two reactions a selected value of D°_{298}(CaF) = 127.5 ± 2.5 kcal. mole^{-1} appears to be appropriate.

The thermodynamic consistency of this value can be tested by considering the following reactions. For example, Reactions 3 and 4 may be combined to give Reaction 2 and indicate a value of D°_{298}(CaF) = 126 ± 3 kcal. mole^{-1}, in good agreement with the result of Reactions 1 and 2. Reactions 5, 6, and 7 lead to identical enthalpies of formation for BeF, and one can infer that the value of D°_{298}(CaF) equal to 127.5 kcal. mole^{-1} is at least as reliable as, and self-consistent with, the $\Delta H^\circ_{298,\ \text{atoms}}$($BeF_2$) and D°_{298}(AlF) values.

From the D°_{298}(CaF) value of 127.5 kcal. mole^{-1} and the enthalpy of Reaction 8 one obtains $\Delta H^\circ_{298,\ \text{atoms}}$($SiF_2$) = 288.7 ± 6 kcal. mole^{-1}, whereas Reaction 9, which is independent of D°_{298}(CaF), implies $\Delta H^\circ_{298,\ \text{atoms}}$($SiF_2$) = 288 ± 2 kcal. mole^{-1}. Thus, these reactions are also consistent with a value of D°_{298}(CaF) = 127.5 kcal. mole^{-1}.

By taking the value of $\Delta H_{298,\ \text{atoms}}$ SiF_2 equal to 288 ± 2, as indicated by Reactions 8 and 9, Reactions 10 to 12 yield the following self-consistent values: D°_{298}(CaF) = 127.5 ± 2.5, D°_{298}(SiF) = 136 ± 4 (Reactions 10 and 12) or 134 ± 2 (Reaction 13), D°_{298}(GeF) = 119.8 ± 3 (Reaction 11), or 126 ± 5 (Reaction 10), all in kilocalories per mole. Hence the CaF dissociation energy is further verified. From Reaction 14 and the known enthalpies of formation, [$\Delta H f^\circ_{298}$(ScF_3) = −383.9 kcal. mole^{-1}] (*11*) and vaporization (*8*, *12*), one calculates D°_{298}(CaF) = 122 ± 8 kcal. mole^{-1}.

Thus the reactions listed in Table I, obtained by a number of different workers, support the value for D°_{298}(CaF) of 127 ± 2.5 kcal. mole^{-1} rather than the alternative value of 135 ± 7 kcal. mole^{-1}. One can similarly show that values of D°_{298}(SrF) and D°_{298}(BaF) lower than those obtained by the spectroscopic method lead to more consistent thermodynamic data. Krasnov and Karaseva (*10*) have also re-evaluated the dissociation energies of the Group IIA subhalides and suggest D°_{298}(CaF) = 125 kcal. mole^{-1} as the most reliable value. The higher values were all obtained by spectroscopic observation of reactions in flames where (*1*) the establishment of equilibrium appears less likely than for Knudsen effusion methods, (*2*) reliable absolute temperature measurements are more difficult, and (*3*) self-absorption, abnormal excitation processes, and quantitative accounting for all elements may create large uncertainties in the interpretation of experimental results.

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Activity Coefficients and Thermodynamics of Hydrobromic Acid in Methanol-Water Mixtures and Anhydrous Methanol From Electromotive Force Studies

