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

$$\text{Pt},H_2/\text{KOH}(m)/K_xHg/\text{KOH}(m_r)/H_2,\ \text{Pt}$$

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

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

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

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.

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[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).

TABLE I

OBSERVED ELECTROMOTIVE FORCE DATA, CORRECTED TO ROUND TEMPERATURES AND UNIT ACTIVITY OF HYDROGEN GAS

| $m$ | 0° | 10° | 20° | 30° | 40° | 50° | 60° | 70° |
|---|---|---|---|---|---|---|---|---|
| 0.2240 | 0.0397 | 0.0418 | 0.0423 | 0.0437 | 0.0456 | 0.0474 | 0.0482 | 0.0492 |
| .2847 | .0497 | .0515 | .0533 | .0551 | .0567 | .0584 | .0591 | .0611 |
| .4829 | .0742 | .0779 | .0808 | .0826 | .0852 | .0868 | .0907 | .0924 |
| .6997 | .0915 | .0954 | .0996 | .1021 | .1042 | .1076 | .1094 | .1129 |
| .9956 | .1104 | .1148 | .1183 | .1226 | .1256 | .1290 | .1325 | .1351 |
| 1.9869 | .1500 | .1569 | .1622 | .1672 | .1720 | .1768 | .1812 | .1846 |
| 2.5141 | .1681 | .1723 | .1785 | .1846 | .1890 | .1942 | .1993 | .2038 |
| 2.9868 | .1802 | .1879 | .1933 | .1982 | .2049 | .2111 | .2138 | .2168 |
| 4.0565 | .2107 | .2173 | .2239 | .2308 | .2380 | .2429 | .2471 | .2520 |
| 5.0212 | .2333 | .2417 | .2491 | .2556 | .2617 | .2663 | .2728 | .2769 |
| 5.6545 | .2515 | .2574 | .2648 | .2714 | .2773 | .2816 | .2861 | .2879 |
| 7.0174 | .2820 | .2902 | .2971 | .3041 | .3116 | .3173 | .3220 | .3273 |
| 8.0473 | .3046 | .3145 | .3217 | .3278 | .3347 | .3412 | .3459 | .3490 |
| 9.0314 | .3284 | .3355 | .3429 | .3498 | .3566 | .3626 | .3683 | .3722 |
| 10.052 | .3483 | .3571 | .3637 | .3714 | .3769 | .3830 | .3867 | .3941 |
| 11.091 | .3701 | .3800 | .3877 | .3941 | .4001 | .4060 | .4109 | .4150 |
| 12.073 | .3922 | .4006 | .4087 | .4154 | .4225 | .4275 | .4327 | .4361 |
| 13.064 | .4111 | .4188 | .4273 | .4341 | .4394 | .4445 | .4512 | .4559 |
| 14.099 | .4321 | .4383 | .4442 | .4501 | .4587 | .4642 | .4703 | .4759 |
| 17.544 | .4948 | .5015 | .5085 | .5156 | .5224 | .5269 | .5308 | .5335 |

ments. The conclusion of Harned and Cook[12] that below four molal the water transfer potential is practically constant in the temperature range from 0 to 35° was confirmed.

**Thermodynamic Properties of Solutions of Potassium Hydroxide.**—The logarithm of the mean ionic activity coefficient of the solute was calculated using the equation

$$\log \gamma = \frac{-u\sqrt{m}}{1 + \sqrt{2m}} + Bm + Cm^2 + Dm^3 + Em^4 \quad (3)$$

where $u$ is the universal constant of the limiting law, and $B$, $C$, $D$, and $E$ are empirical coefficients evaluated as functions of the temperature by the method of least squares. A summary of the results of this process is given in Table II. The extension of the calculation to the other thermodynamic properties of solute and solvent in terms of the constants of equation (3) has been given explicitly by Akerlof and Kegeles.[5] Figures 1 and 2 show the dependence on the concentration of log $\gamma$ and of $(\log a_1)/m$ at the various temperatures at which measurements were made.

