(b) Using the above values and that accepted by Spencer and Mote[8] for the reaction

$$HgO = Hg + \tfrac{1}{2}O_2 \quad \Delta F_{298} = 13{,}850$$
$$3PbO + \tfrac{1}{2}O_2 = Pb_3O_4 = -6{,}910 \quad (4)$$
$$Pb_3O_4 + O_2 = 3PbO_2 = -9{,}580 \quad (5)$$
$$PbO + \tfrac{1}{2}O_2 = PbO_2 = -5{,}500 \quad (6)$$

(c) Using the preceding values and that calculated by Spencer and Mote[8] for the reaction

$$Pb + \tfrac{1}{2}O_2 = PbO \quad \Delta F_{298} = -45{,}100$$
$$3Pb + 2O_2 = Pb_3O_4 = -142{,}210 \quad (7)$$
$$Pb + O_2 = PbO_2 = -50{,}600 \quad (8)$$

(8) Spencer and Mote, THIS JOURNAL, **54**, 4618 (1932).

Summary

1. The potentials of two electrodes have been measured and the potential of a third electrode calculated from these. The values are

$PbO(s)-Pb_3O_4(s)-OH^-$ + 0.2488 ± 0.0005 volt
$Pb_3O_4(s)-PbO_2(s)-OH^-$ + 0.1295 ± 0.001 volt
$PbO(s)-PbO_2(s)-OH^-$ + 0.280 ± 0.001 volt

2. The free energy changes have been calculated from the measured values of the cells.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Compressibility of Aqueous Solutions

BY EDITH H. LANMAN AND BEVERIDGE J. MAIR

Introduction

The compressibility coefficients of many aqueous solutions of both electrolytes and non-electrolytes have been determined during the past fifty years, and the data obtained in this field, prior to the year 1919, have been summarized by Cohen and Schut in "Piezochemie." Since that time, accurate determinations of the compressibility of aqueous solutions of various organic substances have been determined at Harvard, but, at the time this work was undertaken, no further work had been done on solutions of electrolytes. The existing data in this field had been obtained at different temperatures over varying pressure ranges, and at random concentrations. It therefore seemed worth while to redetermine the compressibility coefficients of certain inorganic salts and their acids and bases, all at the same temperature, over the same pressure range, and at equivalent concentrations.

The substances chosen were the chlorides and hydroxides of lithium, sodium and potassium, hydrochloric and acetic acids, and potassium acetate. The compressibility of glacial acetic acid was also determined. Determinations were made at three concentrations for each substance: *i. e.*, one mole of substance to twenty-five moles of water, one to fifty, and one to one hundred. All measurements were made at 25° and between 100 and 300 megabars.

Preparation of Materials and Analysis of Solutions.—The salt solutions were made up from Baker analyzed chemicals. It was not considered worth while to recrystallize these substances, since an impurity of several tenths of a per cent. could not cause a change in compressibility which could be detected (*e. g.*, the difference in compressibility of $NaCl\cdot25H_2O$ and $KCl\cdot25H_2O$ is only 0.78×10^{-6}). The concentrations of the chloride solutions were determined by precipitation with silver nitrate, and the more dilute solutions were made up by adding the calculated amount of water to a weighed portion of the standard solution.

The hydrochloric acid was prepared by distilling one to one C. P. acid, and noting the pressure during distillation. The concentration was then computed from the pressure,[1] and verified by precipitation with silver nitrate. This was then diluted by adding the calculated amount of water to give $HCl\cdot25H_2O$ (and $HCl\cdot50H_2O$ and $100H_2O$).

The sodium hydroxide solution was prepared by dissolving the C. P. base in water in a gold dish to prevent contamination by silica. Only a small amount of water was used in order that the less soluble carbonate might remain undissolved. The solution was then filtered, diluted to the approximate concentration desired, and stored in a Pyrex bottle. Carbonate was then tested for by adding definite amounts of barium chloride solution (of known concentration) to samples of the solution. The precipitates were allowed to settle, the supernatant liquids decanted and Ba^{++} tested for by sulfuric acid. The amount of Ba^{++} necessary to precipitate the carbonate was then calculated and added to the sodium hydroxide solution. After allowing the precipitate to settle, the solution was siphoned into a bottle containing carbon dioxide-free air. The solution was at all times protected from contamination with carbon dioxide by means of soda lime. Solutions of potassium hydroxide and lithium hydroxide were prepared in a similar manner.

The concentrations were determined by titrating against the hydrochloric acid, using phenolphthalein as an indicator. Weight burets were used. The more dilute solutions were made up accurately by addition of the calcu-

(1) Hulett, THIS JOURNAL, **31**, 390 (1909).

lated amount of water, and checked by titration against hydrochloric acid.