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HARNED, Keston, and Donelson (*13*) determined the standard electromotive force of the cell, Pt; H_2 (1 atm.), HBr (m), AgBr, Ag, and the activity coefficients and certain thermodynamic functions of HBr in aqueous solutions over considerable temperature and concentration ranges. Other investigators (*12, 18, 21, 23*) have also reported standard potential of the silver-silver bromide electrode at various temperatures in water. There is as much as 0.37-mv. difference in the reported values. Hetzer, Robinson, and Bates (*16*) redetermined the standard electromotive force of the same cell in an effort to resolve a discrepancy appearing in the literature. Their results are in satisfactory agreement with the work of Harned, Keston, and Donelson, but did not confirm the later values of Harned and Donelson (*12*) and of Owen and Foering (*21*) which were in agreement. The activity coefficients that Hetzer *et al.* derived from three separate studies agreed well, suggesting that the differences in the standard potential might be attributed to differences in electrodes prepared in different ways. Keston (*18*), Harned *et al.* (*13*), and Hetzer *et al.* (*16*) used the thermal type of the silver-silver bromide electrode. Feakins and Watson (*7*) and Kanning and Campbell (*17*), using this type of electrode, measured the electromotive forces of cell 1 in 10 and 43.12 weight % methanol and pure methanol, respectively, at 25° C.

In this study electromotive forces of the reversible cell

H_2 (1 atm.) | HBr (m), X% CH_3OH, Y% H_2O | AgBr-Ag (1)

The standard potentials have been determined for the HBr cell over a range of methanol-water mixtures at 25°, 35°, and 45° C. and the thermodynamic functions of the cell calculated. The thermodynamic function gave evidence of some "uncompensated" structural change occurring in the region of 90 to 100% methanol, where the solutions are considered more basic than anhydrous methanol from Hammett acidity functions and where formation of H_3O^+ and $H_9O_4^+$ ions is postulated from conductivity studies.

were measured over the concentration ranges from 3×10^{-3} to 0.1 molal HBr in 30, 60, 90, 99, and 100 weight % methanol at 25°, 35°, and 45° C. using the thermal type silver–silver bromide electrode. The standard potentials of the silver–silver bromide electrode were calculated, and the thermodynamic functions, $\Delta G°$, $\Delta S°$, and $\Delta H°$, and the activity coefficients of hydrobromic acid in each solvent determined.

EXPERIMENTAL

Materials Used. Anhydrous methanol was prepared by the method of Bjerrum and Zechmeister (*3*) from reagent grade methanol purchased from the Fisher Scientific Co. The resulting methanol had a specific conductance, L, of 5.50×10^{-7} mho per cm. and gave a negative test for aldehydes. That this methanol was anhydrous is indicated by data of Goldenberg and Amis (*11*), who found that addition of 0.3 weight % of water to methanol of the specific conductance given here caused a decrease of 20 units in the equivalent conductance at infinite dilution, Λ_0, of perchloric acid at 25° C. The tremendous influence of this small amount of water on Λ_0 indicated that the methanol originally contained much less than 0.3 weight %, since further addition of water to alcohols (*10*) caused a reversal of the change of Λ_0—that is, an increase—but the amount of water for a similar magnitude of change in Λ_0 was about 40 weight %. Distilled water passed through a column of ion-exchange resin was used. All other chemicals—hydrogen bromide, tetrahydronaphthalene, bromine, etc.—were of reagent grade or were purified before use.

The hydrogen used was commercial tank hydrogen which was purified by passing over hot copper turnings heated to 500° to 600° C. and scrubbed by sulfuric acid and Dehydrite. Dry nitrogen used to purge the cell and the purified hydrogen gases were saturated with solvent at the same temperature at which the electromotive force measurement was being made before either one was introduced into the cell.

Electrodes. The silver–silver bromide electrodes were prepared by the thermal method of Keston (*18*). A mixture of 10% silver bromate and 90% silver oxide was made into a paste with water and painted on a platinum spiral, one end of which had been fused in a glass tube, and the coated electrode was heated at 650° C. for 7 minutes. The electrodes were then allowed to stand in a cell solution of HBr for 24 hours, and the electrodes whose potentials agreed within ±0.05 mv. were used for the measurements.

The hydrogen electrodes were the customary platinized type.

Cell Solutions. For the methanol-water mixtures, an aqueous stock solution of hydrobromic acid was prepared, of such concentration that it could be diluted by weight to the desired concentration of the cell solution. The molality of hydrobromic acid in the cell solutions, m, ranged from 3×10^{-3} to 0.1 and the methanol contents, X, were varied to 30, 60, 90, and 99 weight %.

