[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Chemical and Physical Adsorption of Gases on Carbon Dust

BY ROBERT H. SAVAGE AND CALLAWAY BROWN

The clean-up of hydrogen by fresh carbon or graphite wear-dust,[1] at room temperature, has been interpreted as a chemical adsorption resulting from the opening of the graphite lattice during the process of frictional seizure. The amount of hydrogen adsorbed by the dust was found to be 10^5 times greater than that adsorbed by a typical activated charcoal at the same temperature and pressure, and represented a chemically-active surface of the order of one square meter per gram. The supposition was made that the *total* surface of the dust was considerably greater than this, as roughly indicated by the color of the material; and this possibility was strengthened by a subsequent study with an electron microscope which revealed[2] that the carbon particles occurred in a wide distribution of size and showed a fineness extending beyond the resolving power of the instrument. The suggestion was then made that a determination of the total surface of this carbon by nitrogen adsorption at low temperature[3] would complete the data relating the chemically active surface to the total (physical) surface.

For carbon we have not found published information relating the two types of adsorption. According to the work of Lowry and Hulett,[4] after a charcoal has been outgassed thoroughly at 900–1000° and has been allowed to cool in vacuum to room temperature, such gases as hydrogen, nitrogen, carbon monoxide, can be admitted and subsequently recovered quantitatively at room temperature. The adsorption of these gases is clearly no more than physical. Yet surface films held by primary valences evidently occur since there are recovered large quantities of hydrogen as well as oxides of carbon during the degassing of charcoal[5] at 600 to 1200°. Nitrogen, also, has been recovered in the degassing of graphite[6] at temperatures up to 2200°, and is the predominant gas evolved in the range 1700 to 2200°.

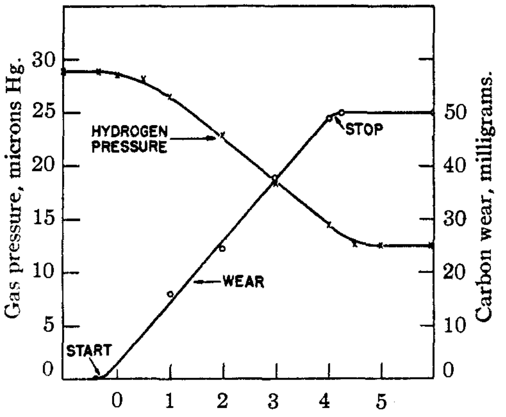

Fig. 1.—Clean-up of hydrogen by graphite wear-dust.

The lack of a detailed knowledge of the surface films on carbon seems to result from the fact that previous work has been concerned almost exclusively with the determination of adsorption characteristics of carbons which are already saturated chemically and which are not cleaned by the usual activation methods involving bake-outs at relatively low temperatures. Since an important part of the surface film may not be removed by such heating alone, the carbon wear-dust as a research material offers the novel advantage of providing *clean* carbon surfaces of exceptional extent by a simple mechanical process, so that the *formation* of the primary films may be measured. Employing the carbon dust we have observed an irreversible (chemical) clean-up at room temperature of hydrogen, nitrogen, oxygen, carbon dioxide, carbon monoxide and methane. This report is concerned particularly with (A) the hydrogen clean-up in relation to (B) a low temperature nitrogen adsorption performed after the clean-up to determine the total surface area.

Experimental

Part A.—Carbon wear-dust was made by operating graphite rods (brushes) against a rotating copper disk in a friction apparatus[1] containing hydrogen at a low pressure. (In the absence of certain vapors required for graphite lubrication, the graphite seizes to the moving base and rapidly disintegrates into a black dust which immediately cleans up the hydrogen. The clean-up is substantially the same whether the dust is formed in hydrogen directly or whether it is formed in vacuum and the hydrogen admitted after wear has stopped. Further, it occurs independently of the presence of copper in the moving base; *i. e.*, it is observed also with graphite rods sliding on a graphite disk.)