The acetic acid solutions were made up by diluting C. P. glacial acetic acid, and were titrated against the lithium hydroxide using phenolphthalein. $KAc \cdot 51H_2O$ and $KAc \cdot 101H_2O$ were prepared by adding equivalent amounts of KOH and HAc.

A set of calibrated weights was used in all analytical work, and vacuum corrections were applied. In the gravimetric analyses, the concentrations were computed from the average of two analyses which checked to within 5 parts in 10,000 (with the exception of the hydrochloric acid. In this case, the analyses checked only within 0.13%, but this concentration was further checked by calculation from the pressure reading during distillation). In the one instance in which the concentration of a diluted solution was determined by analysis as well as computed from the amount of water added, the results checked within 0.02%. The concentrations of solutions determined by titration were calculated from two or more analyses which checked in general to less than 0.03% (never more than 0.1%). The density determinations were accurate to less than one part in 10,000, the greatest difference in accepted results being 0.02%. When plotted against concentration, smooth curves were obtained and points from the data of Baxter and Wallace[2] lay on these curves. The densities represent the weight *in vacuo* of one cc. of solution.

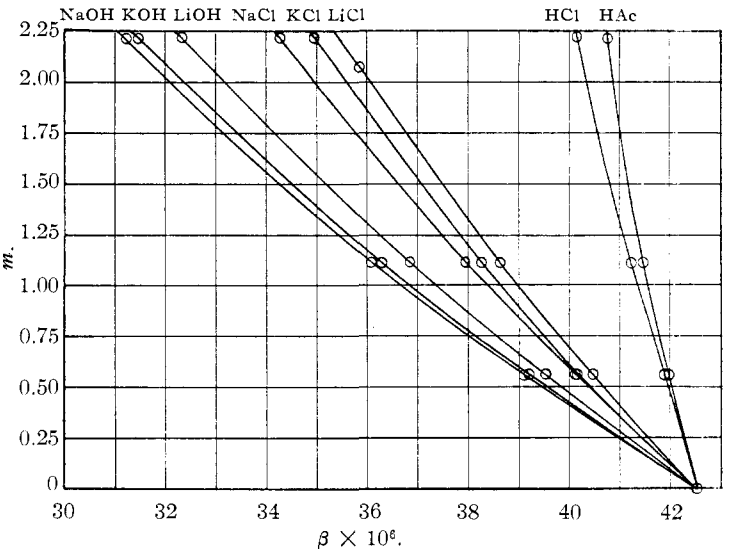

Fig. 2.—The compressibility plotted against m.

Method and Apparatus

The compressibility determinations were made by the method in use at Harvard.[3]

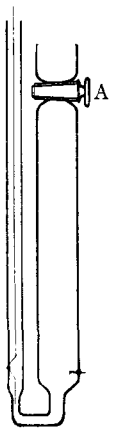

Fig. 1.—Piezometer.

The glass piezometer used is shown in Fig. 1. It was a modified form of the piezometer used for fused salts,[4] and was found simpler to fill than that generally used for liquids.[3] It was fitted at A with a stopcock having a solid barrel, instead of the stopper ordinarily used. An open cup at the top contained mercury into which the platinum wire dipped. Although this stopcock sometimes stuck, especially when in use with the alkali solutions, it was always possible to remove it easily by means of an Achesel stopcock remover. The piezometer was filled with solution by means of a funnel drawn out to a long capillary which was inserted at A. The stopcock, which was well-ground and provided with a minimum amount of Ramsay grease, was then inserted and turned until it "set," *i. e.*, it could be turned no more.

All determinations were made at 25° (±0.01). The pressure was measured fifteen minutes after application, and the compressibility calculated from the following equation

$$\beta_{100-300} = \frac{(w - w_1)\,D}{13.550\,W\,200} + \beta'$$

where β = compressibility per cc. per megabar

β' = compressibility of mercury = 4×10^{-6}

w = weight of mercury added corresponding to a change in pressure of 200 megabars

w_1 = weight of mercury corresponding to 200 megabars (=0.1473 grams) when piezometer is filled with Hg only

D = density of solution

W = weight of solution

13.55 = weight of 1 cc. of mercury at pressure of 300 megabars

Instead of adopting the usual procedure of adding random amounts of mercury and plotting the weights against the corresponding pressure in megabars, and then reading from the curve the weights corresponding to just 300 and 100 megabars, considerable time was saved by taking two points only, one close to 300, and one close to 100, *i. e.*, mercury was added until the pressure on the scale corresponded to approximately 300 megabars. After a period of fifteen minutes, the pressure was determined accurately in the usual manner by adding weights until the circuit was just broken. Mercury was then removed until the scale reading approximated 100 megabars, and, after fifteen minutes, the pressure was accurately determined again. The first point was then checked by putting back the mercury which had been removed. As these two points were close to 300 and 100 megabars, respectively, the weight of mercury corresponding to a change of pressure of exactly 200 megabars was calculated by direct proportion. In the two cases in which both methods were used, the results checked within one part in 3500.

