Employing arbitrary values of k_1, b, and S_∞ it has been found possible to approximately fit the data of Soller, Goldwasser and Beebe[12] on the adsorption time relation of hydrogen and deuterium on copper at 0°. This agreement is sufficiently close to indicate that the kinetics might be applicable; however, the agreement might well be fortuitous because of flexibility introduced by the adjustable constants. Therefore it does not seem possible to decide whether the kinetics are applicable for the calculation of adsorption rates on the basis of available data. Similar data at other pressures and temperatures would permit a decision. Dr. Beebe informs me that such work is in progress in his laboratory.

Application of Kinetics to Other Systems

It has been found that equation (2) may be applied successfully to the adsorption isotherms of hydrogen or iron at 300 and at 400° by Morosov.[15] These isotherms do not include a secondary slow sorption, which was excluded by the method of Ward.[7] The ratio of the value of b at 300° to that at 400° is 1.2. From equations (6) and (7) this corresponds to $E_1 - E_2 = +3.4$ kcal. or $q =$ 4.6 kcal.

The adsorption isotherm of oxygen on silver[16] is compatible with equation (3) but affords no adequate test of its validity, as most of the measurements are in the range approaching saturation. The same authors also give data on the rates of desorption, which could perhaps be treated by equation (1) except for the irreproducible nature of the surface.

The kinetics of the catalysis of water formation from hydrogen and oxygen by silver[17] suggest that the adsorbed oxygen is atomic.

Equation (3) is not applicable to the data of Emmett and Brunauer[18] on the sorption of nitrogen on a promoted iron catalyst. In view of the heterogeneous nature of the catalyst and the probability that some of the adsorbed hydrogen is in the interior, this disagreement is not surprising. No other applications have been attempted.

I wish to express my thanks to Dr. H. H. Storch, under whose direction this work has been done, for his helpful suggestions and to Prof. R. A. Beebe, of Amherst College, who has been kind enough to discuss with me freely some of the experimental aspects of hydrogen adsorption on copper.

Summary

It has been shown that the assumptions of dissociative adsorption on a uniform surface lead to kinetics which account for the observed equilibria in the primary activated adsorption of hydrogen on copper. The possibility of extension of these kinetics to rates and to other systems is discussed.

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(15) Morosov, *Trans. Faraday Soc.*, **31**, 659 (1935).

(16) Benton and Drake, THIS JOURNAL, **56**, 255 (1934).

(17) Benton and Elgin, *ibid.*, **51**, 7 (1929); **48**, 3027 (1926).

(18) Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

PHYSICAL CHEMISTRY SECTION
PITTSBURGH, PENNA. RECEIVED MAY 17, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Gas Density Balance for Determination of the Absolute Density of Protium–Deuterium Mixtures and Other Gases

By Nelson R. Trenner[1]

Small abnormalities in the results of an investigation of the velocity of sound in the best deuterium gas[2] and in an investigation of the photochemical reaction between bromine and deuterium[3] prompted the necessity of examining the absolute density of our best deuterium gas. This was undertaken by use of the suspended gas density balance, similar in principle to those designed by Whytlaw-Gray,[4] Aston[5] and T. S. Taylor,[6] but modified so as to permit reasonable ease of construction, adjustment and operation. Such a balance is described below together with some of the results obtained with it. It has proved of especial value as a primary concentration standard in our work with the hydrogen isotopes.

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(1) National Research Fellow in Chemistry, 1933–1935.

(2) W. T. Richards, *J. Chem. Phys.*, **4**, 563 (1936).

(3) N. R. Trenner, *ibid.*, forthcoming publication.

(4) Whytlaw-Gray, Patterson and Cawood, *Proc. Roy. Soc.* (London), **134A**, 10 (1931).

(5) F. W. Aston, *ibid.*, **89A**, 439 (1914).

(6) T. S. Taylor, *Phys. Rev.*, **10**, 653 (1917).