The observed wear (brush-volume) and the hydrogen clean-up were measured, as shown by Fig. 1. From the observed pressure drop in the system of 5.3-liter volume

TABLE I

CHEMICAL ADSORPTION

Sample, wear dust	Trial a	Trial b
Wear volume from rod, cc.	0.0263	0.0206
Apparent rod density, g./cc.	1.9	1.9
Calcd. weight of dust, g.	0.050	0.0392
Hydrogen adsorbed at S. T. P., cc.	0.101	0.078
Specific adsorption, cc./g.	2.00	1.98
Specific surface (chemical), sq. m./g.	5.16	5.12

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[1] R. H. Savage, *J. Applied Phys.*, **19**, 1 (1948).

[2] Ernest F. Fullam and Robert H. Savage, *ibid.*, July. 1948.

[3] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

[4] H. H. Lowry and G. A. Hulett, *ibid.*, **42**, 1408 (1919).

[5] Robert B. Anderson and P. H. Emmett, *J. Phys. and Colloid. Chem.*, **51**, 1308 (1947).

[6] F. J. Norton and A. L. Marshall, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div.*, **156**, 351 (1944).

we have calculated the adsorption, and also the specific area, of the *chemically active surface*, Table I. For reasons to be discussed, the area saturated per hydrogen molecule was assumed to be 9.6 × 10^{-16} sq. cm. (the area of two C atoms in the plane perpendicular to the graphite hexagonal plane). Several additional runs were then made to increase the amount of dust, and to check these results, after which the bell-jar was removed and a sample of the dust transferred to a small Pyrex tube for determination of surface area.

Part B.—The tube was next sealed into an adsorption apparatus[7] by means of a spherical ground-glass joint. The carbon sample was degassed in vacuum at room temperature and again for one hour at 500°, and the adsorption of nitrogen at −195° was determined after each pumping in the usual manner with helium as the reference gas. (Only the results following the 500° bake-out will be included because these are indicated to be more representative; the other data agreed however within 20%.) The dust was then removed and was replaced, first, with a sample of the original graphite "stock-powder" from which (with the addition of about 2% coked-binder) the brush had been made by pressing and firing to 1350°; and second, with samples of finished graphite rods of apparent density 1.9 g. per cc. Nitrogen adsorption at −195° was determined for each of these and the results are summarized, for comparison with the wear-dust, in Table II. The surface areas were calculated from these adsorption data, shown in Fig. 2, using the Brunauer, Emmett, Teller adsorption equation[3] and the value 16.2 × 10^{-16} sq. cm. for the area covered by a nitrogen molecule.

TABLE II

PHYSICAL ADSORPTION

Sample	g.	V_m (from BET plot) cc. N_2	Specific V_m cc. N_2/g.	Sp. surface (total) m²/g.
Wear dust	0.0786	7.86	100.0	435
Stock powder	2.579	4.53	1.76	7.65
Rod	0.281	0.084	0.30	1.30

Finally the work was extended to include graphite rods of contrasting physical properties, with the results shown in Table III. The electrographitized carbon shown under (2) had been fired to about 2800° in contrast to the natural graphite rod 1, fired at 1350°. The powder under (2) was formed by grinding one of the rods in a high-speed impact grinder to produce a surface area of 4.62 sq. m./g., in striking contrast to the 435 and 390 sq. m./g. areas shown for the two wear-dust samples. The three samples of rod 1 of different cross-section and history show the reproducibility of the results.

