(corr.), and were not hydrolyzed by digestion with concentrated hydrochloric acid.

Anal. Calcd. for $C_{18}H_{16}O_3N_2$: C, 70.10; H, 5.25. Found: C, 70.20; H, 5.17.

2,3-Dimethyl-4-quinazolone.—Incidentally this compound was also prepared from 2-methyl-4-quinazolone (I), by the same method as the two just reported above. It was obtained in thin colorless needles, m. p. 111–111.5° (corr.), which were not hydrolyzed when boiled with concentrated hydrochloric acid. Bogert and Seil[5] obtained it by the action of methylamine upon acetanthranil and gave its m. p. as 110°.

Summary

1. 2-Methyl-4-quinazolone has been condensed with *p*-anisaldehyde and with piperonal to the corresponding styryl derivatives, and the olefin bond of the latter has been saturated by catalytic hydrogenation.

2. These substituted 2-phenylethyl-4-quinazolones have been converted into the corresponding substituted 2-phenylethyl-4-chloro and 4-methoxy quinazolines, of which the 2-(beta-3′,4′-methylene dioxyphenylethyl)-4-methoxyquinazoline is the quinazoline analog of the angostura alkaloid cusparine.

3. The substituted 2-phenylethyl-3-methyl-4-quinazolones were also synthesized, to learn in what respects these N-methyl derivatives differed from their O-methyl isomers.

4. The pharmacological properties of these compounds have not yet been studied.

NEW YORK, N. Y. RECEIVED JULY 10, 1936

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[5] Bogert and Seil, THIS JOURNAL, **29**, 531 (1907).

[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY AND PHYSICS, AMHERST COLLEGE]

A Sensitive Manostat for Low Pressures and its Application to the Adsorption of Hydrogen and Deuterium on Copper

BY THEODORE SOLLER, SEYMORE GOLDWASSER AND RALPH A. BEEBE

In the course of experiments conducted in the Amherst[1] Laboratory of Chemistry on the rates of hydrogen and deuterium adsorption on copper at gas pressures in the region of 2 mm., it became apparent that rate data were needed under conditions of constant pressure. The most sensitive manostat described in the literature is that of Huntress and Hershberg[2] who claim control of pressure to ±0.15 mm. Because this amount of variation was prohibitive for work at 1 to 2 mm. total pressure, a new automatic manostat has been developed which regulates the pressure to better than ±0.005 mm. and is applicable to all pressures. Provision has also been made for the continuous reading of the volume of gas entering the system during the course of adsorption. With the new manostatic technique it has been possible to investigate in detail the relative rates of adsorption of the two hydrogen isotopes on copper at low pressures. At 0° we have found a marked difference in the rates of adsorption of hydrogen and deuterium under identical conditions. Moreover, the temperature inversion in the ratio H_2/D_2 adsorbed has again been observed. This inversion has been found previously by Beebe *et al.*[1] and more recently has been predicted by Pease and Wheeler[3] from a statistical mechanical approach to the problem.

A. The Manostat

The general plan of the control mechanism is as follows. A slight decrease in the pressure of the system causes the mirror of the differential manometer to be tilted downward in such a way as to throw a light beam onto a photo-electric cell. Working through an amplifier, this cell actuates the solenoid which opens the mercury valve, thereby admitting a small amount of gas to the system. The admission of this gas causes a slight increase of the pressure and the valve is closed *via* the mirror, the photo-electric cell, and the solenoid, thus completing the cycle.

The Differential Manometer.—A modified form of the mercury manometer described by Johnson and Harrison[4] was used. To eliminate the rather troublesome task of fusing the platinum strip into a glass roller rod, a 1.6 mm. steel rod was substituted. The platinum strip was then easily attached by spot welding. Three leveling screws supporting the whole float and mirror mechanism made the device more readily adjustable. The whole manometer was placed in a small water thermostat, control of which was necessary to ±0.1° to prevent undue change in the volume of the mercury supporting the glass float. Because a quick response to pressure change was essential, the dead-beat feature of the manometer of Johnson and Harrison was sacrificed by using a 10-mm. tube to connect the mer-

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[1] Beebe, Low, Wildner and Goldwasser, THIS JOURNAL, **57**, 2527 (1935).

[2] Huntress and Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **5**, 145 (1933). The authors also include a complete review of the subject up to 1933.

[3] Pease and Wheeler, *ibid.*, THIS JOURNAL, **58**, 1665 (1936).

[4] Johnson and Harrison, *J. Sci. Instruments*, **6**, 305 (1929).

cury in the two arms of the instrument. This resulted in a slight surging back and forth after the admission of a gas increment but had no undesirable effect on the successful functioning of the control mechanism.