The Balance.—The movement of the balance consisted of two thin-walled Pyrex bulbs A and B (see Fig. 1) fused to the ends of a small Pyrex rod (about 1 mm. in diameter and 8 cm. long) the bulb A being of about 17 cc. volume and sealed off, while bulb B was punctured with several 1-mm. holes and so designed that its total area both internal and external approximately equaled the external area of bulb A. Thus B served both as a counterpoise for A and at the same time nullified any adsorption effects of the gases upon A. For determination of the angular rotation of the balance beam a small mirror, such as is used in high sensitivity galvanometers, was waxed onto the cross bar C. This cross bar C was of Pyrex glass at the ends of which were fused tiny Pyrex to quartz graded seals so that quartz fibers could be drawn from its ends. Quartz fibers were found necessary inasmuch as Pyrex fibers lacked the necessary mechanical strength as well as possessed the bad property of marked creeping under torsional stresses. The suspension was formed by drawing fine quartz fibers E from the ends of the cross bar C using a tiny oxyhydrogen flame. The drawing technique and necessary fineness for these fibers is a matter of experience and trial, and so cannot well be described. The whole movement and suspension of the balance was of less than 2.2 g. weight and could be adequately supported by fibers of the order of $\sim 10^{-2}$ mm. diameter.

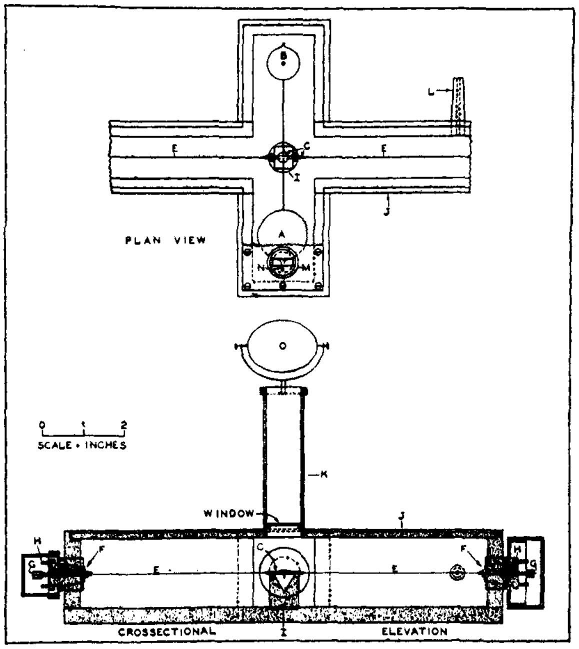

Fig. 1.

The end supports F for the fibers consisted of a cone and screw device which served the dual purpose of adjusting the tension on the fibers as well as changing the zero point of the movement. Thus, by holding the screw G and rotating the cone H, the fibers could be tightened without twisting, while by rotating the screws and the cone simultaneously through the same angle the zero point could be changed without changing the tension. This device proved a great aid in rapidly making final adjustments on the balance. The fibers were fastened to the screws G by threading them through small holes drilled co-axially through the screws and then waxing the loose fibers in with hard de Khotinsky cement while the movement rests upon the beam rest I provided for it in the bottom of the balance housing. This method of attachment proved entirely satisfactory over long periods. Following the waxing operation the movement may be raised from the rest by rotation of the cone and screw device as already described. The balance house J consisted of a rolled[7] brass cross as illustrated. The entire inside, including the under surface of the cover plate, was carefully tinned to fill cracks and flaws in the metal to prevent marked absorption of the gases used. The cover plate was milled and recessed into the main housing and bolted into place. In addition it contained at its center a tube K, which projected up over the thermostat fluid, and at its base a small, waxed in, circular Pyrex window which served to permit the indicator light beam to fall on the mirror of the movement. On top of this tube was mounted a plane mirror, of the type used on microscope substages, which served to deflect the horizontal light beam down into the balance housing. The recess above the cover plate was filled with Apiezon sealing compound "Q." This made the balance quite gas tight, but inasmuch as this material is penetrated readily by liquid water it was necessary to coat it in turn with vaseline, care being taken not to trap air bubbles in the latter. This layer was now unaffected by water and proved very satisfactory as a seal. The caps on the cone and screw devices were sealed similarly. The gases entered through the capillary tube L, which was sealed to the balance housing through a ground joint—glass to brass—by means of a thin film of de Khotinsky cement. The whole balance was mounted on a heavy brass plate equipped with leveling screws. This base plate was in turn set inside the thermostat tank on heavy rubber stoppers to take up vibration. The gas lead-in tube to the balance had a flexible glass spiral inserted in it to take up vibration and allow for movement of the balance during occasional releveling. The aperture M on the cover plate over the small glass hook N on the buoyancy bulb A, and its ground-in plug, was provided to allow for rapid adjustment of the balance when gases of widely different density ranges were to be studied. This was effected by means of small quartz riders which are put on the hook through M. Thus gases in any density range could be measured on the same manometer without loss of accuracy.