Discussion

Tables I and II show the changes in surface which accompany the processes of rod manufacture (pressing and bonding of graphite particles) and of rod wear. The stock powder is a relatively coarse graphite showing an area 7.65 sq. m./g., and this is decreased to 1.3 sq. m./g. as a result of the rod formation. The process of wear results in a fine subdivision of the individual graphite particles, increasing the surface by 335-fold, within the range of the fine colloidal carbon blacks (color blacks). Of the total surface, 99.7% is apparently fresh surface developed in the wearing process. Only a portion of this fresh surface can be chemically active toward hydrogen since the 1.98 cc./g. hydrogen adsorption, although many times larger than that reported for any previous carbon, is only 2% of the monolayer nitrogen adsorption of 100 cc./g. The hydrogen adsorption would seem to represent the proportion of carbon atoms which have been exposed so as to show one or more strong valences of unsaturation, such as those of free radicals. This exposure would not occur if the graphite crystal is simply delaminated or scaled away, but would occur if the crystal is opened both along the main cleavage plane *and* at right angles to this plane (so as to uncover both face atoms and edge atoms).

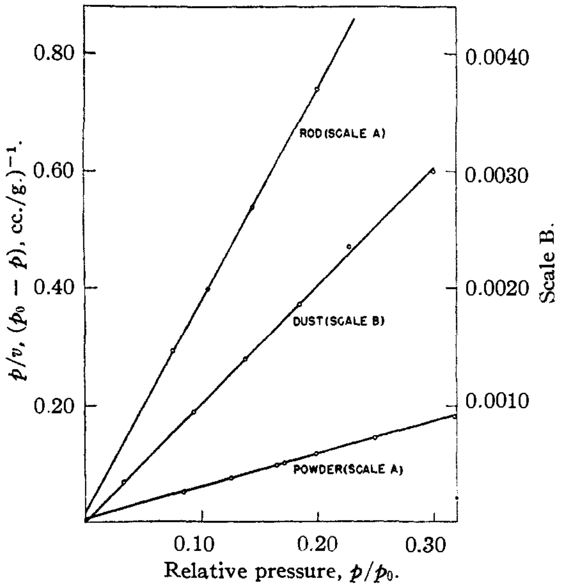

Fig. 2.—Adsorption of nitrogen at −195° on graphite (BET plots).

The laminar structure of graphite, together with the indication that the chemically active surface represents only a small proportion of the total surface, suggests that the wear-dust particles are composed of thin plates, and that only edge atoms combine with hydrogen while face atoms in the main cleavage plane of graphite make up most of the total surface area. In this case the area of the chemically active surface and the fraction of the surface atoms which are chemically active may be readily calculated from the lattice dimensions. The main cleavage plane of graphite consists of carbon hexagons with the smallest interatomic distance 1.42 Å. and the separation between planes 3.39 Å. The area per carbon atom along an edge perpendicular to the main plane is therefore 1.42 × 3.39 = 4.81 sq. Å. If the hydrogen adsorption is due to one-to-one combination of hydrogen atom with edge carbon atoms, the chemically active surface covered by 1.98 cc. per gram is 5.12 sq. m./g. as listed in Table I. Any other lattice points reacting with hydrogen would lead to an even smaller value for the area of the chemically active surface. The remaining total surface, 430 sq. m./g., is considered to represent facial area. Each surface hexagon (equivalent to 2 carbon

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[7] E. O. Kraemer, "Advances in Colloid Science," (by P. H. Emmett). Interscience Publishers, New York, 1942, pp. 1–36.

atoms) occupies 5.24 sq. Å., so the total number of face atoms per g., $n_f = 430 \times 10^4/2.62 \times 10^{-16}$. The proportion of surface atoms which combine with the 1.98 cc. of hydrogen, presumably as edge atoms, is therefore $^1/_{155}$ or 0.65%. Although the "chemical" surface represents only a small fraction of the total surface, its absolute magnitude, 5.12 sq. m./g., is large compared with the *total surface* of the rod from which the dust was worn and is comparable with the *total surface* of natural graphite powders.