TABLE II

EMPIRICAL COEFFICIENTS USED FOR THE CALCULATION OF THE ACTIVITY COEFFICIENT OF THE SOLUTE IN AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE

$$B = 0.06629 + 0.0_36135t - 0.0_411018t^2 + 0.0_74096t^3$$
$$C = 0.010909 - 0.0_317108t + 0.0_516895t^2 - 0.0_87969t^3$$
$$D = -0.0_37351 + 0.0_59973t - 0.0_79347t^2 + 0.0_96215t^3$$
$$E = 0.0_415502 - 0.0_61980t + 0.0_818424t^2 - 0.0_{10}1764t^3$$

| Temp., °C. | $u$ | Temp., °C. | $u$ | Temp., °C. | $u$ |
|---|---|---|---|---|---|
| 0 | 0.487 | 25 | 0.506 | 50 | 0.534 |
| 10 | .494 | 30 | .511 | 60 | .549 |
| 20 | .502 | 40 | .522 | 70 | .565 |

## Discussion

The first amalgam cell measurements on potassium hydroxide solutions were made at 25° by Ming Chow,[13] who used flowing potassium amalgam and mercury–mercuric oxide electrodes. His results were considered unreliable by Knobel,[14] who repeated the work using hydrogen electrodes instead of the mercury–mercuric oxide type. Knobel's experimental results were subsequently recalculated, taking into account the water transfer potential, by Harned,[15] Scatchard,[16] and Harned and Akerlof.[17] In the latter calculations, in which the extrapolations were based on the Debye–Huckel theory, log $\gamma$ values were obtained which are in fair agreement with those here reported. More recently amalgam cell measurements covering a concentration range up to four molal at temperatures from 0 to 35° were reported by Harned and Cook.[12] Our results are on the whole in good agreement with theirs over their entire measuring range.

The electromotive force measurements at 25° of Shibata and co-workers[18] are in excellent agreement with ours at hydroxide concentrations up to seven molal with an average deviation of 0.3 mv. between the two sets of results. This comparison suggests that contrary to previous opinion the mercury–mercuric oxide electrode might function reversibly without undesirable side reactions, at least in dilute alkali solutions. At higher concentrations investigated in the two researches greater deviations are observed. In this connection the

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[12] Harned and Cook, THIS JOURNAL, **59**, 496 (1937).

[13] Chow, *ibid.*, **42**, 488 (1920).

[14] Knobel, *ibid.*, **45**, 470 (1923).

[15] Harned, *Z. physik. Chem.*, **117**, 23 (1925).

[16] Scatchard, THIS JOURNAL **47**, 658 (1925).

[17] Harned and Akerlof, *Physik. Z.*, **27**, 426 (1926).

[18] Shibata, Murata and Toyoda, *J. Chem. Soc. Japan*, **52**, 627 (1931); Shibata and Murata, *ibid.*, **52**, 645 (1931).