The light beam used to indicate the rotation of the balance beam originated from an illuminated ground glass scale located about 1.5 meters from the balance mirror O and was observed through a telescope with internal cross hair. The illuminated scale and telescope were mounted vertically over each other as is usual in suspended galvanometers, but with the scale divisions running vertically.

The pressure in the balance house was measured on an ordinary U type mercury manometer constructed of tubes of 15-mm. internal diameter thus making capillary depression negligible. One arm of this manometer was pumped out continually by the mercury vapor pump. The entire manometer was thermostated by cir-

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(7) An attempt to use a cast brass housing proved a failure due to the presence of numerous leaks in the walls and to marked gassing of the walls even when the leaks were sealed.

culating the thermostat water around it by means of a mechanical circulating pump. This was found to give good temperature control ±0.01°. The thermostat and its regulator were of the usual type. The control was obtained through a vacuum tube relay and mercury switch and heating was obtained by means of a 60-watt electric light bulb. Efficient stirring of the thermostat liquid was effected by means of a motor-driven propeller, the whole being so mounted as to have *no mechanical* connection to the table on which the density balance and thermostat were mounted, thus eliminating vibration due to this source. The whole thermostat tank was mounted on heavy rubber blocks and stood on a rigid table. Pressure readings from the manometer were taken with a heavy one-meter cathetometer.[8] Both cathetometer and manometer were leveled accurately. Finally all connections between the balance and manometer were made of 2-mm. capillary tubing so as to reduce variations during measurements, due to external temperature fluctuations, as much as possible.

The Gas and Pumping Systems.—As a source of pure light hydrogen an all glass electrolytic apparatus, fitted with platinum electrodes was used. The electrolyte was a 15% solution of C. P. sodium hydroxide in distilled water. The hydrogen evolved was passed through a spray trap and cooler (to remove most of the water) packed with glass wool, two hot platinum spirals, a tube packed with soda lime granules to remove possible traces of carbon dioxide, and finally into a 1-liter bulb for storage until use. When used, all the gases were withdrawn from the storage bulbs through a liquid air trap, packed with copper wool, to remove all moisture. The entire purification train was pumped out vigorously before filling.

Pure helium was made from crude tank helium in the following way: 600 mm. of the tank gas was put into an evacuated arcing chamber—which consisted of two platinum tipped electrodes sealed through the opposite sides of a 1-liter round flask with a 1-cm. gap between the ends—and the arc struck. The power to feed this arc was obtained from a 6000 volt 1 Kva. transformer with suitable resistances in the primary to control the current. Following this 100 mm. of pure tank oxygen was added slowly with simultaneous increase of the arc current. Arcing was continued for eight to twelve hours. This treatment served to oxidize all difficultly oxidizable impurities including nitrogen. The products of this combustion, carbon dioxide, water, nitrogen dioxide, etc., are removed continuously by solid soda lime, a layer of which was put into the bottom of the arc chamber. To remove excess oxygen as well as traces of water and carbon dioxide, the gases were circulated for several hours, by means of a Sprengel pump, through a purification train containing hot activated copper (400°), solid sodium hydroxide, a liquid air trap and finally hot metallic calcium turnings (400°). This treatment gave a product containing only possible traces of the other rare gases. These were removed by the fractional desorption technique from chabazite used by Baxter and Starkweather[9] and by Seeliger.[10] The methods of Baxter and Starkweather were followed closely.[11] The helium so produced was found to give excellent agreement with the expected density relative to hydrogen.