Size and Shape of Graphite Fragments.—The values of equivalent particle size in Table III represent the diameter of hypothetical spheres (or the edge of cubes), calculated from the equation $d_3 = 6/\rho S$ where d_3 is in microns when S is in sq. m./g. and the density ρ is in g./cc. (2.25 for graphite). It is convenient to use the spherical model for comparison with the more usual forms of black carbon but a laminar model with a large ratio of area to thickness appears much more likely from the evidence discussed above. For a plate-like particle of area A and thickness t, the surface area may be considered as $2A$ with only a small error if the ratio of edge surface to total surface is small. The mass of the particle is $At\rho$, and the surface area per unit mass $S = 2/t\rho$. As long as the thickness t remains small compared with the area A, the specific surface area of the graphite is *independent of the size and shape* of the plates and is determined by the thickness. For wear-dust 1 with $S = 435 \times 10^4$ sq. cm./g., therefore, the indicated thickness $t = 20.4 \times 10^{-8}$ cm.

TABLE III

Sample	Specific surface, sq. m./g.	Equiv. part.-size, microns
No. 1		
Powder for making rod 1 (natural graphite)	7.65	0.349
Rod 1 (0.25 × 0.25 cm.² cross-section) (used for making dust)	1.3	2.05
Rod 1′ (0.51 × 0.63 cm.² cross-section) (other samples, same stock)	1.19	2.24
Rod 1″ (0.25 × 0.25 cm.² cross-section) (other samples, same stock)	1.13	2.35
Wear dust 1	435	0.0060
No. 2		
Rod 2 (electrographitized coke-bonded black-carbon)	1.88	1.42
Powder from grinding rod 2	4.62	0.58
Wear dust 2	390	0.0068

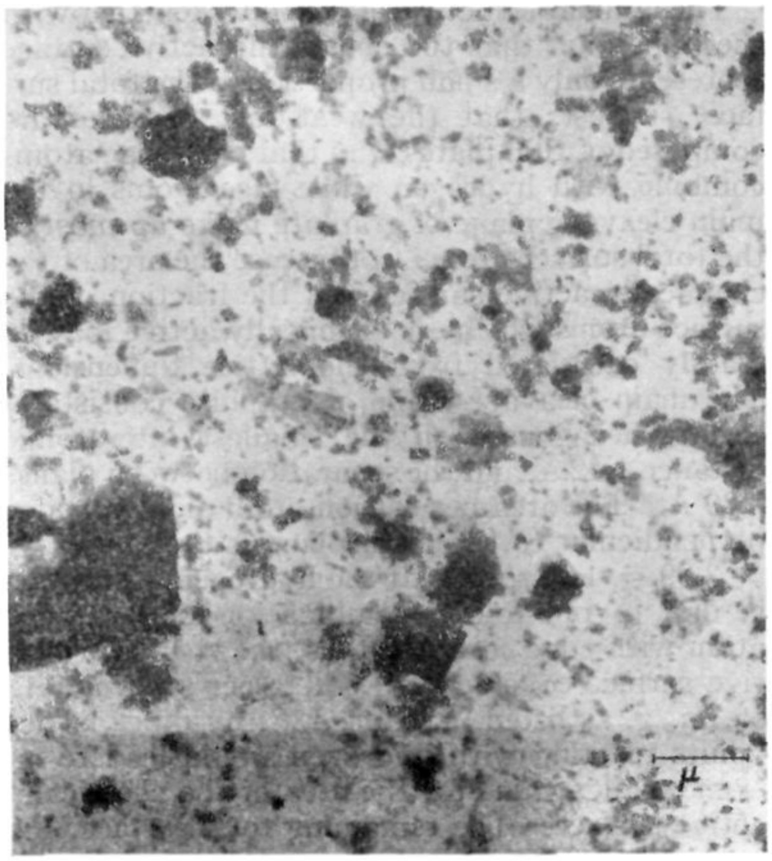

Fig. 3.—Electron micrograph of graphite wear-dust.

