[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Hydrochloric Acid–Hydrobromic Acid Mixtures at Constant Total Molality

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The most extensive studies of the activity relationships of mixed electrolytes at constant ionic strength have dealt with uni-univalent electrolytes with a common ion—usually an alkali or halide ion. The systems salt–acid,[1] salt–salt,[2,3] and salt–base[4] have been investigated in considerable detail. The only comparable work on the remaining combinations, base–base and acid–acid is in a paper by Murdoch and Barton[5] on the activity coefficient of hydrochloric acid in perchloric acid solutions. Their measurements are confined to 25°, and they expressed some doubt regarding the formal relationship observed. The present study of hydrochloric acid–hydrobromic acid mixtures was designed to yield more complete information on acid systems, and to test the reliability of the silver–silver bromide electrode in the presence of considerable concentrations of chloride ions.

For this purpose we have measured the electromotive forces of cells of the type

$$\mathrm{H_2} \mid \mathrm{HCl}(m - mx),\ \mathrm{HBr}(mx) \mid \mathrm{AgBr\text{-}Ag}$$

at 5° intervals from 0 to 45°, and for a total molality $m = 0.5$. The proportion, x, of hydrobromic acid to total solute concentration was varied from 1 to 0.167, or 0.143. At 25° a series of results was also obtained for $m = 1$. The activity coefficient of hydrobromic acid in the presence of hydrochloric acid is given by the relation

$$-\log \gamma_{\mathrm{HBr(HCl)}} = \log m + 1/2 \log x + (E - E_0)/2k \qquad (1)$$

in which E_0 is the electromotive force of the cell containing pure hydrobromic acid at unit activity, and $k = 0.00019844T$.

Materials and Technique.—Two samples of each acid were employed. Samples A were Baker "Analyzed" reagents used without further purification. Samples B were twice redistilled from an all-glass apparatus. The sample B hydrobromic acid was diluted with oxygen-free conductivity water, and kept under pure hydrogen in the dark. All stock solutions were about 1 m, and were analyzed in triplicate by precipitation of the silver salts. To guard against the possibility of a systematic analytical error, the hydrobromic acid concentration was checked by titration against sodium carbonate. Concentrations were established to ±0.05%. All weighings were corrected for buoyancy of air.

Oxygen was excluded by the usual "vacuum technique" employed in preparing the cell solutions, and in filling the cells. Since the weight of water vaporized in this process could not be controlled accurately, the final concentrations of the cell solutions differed by about 1% from exactly 0.5, or 1 m. Proper corrections, amounting at most to a few tenths of a millivolt, were applied to make the observed electromotive forces correspond to the desired round molalities. The usual pressure and temperature corrections were made to adjust the readings to a hydrogen pressure of one atmosphere. Duplicate cells were filled with each solution as a check on the reliability of the electrodes, and the exclusion of air during manipulation. After a given pair of cells had been used over the temperature interval 0 to 20°, they were refilled with fresh solution and fitted with new electrodes before being used for the 25 to 45° range.

The silver–silver bromide electrodes were of the thermal type. They were prepared in the same manner and from the same materials as those of Owen and Foering.[6] The same hydrogen electrodes and measuring equipment were also employed. The standard cells were recalibrated.

Results and Discussion

At constant total molality, the variation of $\log \gamma_{\mathrm{HBr(HCl)}}$ with x is expected[1,2,3,5] to follow the linear relation

$$\log \gamma_{\mathrm{HBr(HCl)}} = \log \gamma_{\mathrm{HBr}} - (1 - x)m\alpha_{\mathrm{HBr(HCl)}} \qquad (2)$$

as a first approximation. Here γ_{HBr} refers to pure hydrobromic acid solutions at concentration m, and $\alpha_{\mathrm{HBr(HCl)}}$ is a parameter, characteristic of the system, but independent of x. We have calculated[7] values of $\log \gamma_{\mathrm{HBr(HCl)}}$ from our electromotive force data by equation (1), and plotted them against x in Fig. 1. The *radii* of the circles represent the effect of an uncertainty of 0.05 mv. in E, or approximately 0.1% in γ. This is the order of the concordance of duplicate cell readings, and since values of $\log \gamma$ can be read easily from the plots with this precision, the usual tabulation of x, E, and $\log \gamma$ has been dispensed with.

It is apparent from the figure that equation (2) is in satisfactory accord with our results over the

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[1] Harned, THIS JOURNAL, **57**, 1865 (1935).

[2] Scatchard and Prentiss, *ibid.*, **56**, 2320 (1934).

[3] Owen and Cooke, *ibid.*, **59**, 2273 (1937).

[4] Harned and Cook, *ibid.*, **59**, 1290 (1937).

[5] Murdoch and Barton, *ibid.*, **55**, 4074 (1933).

[6] Owen and Foering, *ibid.*, **58**, 1575 (1936).