The weight of mercury equivalent to a change of pressure of 200 megabars when the piezometer was filled with mercury alone was first determined (=0.1473 g.). The

(2) Baxter and Wallace, THIS JOURNAL, **38**, 70 (1916).

(3) Richards and Shipley, *ibid.*, **38**, 989 (1916), and previous papers.

(4) Richards and Jones, *ibid.*, **31**, 158 (1909).

compressibility of water at 25° was then determined, giving the value 42.44 × 10^{-6}. Then, after two or more runs on each of twenty-seven solutions, the water value was redetermined: result 42.62 × 10^{-6}. The average value, 42.53 × 10^{-6}, which was used in calculations, differs from the extremes by less than 0.3%. No results on the solutions were accepted which did not check to 0.3%; in general, they were in better agreement than this.

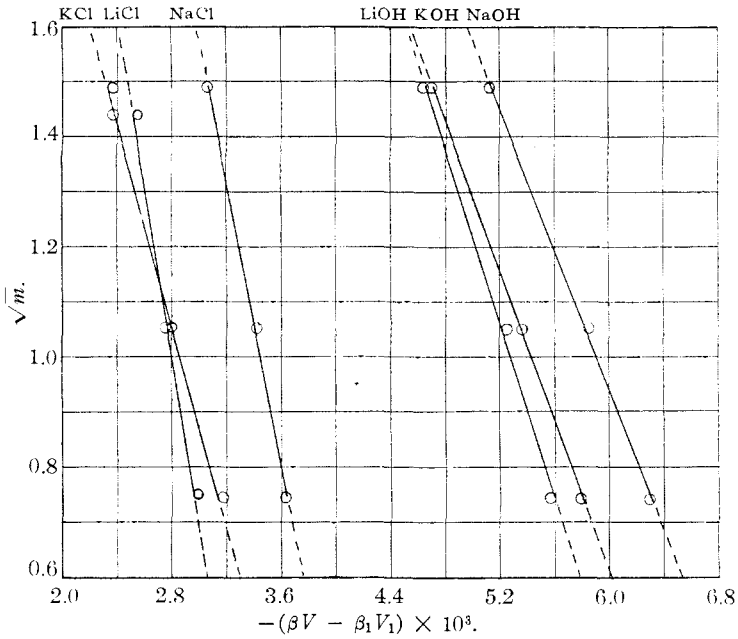

Fig. 3.—The apparent molal compressibility plotted against $\sqrt{m}$.

Data and Results

All data are recorded in Table I. Concentrations are expressed both in moles of water per mole of solute (column 1); and in moles of solute per 1000 g. of water (m, column 2). V and V_1 are, respectively, the volume of solution containing one mole of solute, and the volume of water in which the mole of substance is dissolved. β is the compressibility coefficient of the solution, and β_1 that of water. The apparent molal compressibility ($\beta V - \beta_1 V_1$) of each substance has been calculated and recorded in column 7.

The compressibility coefficients are plotted against the concentrations (expressed in moles of solute per 1000 g. of water) in Fig. 2. At equivalent

TABLE I

Solute	Moles H_2O per mole of solute	m	Density	V	V_1	$10^6\beta$	$10^3(\beta V - \beta_1 V_1)$
LiCl	26.74	2.0757	1.04405	502.07	483.20	35.85	−2.55
	49.99	1.1103	1.02334	921.53	903.31	38.64	−2.80
	98.46	0.5638	1.01094	1796.52	1779.04	40.44	−2.99
NaCl	25.02	2.2182	1.08013	471.50	452.16	34.28	−3.06
	50.04	1.1094	1.04061	922.42	904.10	37.97	−3.42
	100.08	0.5546	1.01952	1825.82	1808.35	40.12	−3.63
KCl	24.99	2.2216	1.09043	481.17	451.45	34.96	−2.37
	49.93	1.1117	1.04642	930.83	902.17	38.26	−2.75
	100.04	0.5549	1.02256	1835.43	1807.62	40.15	−3.17
KAc	51.29	1.0823	1.04534	977.77	926.72	37.02	−3.21
	101.17	0.5487	1.02274	1878.05	1828.04	39.55	−3.45
LiOH	25.04	2.2168	1.05265	451.29	452.45	32.35	−4.64
	50.08	1.1083	1.02640	902.42	904.97	36.82	−5.25
	100.12	0.5544	1.01230	1805.54	1809.14	39.52	−5.57
NaOH	25.01	2.2192	1.08670	451.46	451.94	31.23	−5.12
	50.09	1.1081	1.04391	902.84	905.15	36.15	−5.85
	100.15	0.5542	1.02114	1806.12	1809.65	39.12	−6.29
KOH	25.05	2.2160	1.09853	461.85	452.59	31.49	−4.70
	50.03	1.1095	1.05039	911.44	903.94	36.29	−5.36
	100.16	0.5542	1.02461	1815.88	1809.81	39.19	−5.79
HCl	24.99	2.2218	1.03370	470.79	451.53	40.17	−0.29
	50.09	1.1082	1.01623	923.87	905.08	41.22	−0.40
	100.16	0.5542	1.00704	1828.09	1809.85	41.93	−0.31
HAc	25.24	2.1992	1.01315	508.06	456.06	40.81	+1.34
	50.16	1.1065	1.00578	958.211	906.40	41.47	+1.20
	100.20	0.5540	1.00173	1861.99	1810.52	41.99	+1.20
HAc	Glacial		1.04484			76.52	
H_2O			0.99704			42.52	