From the specific surface area alone there is no limitation on the size and shape of plate-like particles; only the thickness is determined. A probable limitation on the face to edge surface ratio appears in the ratio of total surface, from nitrogen adsorption at −195°, to "chemical" surface, from hydrogen clean-up at room temperature. The ratio of total surface atoms to hydrogen atoms adsorbed has been calculated to be 155. If this is assumed to represent the ratio of face atoms to edge atoms, the average size of the plates may be calculated. For a plate of area A, perimeter p, and thickness t, the total number of facial atoms $n_f = 10^{16} \times 2A/2.62$; the number of edge atoms in each basal plane $10^8\ p/1.42$, and the number of basal planes $10^8\ t/3.39$ approximately. The total number of edge atoms, therefore, $n_e = 10^{16}\ pt/4.81$ and the ratio of face to edge atoms, $n_f/n_e = 3.67\ (A/pt)$. When the thickness $t = 20.4$ Å. and the ratio $n_f/n_e = 155$, the ratio of area to perimeter, $A/p = 862 \times 10^{-8}$ cm.

In the limiting case of a circle of radius r, $A/p = r/2$; then $r = 1720$ Å. Circular plates of average radius 1720 Å. and thickness 20.4 Å. thus satisfy the requirements for both "total" and "chemical" surface, assuming combination of hydrogen with edge atoms. Plates of shape other than circular still satisfy the total surface requirement if the thickness is 20.4 Å. but must be of larger area than $\pi(1720 \times 10^{-8})$ sq. cm. in order for the ratio of face to edge atoms to remain at 155.

Evidence from Electron Microscope and X-Ray Diffraction.[8]—A typical electron micrograph of the wear-dust appears in Fig. 3. The electron microscope studies are discussed more fully elsewhere[2] but it is clear that a large range of sizes is present extending from 10000 Å. down to 100 Å. or less in diameter. A number of particles semi-transparent to the electron beam are present and these are certainly of a thickness considerably less than 100 Å. Furthermore the thin plates are

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(8) The authors wish to thank Ernest F. Fullam for the electron micrograph, and David Harker for the X-ray data and its interpretation.

seen to vary in respect to thickness from opacity to invisibility; and since the gradation is continuous we cannot determine the concentration of particles too thin to be visible. Quantitative treatment is thus complicated by the large range of sizes present and by the transparency to the electron beam of very thin platelets.

X-Ray diffraction results provide interesting independent evidence for the structure of the wear-dust particles. Diffraction of copper Kα radiation from a thin layer of the wear-dust powder was carried out in a Geiger counter X-ray spectrometer. The output of the recorder, which plots intensity of the diffracted radiation against the diffraction angle, is shown in Fig. 4.

The sharp peak at 27° corresponds to the 00.2 reflection of massive graphite. (This reflection is from the cleavage planes.) The graphite crystals responsible for this reflection must be thicker than about 1000 Å. The sharp peak just mentioned is superimposed on a very broad maximum of about 10° width at half height. Such a diffraction effect is consistent with the assumption of either (a) distortion of the crystal lattice, (b) extremely small particle size or (c) both. The electron microscope evidence points toward alternative (b). If the line broadening is due entirely to particle size, the particles must be of the order of five times the interplanar distance or 20 Å. in thickness. This reflection provides no information on particle size in directions other than normal to the cleavage plane of graphite.

Thus the electron micrographs and X-ray diffraction show that the particles are predominantly very thin perpendicular to the hexagonal plane and of comparatively large diameter. Although a portion of the powder appears to consist of relatively thick fragments the results on the whole are in excellent agreement with the thin plate model. This supports the assumption that hydrogen reacts quantitatively with edge atoms. It should be noted that the estimate of 20 Å. thickness from the surface area is independent of the location of the chemisorbed hydrogen. Only the estimate of the face dimension depends on the ratio of edge to face atoms.

Clean-up of Other Gases.—Preliminary studies of nitrogen clean-up by the carbon wear-dust have indicated this is considerably less than for hydrogen. On two carbons it has been indicated to be 180 cu. mm. (STP)/g. or higher. The fact that it is appreciable seems to us to be rather remarkable since molecular nitrogen does not react with charcoal.[9] Preliminary data for methane showed an adsorption of roughly one-half that obtained with hydrogen; that is, roughly the same number of hydrogen atoms were involved per gram of carbon dust. The carbon monoxide adsorption was indicated to be somewhat higher than that of hydrogen.