[7] The values of E_0 employed are given by equation (2) of the paper by Owen and Foering.[6]

range in x covered by the data. The slopes of the lines yield values of α which can be expressed by

$$\alpha_{\mathrm{HBr(HCl)}} = 0.018_0 - 0.62 \times 10^{-4}t \qquad (3)$$

for the $m = 0.5$ series from 0 to 45°. The dashed line for the $m = 1$ series at 25° yields $\alpha_{\mathrm{HBr(HCl)}} = 0.016_0$. The *relative* accuracy with which α may be read from the plots is probably no better than ±0.0005. At 25° $\alpha_{\mathrm{HBr(HCl)}}$ may therefore be considered constant between $m = 0.5$ and $m = 1$, and, judging by the behavior of other systems,[1] this approximate equality probably is maintained over a considerable temperature range.

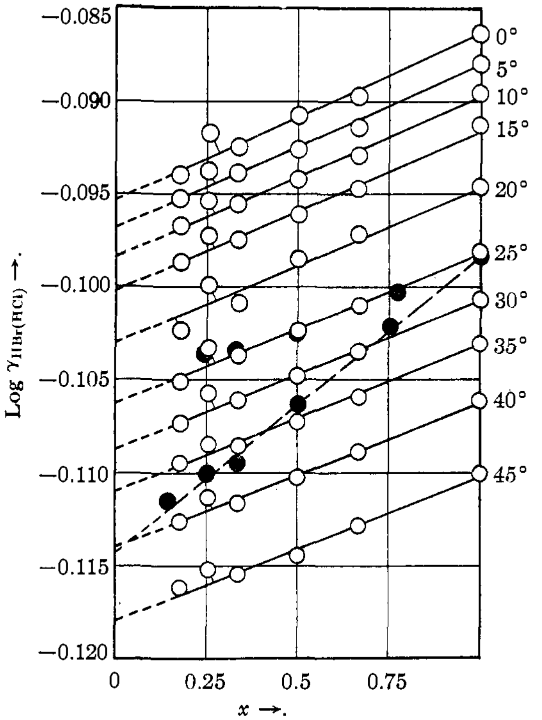

Fig. 1.—Determination of $\alpha_{\mathrm{HBr(HCl)}}$: ○, Samples A; ●, samples B. Dashed line is for $m = 1$ at 25°. Ordinates for this series have been lowered by 0.04586 to bring it within the plot.

The value of $\alpha_{\mathrm{HCl(HBr)}}$ can be calculated from $\alpha_{\mathrm{HBr(HCl)}}$ and the osmotic coefficients of the pure acid solutions by[1,3]

$$\alpha_{\mathrm{HCl(HBr)}} = \alpha_{\mathrm{HBr(HCl)}} - (\varphi_{\mathrm{HBr}} - \varphi_{\mathrm{HCl}})\,0.8686/m \qquad (4)$$

upon the assumption that hydrochloric acid obeys a relation analogous to equation (2). The osmotic coefficients have been evaluated from the results of Harned, Keston and Donelson[8] on hydrobromic acid, and of Harned and Ehlers[9] on hydrochloric acid. All of the quantities involved in equation (4) are recorded in Table I.

TABLE I

SUMMARY OF RESULTS

$t°$	m	φ_{HBr}	φ_{HCl}	$\alpha_{\mathrm{HBr(HCl)}}$	$-\alpha_{\mathrm{HCl(HBr)}}$
0	0.5	0.999	0.984	0.018	0.008
15	0.5	.995	.978	.017	.013
25	0.5	.993	.974	.016	.017
35	0.5	.989	.970	.016	.017
45	0.5	.985	.966	.015	.018
25	1	1.072	1.039	.016	.013
	±Δ	0.004	0.001	.002	.006

It will be observed that the temperature coefficients of $\alpha_{\mathrm{HBr(HCl)}}$ and $\alpha_{\mathrm{HCl(HBr)}}$ are both negative. Harned[1] has shown that the temperature coefficient of $\alpha_{\mathrm{HCl(NaCl)}}$ is negative, while that of $\alpha_{\mathrm{NaCl(HCl)}}$ is positive. Both $\alpha_{\mathrm{HBr(HCl)}}$ and $\alpha_{\mathrm{HCl(HBr)}}$ show negligible variation with concentration within the limited range studied. Their sum is very small at all temperatures and concentrations, indicating that the osmotic coefficient of the mixtures closely approximates the linear variation with x originally postulated by Brönsted.[10] The consistency of the data plotted in Fig. 1 and the fact that the concordance of duplicate cells was usually better than 0.05 mv. indicate that the silver–silver bromide electrode is reproducible and reversible in the presence of considerable concentrations of chloride ions. This is also borne out by the work of Reedy[11] on decomposition potentials.