For the anhydrous methanol cell solutions, dry hydrogen bromide was prepared by the action of bromide on tetrahydronaphthalene (*4*) and was bubbled through anhydrous methanol. Appropriate measures were taken to ensure the absence of water from the system.

The stock solutions of hydrogen bromide and the higher concentrations of the cell solutions were standardized gravimetrically by the precipitation and weighing of silver bromide. Solutions of lower concentrations were prepared by weight dilution of the appropriate stock solutions.

Cells and Measurement of Electromotive Force. For the solvents of 30, 60, 90, and 99 weight % methanol the usual H-type cells with a vacuum cock between the two electrodes were used. The cell solutions were introduced into the side of the cell containing the silver–silver bromide electrode, and argon was bubbled through the solution long enough to render the system air-free. The stopcock was then opened and the solution introduced into the side containing the hydrogen atmosphere and electrode. The electromotive force came to equilibrium within 30 minutes to 1 hour and repeatable measurements could be made for at least 6 hours.

For the anhydrous methanol solvent the cells were constructed entirely of glass and were so designed that solutions or solvent could be introduced into or removed from the cell without contact with the atmosphere. In this manner measurements were made over a range of concentrations with one silver–silver bromide electrode. The hydrogen electrode was changed with each measurement to avoid poisoning of the electrode by the methanol.

The measurements of the cell potentials were made with a Leeds and Northrup Type K-3 potentiometer, a Type 29 General Electric galvanometer, and a standard cell which was checked frequently against a standard cell certified by the National Bureau of Standards.

Solvent Properties. The densities of the solvents at 25°, 35°, and 45° C. were interpolated from the data of Foster and Amis (*9*) and the dielectric constants were interpolated from the data of Akerlof (*1*). The density, d_0, dielectric constants, D, and total vapor pressure (*5, 6*) P, of the solvents are shown in Table I (N is the mole fraction of methanol).

Table I. Properties of Solvent

Wt. % MeOH	T, ° C.	N	d_0, G./Ml.	D	P, Mm.
30	25	0.1940	0.9491	64.36	53.5
	35		0.9438	61.12	91.2
	45		0.9380	58.06	150.5
60	25	0.4574	0.8887	49.88	80.2
	35		0.8805	46.96	131.2
	45		0.8726	44.28	216.5
90	25	0.8350	0.8157	35.77	111.8
	35		0.8064	33.63	179.5
	45		0.7981	31.58	298.5
99	25	0.9824	0.7900	31.96	124.0
	35		0.7811	30.20	206.0
	45		0.7719	28.61	317.5
100	25	1.0000	0.7865	31.52	126.6
	35		0.7778	29.86	217.0
	45		0.7688	28.23	330.5

Table II. Measured Potential of HBr Cell in Water at 25° C.

m	E, Volt
0.00191	0.39615
0.00447	0.35370
0.01260	0.30166
0.02329	0.27217
0.03330	0.25242
0.04080	0.24473
0.05494	0.23040
0.07063	0.21836
0.07963	0.21267
0.09013	0.20704

RESULTS

The electromotive forces of cell 1 were measured in water at 25° C. and the data are given in Table II.

A standard molal potential of 0.07118 volt for the silver-silver bromide electrode was calculated from these data using Equation 3 and averaging all of the values over the molality range studies as done in the work by Oiwa (*20*) on HCl in methanol and water at 25° C.

Keston (*18*), Harned *et al.* (*13*), and Hetzer *et al.* (*16*) have reported values of 0.0711, 0.07105, and 0.07106 volt, respectively, for the silver-silver bromide electrode in water at 25° C.