The deuterium samples were obtained in a manner very similar to that used for the light hydrogen except that, for special reasons to be presented in another place, the D_2 and O_2 were generated in a single compartment and, consequently, the O_2 had to be removed by freezing out. The low temperature trap used for this process is described in another place.[12] In brief, by pumping off liquid air in this special trap, a temperature of about −232° was attained which served to remove the oxygen very efficiently. Residual traces were removed on a glowing platinum wire and any water formed removed in a liquid air trap packed with glass wool. Starting with about 17 cc. of a 2% sodium hydroxide solution in 50% D_2O and electrolyzing on platinum electrodes gave deuterium gas of about 10–15% D initial concentration. With continued electrolysis the D content of the gas steadily rose until the final concentration was about 95%. Thus, a continuous range of deuterium gas samples could be obtained varying between 15 and 95% D, and their D content analyzed on the gas balance. Separation factor studies of the hydrogen isotopes were made using this method and an account of the results of those studies will be published shortly. The pumping system consisted of the usual two-stage mercury vapor pump backed by a Hyvac pump.

Adjustment and Characteristics of the Balance for Hydrogen.—To adjust the balance for use with the hydrogen isotopes and helium the balance house was first evacuated thoroughly for a time and then filled with hydrogen to about 600-mm. pressure. If the balance failed to move to the proper position the quartz rider was made heavier or lighter according to the indication of the previous test. The evacuation and filling was then repeated and the rider further corrected until an approximate balance was attained. The final adjustment was then made with the cone and screw device as previously indicated. This is a somewhat tedious procedure at first but when once a set of suitable riders is made, one for each pair of gases to be investigated, the range is changed quickly at will. The tension on the fibers was also changed until the most sensitive adjustment was found.

In filling the gases into the balance they were allowed to flow into the thoroughly outgassed housing through an all-glass leak from the purification train at atmospheric pressure, or pumped in slowly with a Toepler pump when individual samples were being investigated. This always took place through a glass wool packed liquid-air trap. When sufficient gas pressure had built up in the balance to give almost the desired balance point the gas flow was stopped. Final adjustment of the pressure was then attained by electrically warming the platinum filament in a small bulb connected to the balance-manometer tube through a stopcock. This heating served to increase the pressure in the system slowly and by observing through the telescope while adjusting the heating current, a precise balance was obtained easily. This accomplished, the

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(8) The author is much indebted to the Palmer Physical Laboratory for the loan of this instrument.

(9) Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **11**, 231 (1925); Baxter and Starkweather, *ibid.*, **12**, 20 (1925).

(10) Seeliger, *Physik. Z.*, **22**, 563 (1921).

(11) The excellent sample of purified chabazite used in this work was given the author through the kindness of Dr. A. Tiselius for which he wishes to express his thanks.

(12) Trenner, Morikawa and Taylor, *J. Chem. Phys.*, **5**, 203 (1937).

stopcock between heater and balance was closed and the pressure read on the manometer with the cathetometer. The gas balance so set up and adjusted was found to be free of vibration, to undergo no annoying drifts even over long periods of time (eight hours) and, for a given zero point setting, gave reproducible pressures in successive runs made over periods of an eight-hour day. The gas balance was always stored—at balance—in a hydrogen atmosphere when not in use so as to avoid distortional strains causing the fibers to creep unduly. Evacuations of an hour were always employed before introducing the next gas since pumping through the capillary tubing and spiral proved a long slow process even with hydrogen. The sensitivity of the balance when filled with light hydrogen was found to be 2 mm. of pressure change per scale division. Since the balance could be set to within ±0.1 scale division the pressure adjustment is accurate to ±0.2 mm. The precision of reading with the cathetometer was 0.1 mm. on each arm or a total of 0.2 mm. Thus the maximum error in setting and reading the pressure was about 0.5 mm. These characteristics are illustrated by the data in Table I. The deuterium used in these experiments was the ***best electrolytic*** gas obtainable with the generator system used and was obtained from deuterium oxide previously subjected to prolonged electrolysis before use. The percentages given in column 4 of the table are expressed as atom per cent. of deuterium (D) in the gas.