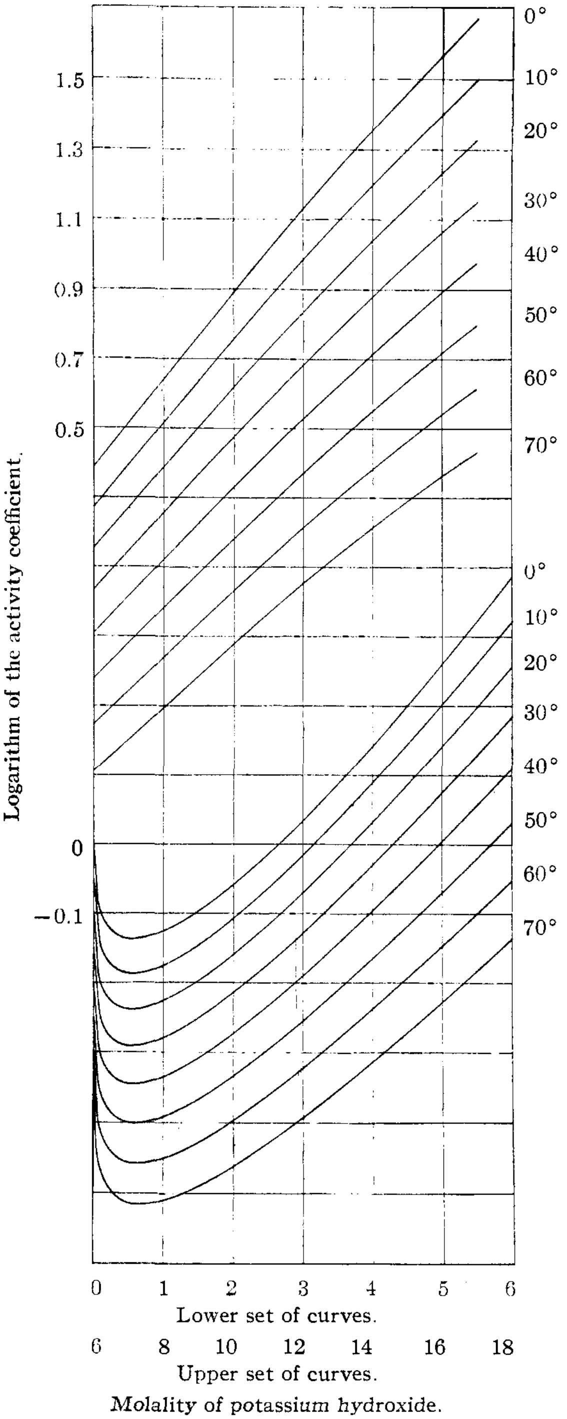

Fig. 1.—Isotherms for the logarithm of the activity coefficient of potassium hydroxide. The curves for the concentration range 6 to 17.5 molal are plotted on half the scale of those for the range 0 to 6 molal. The figures on the ordinates are for 0°; for each 10° rise in temperature the ordinate is shifted by 0.05 for the lower set of curves, and by 0.1 for the upper set.

possibility of specific effects arising in very concentrated hydroxide solutions cannot be ignored.

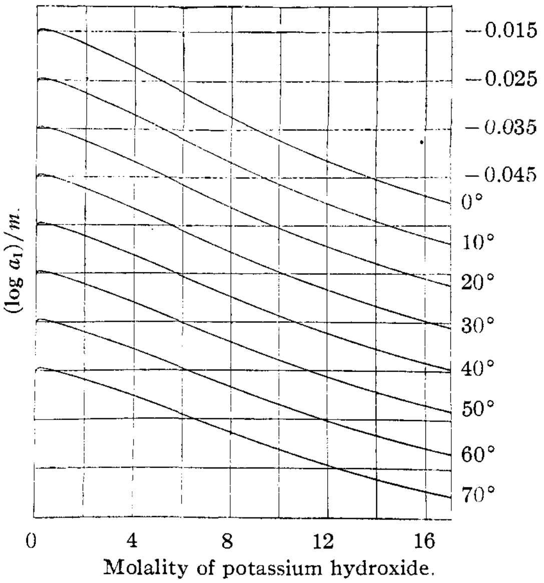

Fig. 2.—Isotherms for the function (log $a_1$)/$m$ for aqueous solutions of potassium hydroxide. The figures on the ordinates are for 0°; for each 10° rise in temperature the ordinate is shifted by 0.010.

In a comparison of the curves for log $\gamma$ for sodium and potassium hydroxides and hydrochloric acid we find that with increasing temperature and concentration they approach each other rapidly, the large individual differences observed at lower temperatures and moderate concentrations tending to disappear. A study of the behavior of these curves at concentrations or temperatures considerably above those previously employed would be of great interest.

A direct determination of log $a_1$ from electromotive force measurements on the cell Pt,$H_2$/$KOH_{(m)}$/HgO-Hg has been attempted by Shibata, Kobayashi and Furukawa,[19] but the values reported by them differ appreciably from ours, which are in good agreement with the available experimental vapor pressure data.

An attempt to determine the relative partial molal heat contents and heat capacities subjects the original data to a very severe test, since the evaluation of these quantities involves the first and second differential coefficients of the original results with respect to the temperature. Values have been calculated for the relative partial molal heat content of the solute and compared with those of Harned and Cook[12] and Rossini,[20] whose computation was based on the calorimetric determinations of Richards and Rowe[21] and Pratt.[22] The calculation gives in both cases what might seem to be only fair agreement. This is due partly to the very high accuracy required in the basic experimental work, and partly to the method of compu-

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(19) Shibata, Kobayashi and Furukawa, *J. Chem. Soc., Japan*, **52**, 404 (1931).

(20) Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

(21) Richards and Rowe, This Journal, **43**, 770 (1921).