concentrations, the bases are the least compressible, the acids the most, and the salts occupy the intermediate position. The order of increasing compressibility of the alkali bases and chlorides is not, however, in the order of increasing atomic weights, as is the case with the solid chlorides.

A study of the existing compressibility data has been made by Gucker[5] in which it has been shown that the apparent molal compressibility is a linear function of the square root of the concentration, over a wide range of concentration, temperature, and pressure. Results based on the data given in this paper were included in this study, and were found to be in agreement with this relationship, as is shown in Fig. 3.

Fuller discussion of these results is taken up in a later paper by Gucker.[6] He states here that Scott,[7] who has made a more complete study of the compressibility of the alkali halides, has independently reached similar conclusions.

(5) Gucker, THIS JOURNAL, **55**, 2709 (1933).

(6) Gucker, *Chem. Rev.*, **8**, 117 (1933).

Summary

The compressibility coefficients of aqueous solutions of LiCl, NaCl, KCl, LiOH, NaOH, KOH, HCl, HAc, and KAc have been determined, each one at three concentrations; one mole of solute to twenty-five moles of water, one to fifty, and one to one hundred. The compressibility of glacial acetic acid was also determined. All measurements were made at 25°, and between 100 and 300 megabars.

The linear relationship between the apparent molal compressibility and the square root of the concentration which was pointed out by Gucker, has been confirmed by these data.

(7) Scott, to be submitted to *J. Phys. Chem.*

BRYN MAWR, PA. RECEIVED NOVEMBER 8, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OREGON STATE COLLEGE]

Studies on Hydrazine: The Dissociation Pressures of Hydrazinium Dichloride and Dibromide

BY B. E. CHRISTENSEN AND E. C. GILBERT

It has been shown by Hantzsch, Brönsted, Hall and others[1] that the strength of an acid in a given solvent depends upon three factors, the nature of the solvent, its dielectric constant, and the intrinsic affinity of the anion for the proton. In the case of acids such as hydrobromic and hydrochloric in the solvent water, the affinity of the solvent for the proton is so much greater than that of the anion that the reaction

$$HX + H_2O \longrightarrow X^- + H_3O^+$$

goes practically to completion and there is no marked difference in the strength of the two acids. In a solvent which did not have as great affinity for the proton, differences in the third factor, *i. e.*, the intrinsic affinity of the anion, should be more apparent. Measurements in other solvents[1a,1b,2] have indeed shown that under such conditions hydrobromic acid is stronger than hydrochloric, *i. e.*, the bromide ion shows less affinity for the proton than does the chloride ion.

The thermal dissociation of the phosphonium and ammonium halides[3] offers an interesting verification of this same viewpoint. Since this reaction involves the formation of gaseous molecules from the halide ion and a proton in a "solvent" (air or the vapor phase) which has no proton affinity, it might be expected that the halide ion having lesser affinity for a proton would form fewer molecules and its salt would show a lower dissociation pressure This is found to be true, the bromide exhibiting a lower dissociation pressure than the chloride.

The hydrazinium dihalides might be expected to furnish further verification. When heated slightly above 100° the solid salts dissociate.[4]

$$N_2H_4{\cdot}2HX \rightleftharpoons N_2H_4{\cdot}HX + HX$$

The dissociation is reversible and the extent depends upon the temperature. The dissociation pressures, however, have never been determined. The difluoride is volatile and sublimes undecomposed, while the iodide decomposes upon heating.[4] Curtius and Schultz, however, pre-

(1) (a) Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923); (b) Brönsted, *Ber.*, **61**, 2048 (1928); (c) Hall, *J. Chem. Ed.*, **7**, 782 (1930).

(2) Schreiner, *Z. physik. Chem.*, **111**, 419 (1929).

(3) Landolt-Börnstein-Roth, "Tabellen," Fourth edition, 1912, p. 400.

(4) Curtius and Schultz, *J. prakt. Chem.*, [2] **42**, 521 (1890).