The Photo-electric Relay.—The photo-electric relay circuit is a modification of one suggested by F. H. Shepard.[5] Its advantages are the use of standard parts and operation directly from 110-volt, 60-cycle power circuit, no rectifier being necessary. The diagram of the circuit used is given in Fig. 1.

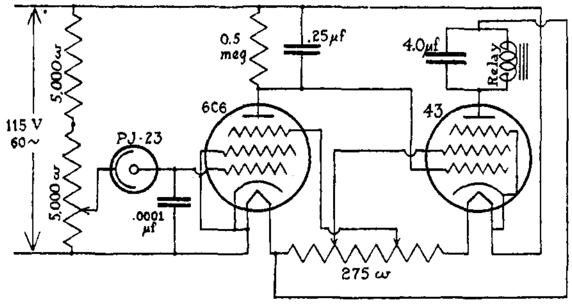

Fig. 1.—Diagram of photo-electric relay circuit.

Light from a straight-line filament lamp operating on 10 volts and 3.5 amperes falls on the mirror of the differential manometer, is reflected and brought to a focus at the PJ-23 photo-cell by a lens of one meter focal length. The sensitivity of the circuit is controlled by the position of the moving contact of the 5000 ohm potentiometer. The relay used in the output of the 43 tube is a Struthers Dunn ASBTS, operating on 15 m.a. half wave rectified current, having an A. C. core, No. 190 coil, and secondary contacts capable of carrying 10 amperes at 110 volts.

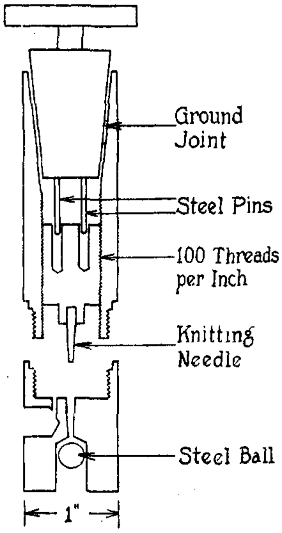

Fig. 2.—Adjustable leak.

The Adjustable Leak.—A rather large variation in rates of adsorption was anticipated during the different stages of the various processes to be studied. Moreover, it was found desirable for the effective functioning of the control mechanism that the rate of flow of the gas entering the system with the mercury valve open be of the same order of magnitude as the rate of removal of gas from the system by adsorption. The adjustable steel leak shown in Fig. 2 has met this requirement very satisfactorily. Because of the rigid construction of the glass apparatus, it was necessary that the leak be designed in such a way that neither the inlet nor the outlet glass tube should be moved during adjustment of the leak. For convenience in construction, the leak was made in two parts which fitted together at the joint J. This joint, which was in a fixed position while in use, was made vacuum tight with picene cement.

Gas Buret.—The gas buret, operated under reduced pressure for increased sensitivity, is maintained at constant pressure by an electrolysis device (see Fig. 3) built on the same principle as that of Taylor and Strother.[6] When the mercury touches the platinum tipped tungsten contact C, a 0.25 ampere current is allowed to flow between C and D; this current, acting through a simple relay, closes a switch which permits a 3 ampere current to flow through the solution of the electrolytic cell between the electrodes E and F. This relay system reduced difficulties from sparking at the contact C. A specially designed iron plate float with a platinum center helps to eliminate trouble from clinging of the mercury to the contact C, thus giving closer control of the pressure in the gas buret. The quantity of gas leaving the buret over any time interval is a linear function of the change in height of the mercury column. For the buret tube used, a change in height of 1 mm. represented 0.0132 cc. of gas at standard conditions when the buret pressure was 10 cm.

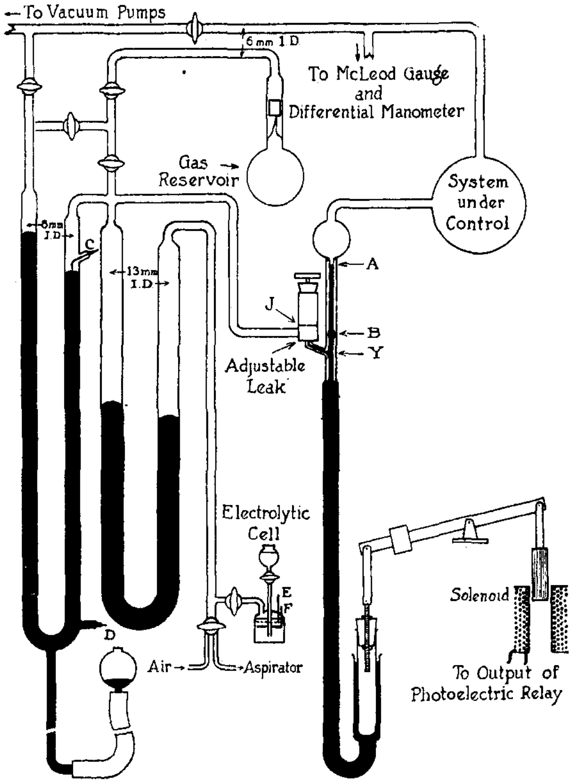

Fig. 3.