(22) Pratt, *J. Franklin Inst.*, **186**, 663 (1918).

tation employed. The use of quadratic equations instead of cubic equations for the coefficients of equation 3 changes the value of $\overline{L}_2$ by over 70 calories per mole at a concentration of 2 molal and 18°, although the changes so produced in the values of the coefficients themselves amount to a few tenths of a per cent. at most. Actually the agreement between our results and those obtained by Rossini is quite respectable, as is shown by the following comparison for a temperature of 18°

| $m$ | 0.09 | 0.16 | 0.25 | 0.36 | 0.64 | 1.00 | 1.44 | 1.96 |
|---|---|---|---|---|---|---|---|---|
| $\overline{L}_2$, cal./mole, this study | 145 | 168 | 186 | 198 | 218 | 242 | 292 | 374 |
| $\overline{L}_2$, cal./mole, Rossini | 131 | 145 | 148 | 147 | 147 | 137 | 164 | 207 |

No direct comparison with the work of Shibata and associates[18] is possible, but from their measurements can be derived values of $E$ and $\mathrm{d}E/\mathrm{d}T$ for the cell

$$\mathrm{Hg-HgO/KOH}(m)/K_x\mathrm{Hg/KOH}(m_\mathrm{r})/\mathrm{HgO-Hg}$$

for which there holds the relation

$$FE - FT\,(\mathrm{d}E/\mathrm{d}T) = \overline{L}_2(m) - \overline{L}_2(m_\mathrm{r}) + {}^1/_2\overline{L}_1(m_\mathrm{r}) - {}^1/_2\overline{L}_1(m) \quad (4)$$

Values of the right-hand side of the equation calculated from their data differ by an average of 100 calories from those calculated for the left-hand side from our data, over a concentration range from one to twenty molal at 25°.

In the case of the relative partial molal heat capacity of the solute, our values differ from those of Harned and Cook[12] by an average of only one calorie per degree per mole for concentrations up to four molal in the temperature range from 0 to 25°. The average difference between our results and the direct calorimetric measurements of Gucker and Schminke[23] at 25° is less than three calories per degree per mole.

In the calculation of the relative partial molal entropy of the solute and solvent an interesting result was obtained. At high solute concentrations on each isotherm the values obtained for these quantities were constant within the experimental error, the entropy level for both solute and solvent changing almost linearly with the temperature. This behavior is illustrated for the solute in Fig. 3. The deviations of the entropy changes of the solvent in concentrated solutions from the requirements of the limiting law should be connected with definite structural changes, and they will be of the greatest interest when a more adequate theory is available. The practically constant values obtained for the relative partial molal entropies at high concentrations of potassium hydroxide would seem to suggest evidence for a structural constancy of the solutions over a large concentration range.

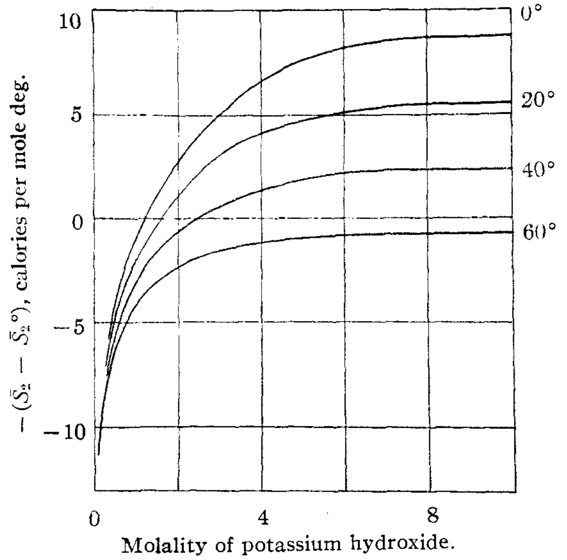

Fig. 3.—Isotherms for the relative partial molal entropy of the solute in aqueous solutions of potassium hydroxide.

## Summary

The electromotive force of the cell Pt,$H_2$/KOH($m$)/$K_x$Hg/KOH($m_r$)/$H_2$,Pt has been measured at a number of hydroxide concentrations up to 17 molal over the temperature range from 0 to 70°. Various thermodynamic properties of both solute and solvent were computed and compared with earlier, pertinent data in the literature.

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[23] Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932).