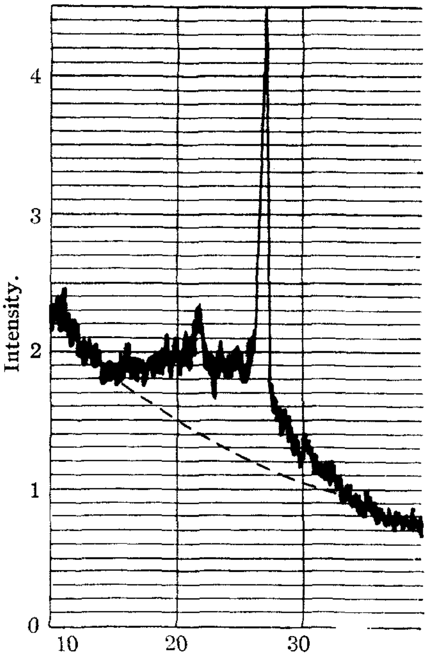

Fig. 4—X-Ray diffraction record for graphite wear-dust.

In measuring the chemical clean-up of these gases during the initial stages of the work, the bell-jar trap was chilled with liquid nitrogen to condense traces of water vapor. The trap was observed to collect a much larger proportion of the wear-dust when chilled than when held at room temperature, and because of the large carbon surface involved, there resulted considerable physical adsorption of such gases as nitrogen and methane at the low temperature. This complicated the chemical measurements, and to correct this difficulty in a later series of experiments the trap was retained at room temperature during the clean-up. Another complication was found to occur when the trap was warm, *viz.*, a slow evolution of water vapor which tended to compete in the clean-up and to modify the pressure reading. Further work is under way to bring the data on the other gases up to the degree of reproducibility found for hydrogen.

Summary

1. Carbon dust, formed by the high wear of graphite rods rubbing against a rotating base in vacuum, has been found to adsorb hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide and methane irreversibly at room temperature. The hydrogen clean-up, 2 cc./g. of dust, is 10^5 times the adsorption shown by representative activated charcoals at room temperature and low pressures of the order of 10 microns.

2. In a typical case the *chemically active* specific surface of the dust is indicated by the hydrogen clean-up to be 5.12 sq. m./g. The total (physical) specific surface is found by nitrogen adsorption at −195° to be 435 sq. m./g., as calculated from the

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[9] R. B. Anderson and P. H. Emmett, *J. Phys. Colloid. Chem.*, **51**, 1327 (1947).

measured adsorption of 100 cc. of N_2/g. for the monolayer. This total surface of the *graphite* dust is comparable with those of the best commercial activated carbons, and in addition 1.2% of this total surface showed a powerful chemical activity.

3. Nitrogen adsorption isotherms on graphite powder (raw material), finished graphite rods (brushes), and powder formed by pulverizing the rods in a high-speed impact grinder indicated surface areas of 7.7, 1.3 and 4.6 sq. m./g., respectively, compared with 435 sq. m./g. for the wear-dust.

4. It is shown that for a laminar model of graphite fragments in which the ratio of edge area to face area is small, the surface area per unit weight is independent of size and shape and depends only on the thickness of the fragments. A thickness of 20.4 Å. is indicated for the carbon wear-dust. A minimum average diameter of 3500 Å. is indicated for the face dimension on the assumption that hydrogen reacts quantitatively with edge atoms.