The Mercury Valve.—The mercury valve is so arranged that in its closed position the difference in height in mm. between the top of the mercury column A, Fig. 3, and the top of the ball valve in the metal adjustable leak slightly exceeds the gas pressure in mm. in the gas buret. This prevents any passage of gas when the mercury valve is closed. In the open position of the mercury valve, the mercury column stands, of course, slightly below the junc-

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[5] F. H. Shepard, *Electronics*, **8**, 304 (1935).

[6] Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

tion Y. The vertical glass section just above the Y junction is of 3 mm. inside diameter to eliminate appreciable expansion or compression of the gas in the system under control because of changes in volume of the system during the opening or closing of the mercury valve. A small enlargement, B, in the bore of the tube serves to prevent trapping of a short mercury column above the incoming gas increment. It was found that the amount of each increment could conveniently be made as small as 0.008 cc. (at standard conditions).

The successful operation of the apparatus is illustrated in Fig. 4. Volumes of gas delivered from the buret to the system under control are plotted against time. In obtaining the data for curve 2, the system to be controlled was initially at 1.003 mm. pressure. Gas was allowed to leak out of the system through a very narrow glass capillary tube (not shown in Fig. 3) directly to the mercury diffusion pump; gas then entered the system through the mercury valve at a rate sufficient to maintain the pressure constant to ±0.005 mm. as was shown on a McLeod gage. The straight line obtained in curve 2 under these conditions is evidence that all parts of the apparatus were functioning properly. For curve 1, the gas leaked out through a still finer capillary at first, but at point A the path of the leak was changed to the coarser capillary used for curve 2. For curve 3, the gas was allowed to leak out of the system, the pressure in which was 1.325 mm. at the start, into an evacuated bulb (not shown in Fig. 3). Because the rate of leak out of the system decreased with time as the pressure in the initially evacuated bulb was built up, a corresponding decrease was obtained in the rate of leak into the system as is shown in Fig. 4. For adsorption measurements, the tube containing the adsorbent would correspond to the bulb and capillary attachment used for curve 3.

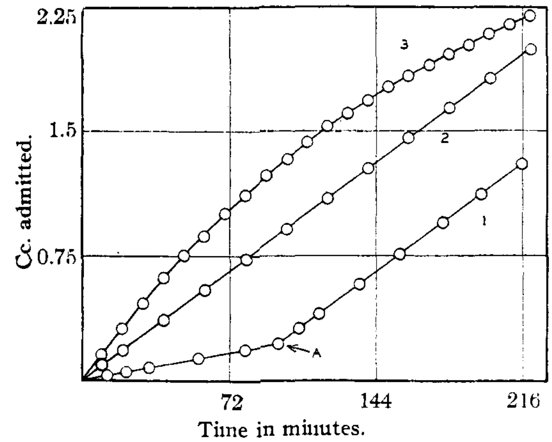

Fig. 4.

Owing to its differential principle, the manometer and consequently the manostat should operate satisfactorily at all pressures up to 760 mm. Obviously the percentage of variation in the pressure would be much less at higher pressures. Moreover, by drawing gas out of the system under control through the adjustable metal leak and mercury valve into an evacuated system, the manostat should be equally adaptable to control in a system in which gas is slowly being evolved or admitted from outside.

B. Adsorption Experiments

Apparatus.—The apparatus was that referred to and described above. All the measurements were made at 2.63 ± 0.005 mm. pressure.

Materials.—The copper powder supplied through the courtesy of the General Metals Powder Company was prepared in the same way as copper 3 described in the earlier work;[1] it came from a different batch, however. The copper was outgassed for fourteen to sixteen hours at 170° before each run.

The deuterium gas containing less than 0.5% of hydrogen was received from the Princeton Laboratory of Chemistry in October, 1935.

The sources of the hydrogen and helium have been described previously.[1]

Experimental Results

The relative rates of adsorption of hydrogen and deuterium at 0° are shown in Fig. 5. For example, the average rates from 0.20 cc. to 0.50 cc. absorbed bear the ratio: $H_2/D_2 = 5.5$. The rates which were investigated at the higher temperatures were too rapid to make the H_2/D_2 ratio significant.