Considering the *precision* of the various data used in our calculations, we regard the above conclusions as satisfactorily established, but the *absolute* magnitudes of some of the quantities in Table I are in considerable doubt. To illustrate the uncertainty in absolute magnitudes, we have estimated the *maximum* errors produced by given uncertainties in the original data. For this purpose we assume errors of ±0.4 mv. in the evaluation of γ_{HBr}, ±0.1 mv. in γ_{HCl}, and ±0.2 mv. in the variation of $\gamma_{\mathrm{HBr(HCl)}}$ with x. These assumptions are based upon considerations discussed in the concluding paragraphs. Their effects upon the derived quantities are indicated in Table I as ±Δ.

Although the evaluation of $\alpha_{\mathrm{HBr(HCl)}}$ is independent of E_0, and the absolute magnitude of log $\gamma_{\mathrm{HBr(HCl)}}$, it is subject to the condition that the silver–silver bromide electrode is thermodynamically reversible. Recent investigations[6,8,12] of this electrode attest its reversibility, but

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[8] Harned, Keston and Donelson, THIS JOURNAL, **58**, 989 (1936).

[9] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

[10] Brönsted, *ibid.*, **45**, 2898 (1923).

[11] Reedy, *Am. J. Science*, **40**, 281, 400 (1915).

[12] (a) Harned and Donelson, THIS JOURNAL, **59**, 1280 (1937); (b) Keston, *ibid.*, **57**, 1671 (1935).

it has been pointed out[8] that the discordance between the results of the several studies is as much as 0.2 to 0.5 mv. Analogous studies with the silver–silver chloride electrode[9,13] agree within 0.1 mv. Our own electromotive forces in pure hydrobromic acid solutions at 25° are 0.1185 and 0.0775 v. at 0.5 and 1 m, respectively, which are 0.3 to 0.6 mv. lower than results previously reported.[8] It is improbable that this discordance is due to analysis, as it corresponds to errors of the order of 0.5 to 1%. It is attributed more readily to impurities in the solution and electrode constituents, but further purification of the commercial reagents employed was shown to be without effect in this as well as in a previous study.[6] It is noteworthy in this connection that sample B of hydrobromic acid, which was protected from oxygen and exposure to light, gave the same results as the unprotected sample A. As a check on the preparation of the thermal type electrodes, the measurements on four cells were repeated with the electrolytic variety. The concordance was within 0.1 mv. In fact, the only irregularities apparent in our measurements occurred when x was less than 0.1, or when the cells had been in operation all day. In the latter case a drop in e. m. f. of about 0.1 mv. in six or eight hours undoubtedly caused the irregularity in temperature coefficient which can be observed in Fig. 1 between 20 and 25°.

At 25° we made $x = 0.063$ for sample B acids at 0.5 and 1 m, and obtained readings 0.44 and 0.34 mv. higher than required by the extensions of the lines in Fig. 1. Unfortunately the time available for measurements did not allow us to investigate the reproducibility of these "high" results. Accordingly we have disregarded them entirely, and *limited our conclusions to values of x greater then one-seventh.*

Summary

1. The silver–silver bromide electrode was studied in mixtures of hydrobromic acid and hydrochloric acid and found to give reproducible results over a sevenfold change in relative concentration.

2. Log γ for hydrobromic acid was determined in the mixtures at constant total molality from 0 to 45°. It was shown to vary linearly with relative concentration. The rate of variation decreases with rise in temperature, but is practically independent of concentration between 0.5 and 1 m.

3. The rate of variation of log γ for hydrochloric acid in the mixtures was estimated, and found to be of the same order of magnitude as that for hydrobromic acid, but of opposite sign. Its temperature coefficient is also negative.

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[13] (a) Randall and Young, THIS JOURNAL, **50**, 989 (1928); (b) Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936).

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Composition of Coconut Shells[2]

BY L. C. FLECK,[3] W. G. VAN BECKUM[4] AND GEO. J. RITTER[4]

Although coconut shells have been used extensively for making a highly absorbent charcoal, little if any published information on their composition is available. In order to supply some information on the subject, the Forest Products Laboratory presents the following results of an analysis of the shells made in coöperation with the Barnebey–Cheney Engineering Company of Columbus, Ohio. The standard methods employed on woods were used in this analysis.

Analysis and Results

Coconut shells in the form of a meal (60–80 mesh) were analyzed according to the following determinations: moisture, ash, cold water soluble material, hot water soluble material, 1% sodium hydroxide soluble material, ether soluble material, pentosans, methoxyl, and acetic acid by methods described by Schorger;[5] holocellulose by the chlorine–alcohol–ethanolamine method developed by Van Beckum and Ritter;[6] Cross and Bevan cellulose by a modified Cross and Bevan method

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[1] Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

[2] Presented before the American Chemical Society, Rochester, N. Y., September, 1937.

[3] Formerly with the Forest Products Laboratory.

[4] U. S. Forest Products Laboratory, Madison, Wis.

[5] A. W. Schorger, *Ind. Eng. Chem.*, **9**, 556 (1917).

[6] W. G. Van Beckum and Geo. J. Ritter, *Paper Trade J.*, **104**, 19, 49 (1937).