5. It is suggested that the chemically active portion of the dust represents unsaturated carbon valences at points of cleavage at right angles to the main cleavage plane. The wear dust appears to differ from previous carbon samples studied in that these strong valence bonds have been freshly opened, mechanically, and occur in large numbers; whereas the corresponding bonds in other carbons are ordinarily saturated by chemisorbed gas and are not opened by ordinary outgassing procedures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Thermodynamics of Aqueous Solutions of Potassium Hydroxide[1]

BY G. C. AKERLOF[2] AND PAUL BENDER[3]

Introduction

The results presented in this paper represent a continuation of a program of studies of the thermodynamic properties of concentrated aqueous electrolytic solutions in which measurements on hydrochloric acid[4] and sodium hydroxide[5] solutions have already been reported. A detailed description of the experimental procedure and the method of calculation employed here has been given previously.[5] In the following all symbols agree with common usage or with those in earlier papers.

Preliminary Treatment of the Data.—The cell measured has the composition

$$Pt, H_2/KOH(m)/KxHg/KOH(m_r)/H_2, Pt$$

The cell reaction and the resulting electromotive force expression are given, respectively, by

$$KOH(m) + H_2O(m_r) + {}^1/_2H_2(m) \rightarrow KOH(m_r) + H_2O(m) + {}^1/_2H_2(m_r) \quad (1)$$

$$E = -\frac{RT}{F}\ln\frac{a_{KOH(m_r)}a_{H_2O(m)}a^{1/2}_{H_2(m_r)}}{a_{KOH(m)}a_{H_2O(m_r)}a^{1/2}_{H_2(m)}} \quad (2)$$

The reference concentration m_r was held constant at 0.09154 molal for twenty concentrations m of potassium hydroxide ranging from 0.2240 to 17.544 molal. The method employed to eliminate carbonate from the solutions has been described previously.[6] Measurements were made at ten-degree intervals from 0 to 70°; a small linear correction was applied to the observed electromotive force values to correct them to round temperatures.

A critical survey of the vapor pressure measurements of Smits,[7] Tammann,[8] Paranjpe[9] and Kobayashi[10] provided the information necessary for the correction of the observed electromotive forces to unit activity of hydrogen gas in each half-cell. Since all the measurements available were made by the static method, which tends to give too high values because of difficulty in the complete elimination of air from the solutions, somewhat greater weight was assigned to the lower vapor pressure values reported at a given concentration. The resulting correction reached a maximum value of 4.5 millivolts at 70° and 17.54 molal. The corrected electromotive force values are summarized in Table I; the average deviation of the observed points from smoothed values obtained by the method of least squares, assuming a quadratic dependence on the temperature, is less than 0.4 millivolt.

The water transfer potentials

$$\Delta E_{H_2O} = -\frac{RT}{F}\ln\frac{a_{H_2O(m)}}{a_{H_2O(m_r)}}$$

were evaluated by the method suggested by Akerlof and Kegeles[5] and more recently generalized by Stokes.[11] Their validity was checked by comparison with those calculated from the final log a_1 values; the agreement was well within the experimental error of the electromotive force measure-

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(1) This paper is based on the dissertation presented in 1942 to the Faculty of the Graduate School of Yale University by Paul Bender in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: Mellon Institute, Pittsburgh 13, Pennsylvania.

(3) Present address: Department of Chemistry, University of Wisconsin, Madison 6, Wisconsin.

(4) Akerlof and Teare, THIS JOURNAL, **59**, 1855 (1937).

(5) Akerlof and Kegeles, *ibid.*, **62**, 620 (1940).

(6) Akerlof and Bender, THIS JOURNAL, **63**, 1085 (1941).

(7) Smits, *Arch. Neerland.* 2, **1**, 111 (1898); *Z. physik. Chem.*, **39**, 385 (1905).

(8) Tammann, *Mem. Acad. Petersburgh* 7, **35**, Nr. 9 and 64 (1887).

(9) Paranjpe, *J. Indian Inst. Sci.*, **2**, 59 (1918).

(10) Kobayashi, *J. Sci. Hiroshima Univ.*, **A2**, 274 (1931-32).

(11) Stokes, THIS JOURNAL, **67**, 1686 (1945).