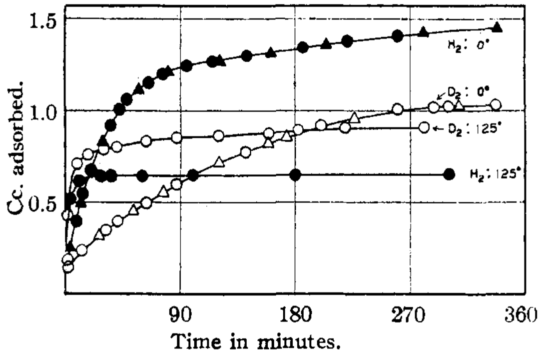

Fig. 5.—Adsorption of hydrogen and deuterium on 109 g. of copper powder.

The temperature inversion in the amounts of hydrogen and deuterium adsorbed is also apparent in Fig. 5, hydrogen being adsorbed in greater amount at 0° but in lesser quantity than deuterium at 125°. We estimate from these experiments at 0 and 125° together with experiments at 100° not shown, that the inversion temperature for this sample of copper was approximately 95°. This is to be compared with 60° previously observed on another copper sample.

The order of experiments was: H_2 at 0°, H_2 at 0°, H_2 at 100°, D_2 at 0°, D_2 at 100°, H_2 at 100°, D_2 at 125°, H_2 at 125°, D_2 at 0°, H_2 at 0°. In Fig. 5, points for 0° represented by circles are plotted from data taken at the beginning of the series, and those represented by triangles at the end of the series of rate measurements. The reproducibility of the data at 0° indicates the stability of the copper surface as well as the dependability of the manostatic technique throughout the whole series of measurements.

Discussion

The large difference in the rates of adsorption which we have observed appears to be in disagreement with the recent work of Melville and Rideal,[7] who have investigated the adsorption of hydrogen and of a 70% deuterium to 30% hydrogen mixture on copper at low pressures over the temperature range 71 to 171° and have found no difference in rates in the lower part of the temperature interval. The fact that we have found a threefold difference in rates for the two isotopes makes it seem probable that the results obtained by Melville and Rideal would have been different if they had used pure deuterium although the apparent discrepancy between their results and ours may conceivably be attributed to a difference in the nature of the copper surfaces studied.

Moreover, Melville and Rideal have not reported the temperature inversion of H_2/D_2 adsorbed which has been found in the Amherst laboratory by two different experimental methods. It seems probable that their failure to observe this phenomenon is due to the limited time interval over which the process was studied. For instance, referring to Fig. 3, p. 85, of their paper it would appear that the rate curve at 137° for the 70% deuterium mixture would actually cross the hydrogen curve, if extrapolated, instead of bending downward as shown. This would mean that although the rate for hydrogen was greater, more deuterium would be adsorbed at equilibrium at the higher temperatures.

Using the value 5.5 as the H_2/D_2 ratio of the average rates of adsorption on copper from the second to the forty-second minute at 0°, it is possible to show that the difference in activation energies is 0.75 kcal., making due allowance for the $\sqrt{2}$ collision factor. From this it may be inferred that the difference in zero point energies of hydrogen and deuterium in the activated state is 1.05 kcal. This result, which indicates that not all the zero point energy is contributed to the energy pool in the activating collision, is in accordance with the data of other investigators[7] (p. 77) for several homogeneous reactions.

The work of Pace and Taylor[8] as well as that of Kohlschütter[9] indicates that the rates of adsorption of hydrogen and deuterium on chromic oxide are identical at atmospheric pressure. Because our results make it clear that there is a marked difference in the rates for the two isotopes on copper at low pressures, it seems apparent that the adsorption of the two gases should be studied on both the adsorbents mentioned over a wide range of pressures. This series of measurements for copper adsorbent is now being undertaken making use of the constant pressure technique.

Our thanks are due to the Committee on Grants-in-Aid of the National Research Council for supplying funds for technical assistance in this work.

Summary

1. A device is described for the control of gas pressures to ±0.005 mm. and its applicability to the measurement of adsorption rates at low pressures is demonstrated.

2. At 0° and 2.63 mm. the relative rates of adsorption of hydrogen and deuterium on copper bear the ratio 3.35 to 1; and the difference in activation energies of adsorption for the two isotopes on copper at 0° is 0.48 kcal.

3. The temperature inversion in the ratio of adsorbabilities of hydrogen and deuterium on copper, which had been observed previously, has been confirmed using the new manostatic technique.

AMHERST, MASS. RECEIVED JUNE 30, 1936

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(7) Melville and Rideal, *Proc. Roy. Soc.* (London), **A153**, 89 (1935).

(8) Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

(9) Kohlschütter, *Z. physik. Chem.*, **A170**, 300 (1934).