TABLE I

Gas	Temp., °C.	Pressure	Remarks	Date
H_2	25.00	691.6	Measurements taken over six hours	1/16/35
H_2	25.00	691.2		
H_2	25.00	691.7		
H_2	25.00	691.5		
H_2	25.00	635.3	Balance readjusted	
H_2	25.00	635.8	β_D	
H_2	25.00	635.9		3/23/35
D_2	25.00	320.4	98.56 At. % D	
H_2	25.00	636.8		
D_2	25.00	321.4	98.25	
H_2	25.00	636.0		3/28/35
D_2	25.00	320.5	98.56	
D_2	25.00	318.9	98.46	
H_2	25.00	632.5		
H_2	25.00	633.6		4/18/35
D_2	25.00	319.2	98.61	
		Mean	98.52	

Methods of Calculation of Results.—In the derivation of the equations which were found useful in converting the results obtained from the gas density balance to analytical quantities such as atom or weight percentages or apparent molecular weights it was assumed—in the cases of the hydrogen isotopes and helium—that the perfect gas laws applied. This assumption is justified adequately by existing data on the pressure coefficients of hydrogen and helium and also for deuterium.[6,9,13] Now since the gas balance was used as a constant density, constant volume and constant temperature device, it follows that $P_{H_2}M_{H_2} = P_xM_x = \textit{constant}$, where P_x is the pressure at which the gas x has the same density as that of hydrogen at the pressure P_{H_2} and M_x is the apparent molecular weight of x gas if that of hydrogen be M_{H_2}. The results given in Table II were calculated using the above equation.

TABLE II

Gas	Temp., °C.	Pressure	Apparent mol. wt.	Date
He (tank)	25.00	259.9	4.915	
H_2	25.00	633.8	(2.0156 used in calcns.)	
He (pure)	25.00	319.4	3.998	
H_2	25.00	633.2	...	3/19/35
He (pure)	25.00	318.8	4.004	
H_2	25.00	633.5	...	
He (pure)	25.00	318.8	4.005	
H_2 (tank)	25.00	572.6	2.230	
D_2	25.00	319.2	4.000	98.58 At. % D

In all calculations the following accepted values of atomic weights were used: H = 1.0078, He = 4.002, and the best mean value for D = 2.0144 obtained from recent determinations of Livingston, Bethe, Oliphant and Aston.

It is shown easily that the relationship between the *atom* per cent. of D = β_D in an *equilibrated* mixture of the hydrogen isotopes, and P_x is given by

$$\beta_D = \frac{[(P_{H_2}/P_x) - 1]\,M_{H_2}}{2\,(M_{HD} - M_{H_2})} = 1.00119\left[\frac{P_{H_2}}{P_x} - 1\right] \qquad (1)$$

and that for weight per cent. of D = γ_D is given by

$$\gamma_D = 2.00119\left[1 - \frac{P_x}{P_{H_2}}\right] \qquad (2)$$

If equilibrium was established at temperatures sufficiently high that

$$K = \frac{[HD]^2}{[H_2] \times [D_2]} = 4$$

then the mole per cent. = α of each of the molecular species is given by

$$\alpha_{D_2} = (\beta_D)^2;\ \alpha_{HD} = (2\beta_D - 2\beta_D^2);\ \alpha_{H_2} = (1 - \beta_D)^2 \qquad (3)$$

The results presented in Tables I and II were calculated using equation (1).

