the by-pass valve. The zero reading is now made by running the screw rod down until electrical contact with the mercury is made, as shown by the deflection of the galvanometer needle, and then slowly screwing the rod upward until the circuit is just broken. The relative position of the top of the rod on breaking the circuit is determined by measurement with the depth gage from the reference plane. The micrometer gage reads directly to 0.025 mm. (0.001 in.) but the graduations on the barrel permit estimation to 0.0025 mm. (0.0001 in.). The mean of several such readings agreeing within 0.025 mm. (0.001 in.) is taken as the zero reading. This procedure gives very reproducible results. The source of e. m. f. for the circuit is a copper–constantan thermocouple immersed in ice water. The couple is very satisfactory for this purpose as the feeble current so produced minimizes arcing at the mercury surface. After making the zero readings the rod is run up to a greater height than the mercury level anticipated in the ensuing experiment, the by-pass valve is closed

and the upstream valve opened. The mercury now rises to its equilibrium position and the observations are again made. In each case the mercury approaches its equilibrium level from below, which tends to introduce a compensation of errors on taking the difference of the two average readings to obtain the apparent pressure differential. The true differential is obtained on applying the corrections previously mentioned. At the conclusion of a series of experiments the pressure in the flowmeter is relieved in order to avoid forcing mercury over into the trap should a leak develop at the rod packing.

Results

The absolute accuracy of the measurement of the pressure differential is not known but in view of the compensation remarked above the error should never exceed the average deviation observed in making a series of zero readings. In Table I a series of consecutive, average zero readings is given which was made over an eight-day period at gage pressures ranging from zero to 3000 lb. per sq. in.

TABLE I

CONSECUTIVE MEAN ZERO DETERMINATIONS, IN INCHES

2.4249	2.4247	2.4265	2.4247
39	56	71	45
82	62	76	57
74	60	73	67
26	73	45	43
57	59	45	44
43	61	51	43

Grand average	2.4256
Maximum deviation	0.0030
Average deviation	.0011

The tabulated results show the zero reading to be reproducible and indicate that the error in the measurement of a pressure differential does not exceed 0.025 mm. (0.001 in.). Such accuracy is sufficient for most purposes.

Conclusion

While the instrument described above was satisfactory, certain changes are recommended for future work. The use of a larger riser well will eliminate capillarity effects and also allow the use of a larger screw rod whose greater rigidity will make the micarta centering disk unnecessary. In addition the screw rod assembly should be made in two pieces, the lower or contact rod being threaded into the screw rod proper and secured in place by lock nuts. This would necessitate a larger screw rod, which would facilitate packing the rod. Moreover, the bushing through which the rod handle ran and the pin driven into the bushing might well be eliminated.

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Summary

A manometer has been developed which is capable of measuring by electrical means pressure differentials of an inch of mercury with an accuracy of one part in 1000 at a pressure of 3000 lb. per sq. in. The instrument is direct reading and requires neither calibration nor the use of very clean mercury.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE THERMAL HYDROGEN–OXYGEN COMBINATION. FORMATION OF HYDROGEN PEROXIDE, AND THE INFLUENCE OF SURFACE NATURE[1]

BY ROBERT N. PEASE[2]

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Hydrogen peroxide has not before been reported as a product of the slow reaction between hydrogen and oxygen which takes place in the neighborhood of 550° and 1 atm. Indeed Rowe[3] states that none could be detected by the sensitive titanium sulfate test. This paper reports the results of some flow experiments in which easily detectable quantities were obtained. In addition there are reported some data on the effect of the nature of the reaction tube surface on the hydrogen–oxygen reaction.

The experiments were of the flow type. Compressed hydrogen and oxygen were passed through flowmeters and a drying system to a cylindrical reaction tube of pyrex glass to the ends of which were sealed 2-mm. capillaries. The off-gas passed through a weighing tube cooled to −79°. The reaction tube was contained in an electrically heated furnace the temperature of which was automatically controlled to about ±2°. Hydrogen peroxide was determined by washing out the weighing tube and titrating the product with 0.02 normal potassium permanganate in sulfuric acid solution.

[1] This paper contains results obtained in an investigation entitled "Catalytic Methods Applied to Petroleum Hydrocarbons" listed as Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor, of Princeton University, is Director of Project No. 7.

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[3] Rowe, *Z. physik. Chem.*, **59**, 41 (1907).