Discussion

From the measured sensitivity of the gas balance it is evident that the pressure readings were accurate to one part in 1000 so that the total error in the final analysis was 0.2%. This was the

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(13) J. B. M. Coppock, *Trans. Faraday Soc.*, **31**, 913 (1935).

variation actually found for the hydrogens. The intercheck between the purified helium and the light hydrogen is satisfactory and clearly points to the purity of the light hydrogen used as the standard gas being certainly better than 99.9% with respect to any impurity likely to be present. Thus, the analytical values of the deuterium samples must be correct to within 0.2% of the real absolute value if one accepts Livingston's value for the atomic weight of D. This latter value would certainly seem to be much more accurate than 0.1% so that the deuterium analyses may be accepted within the limits of error found. More discussion of the significance of this point will be forthcoming in another paper in which the results —obtained using this gas balance as an analytical device—of a recent investigation of the electrolytic separation factors for the hydrogen isotopes will be published. The gas balance has proved very useful as a primary standard in preparing samples of the hydrogen isotopes of known deuterium concentration for use in calibrating other analytical devices of the relative type such as thermal conductivity gages of the Farkas form and another form, details of which are published elsewhere.[14] It is of some interest for practical reasons to note two other results in the data of Table II, namely, those obtained from measurements made on ordinary tank helium and hydrogen. The measurements have been expressed in terms of the apparent molecular weights of the tank gases in order to facilitate comparisons with the purified gases. Both gases obviously contain very appreciable amounts of heavier impurities. In the case of the helium this impurity may have been due largely to nitrogen because during the arcing process the brown fumes of nitrogen peroxide were clearly visible. With proper precautions many kinds of two component—as well as three component equilibria of known equilibrium constants—gaseous combinations could be analysed using this balance.

Summary

1. A simple type of quartz fiber suspended gas density balance which can be constructed easily has been described.

2. The method of adjustment and use of this gas balance as well as its characteristics have been described and illustrated by experimental results.

3. The use of this gas balance as an analytical device and as a primary standard for (making up) samples of the hydrogen isotopes of known deuterium concentration has been illustrated.

PRINCETON, N. J. RECEIVED MARCH 1, 1937

[14] N. R. Trenner, *J. Chem. Phys.*, **5**, 382 (1937).

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, E. R. SQUIBB & SONS]

Crystalline Vitamin B$_1$ from Natural Sources

BY R. D. GREENE AND A. BLACK

This paper deals with a study of vitamin B$_1$ which was carried out in this Laboratory during the past three years, a portion of which was referred to in a preliminary report.[1] Several workers[2–7] have developed methods for the isolation of the vitamin from natural sources. Since the beginning of this work two different groups of workers[8–9] have developed processes for the synthetic production of vitamin B$_1$. While it had been our purpose to provide a less expensive method for the isolation of the naturally occurring vitamin, it is not claimed that the process herein described can meet the synthetic methods on a competitive basis. Rather it is submitted because it contains certain features which have proved successful in the production of pure natural vitamin B$_1$ and which may be useful in the fractionation of the B complex.

Adsorption

Since Seidell's discovery in 1916 of the adsorption of vitamin B$_1$ by certain agents, such as fullers' earth, this procedure has been used by nearly everyone in their attempts at concentration. We have studied the adsorptive capacities of a num-

[1] Greene and Black, *Science*, **84**, 185 (1936).

[2] Jansen and Donath, *Mededeel. Dienst Volksgezondheid Nederland Indië*, *pt. 1*, 186 (1926).

[3] Ohdake, *Proc. Imp. Acad.* (Tokyo), **7**, 102 (1931).

[4] Windaus, *Nachr. Ges. Wiss. Göttingen*, 209 (1932).

[5] Seidell and Smith, THIS JOURNAL, **55**, 3380 (1933).

[6] Kinnersley, O'Brien and Peters, *Biochem. J.*, **27**, 232 (1933).

[7] Williams, Waterman and Keresztesy, THIS JOURNAL, **56**, 1187 (1934).

[8] Williams and Cline, *ibid.*, **58**, 1504 (1936).

[9] I. G. Farbenindustrie A. G., British Patents 456,735, and 456,751 (1936).