Table III gives the data for cell 1 at all three temperatures

Table III. Electromotive Force Measurements of HBr in Methanol-Water Solvents

25° C.			35° C.			45° C.		
Molality	E_{exptl}	$E_{\text{exptl}} - E_{\text{calcd}}$	Molality	E_{exptl}	$E_{\text{exptl}} - E_{\text{calcd}}$	Molality	E_{exptl}	$_{\text{exptl}} - E_{\text{calcd}}$
				30% CH_3OH				
0.00318	0.35772	0.00005	0.00318	0.35953	0.00007	0.00318	0.36070	−0.00015
0.00454	0.34002	−0.00015	0.00488	0.33785	−0.00003	0.00488	0.33823	0.00000
0.00488	0.33652	−0.00009	0.00845	0.31974	0.00000	0.00845	0.30949	−0.00004
0.00567	0.32893	−0.00014	0.01355	0.29595	−0.00003	0.01355	0.28265	−0.00023
0.00789	0.31289	0.00000	0.01412	0.28364	−0.00028	0.01414	0.28506	0.00000
0.01158	0.29405	−0.00010	0.03154	0.24420	0.00020	0.03083	0.24255	−0.00026
0.01353	0.28646	−0.00015	0.05029	0.22108	0.00004	0.03167	0.24161	−0.00006
0.01577	0.27937	0.00018	0.07901	0.19897	0.00003	0.04922	0.21917	0.00001
0.02488	0.25729	0.00006	0.08365	0.19574	0.00001	0.05060	0.21755	−0.00008
0.03167	0.24597	0.00028				0.07971	0.19532	0.00031
0.05060	0.22327	−0.00014				0.08365	0.19314	0.00050
0.07442	0.20517	0.00001						
0.07971	0.20194	0.00001						
				60% CH_3OH				
0.00282	0.35070	−0.00007	0.00585	0.31293	0.00010	0.00585	0.30966	0.00037
0.00875	0.29614	0.00031	0.00875	0.29274	0.00034	0.00876	0.28878	0.00012
0.00996	0.29870	−0.00005	0.00899	0.29091	−0.00016	0.00900	0.28724	−0.00001
0.02705	0.24269	−0.00007	0.01613	0.26252	0.00001	0.00997	0.28215	−0.00001
0.03674	0.22818	−0.00023	0.02706	0.23861	0.00012	0.01615	0.25765	−0.00023
0.05564	0.20936	0.00003	0.03674	0.22270	−0.00005	0.02711	0.23196	−0.00007
0.07437	0.19606	0.00003	0.05451	0.20402	−0.00032	0.03685	0.21674	−0.00009
0.08772	0.18847	−0.00004	0.07792	0.18690	−0.00028	0.07482	0.18228	−0.00008
			0.08772	0.18165	−0.00023	0.07841	0.18015	0.00001
				90% CH_3OH				
0.00677	0.24578	0.00029	0.00677	0.23107	0.00003	0.00677	0.23825	0.00012
0.00853	0.23466	−0.00001	0.00854	0.21728	−0.00004	0.00853	0.22793	0.00020
0.01111	0.22263	0.00028	0.01112	0.20464	0.00033	0.01556	0.19818	−0.00029
0.02470	0.18551	−0.00019	0.01558	0.18738	−0.00047	0.02421	0.17795	−0.00007
0.03883	0.16494	−0.00026	0.02425	0.16646	−0.00023	0.02475	0.17703	0.00016
0.05013	0.15362	−0.00006	0.02475	0.16537	−0.00011	0.03895	0.15595	0.00000
0.05632	0.14887	−0.00014	0.05033	0.13167	0.00016	0.07417	0.12734	−0.00021
0.07374	0.13624	−0.00008	0.08727	0.10557	0.00002	0.08666	0.11918	0.00008
0.08666	0.12912	0.00005	0.09345	0.10267	0.00031	0.09345	0.11604	−0.00002
				99% CH_3OH				
0.01642	0.12876	0.00031	0.01196	0.13067	−0.00025	0.01350	0.11277	−0.00011
0.02900	0.10459	−0.00032	0.02388	0.10041	0.00027	0.02269	0.09034	+0.00048
0.02915	0.10442	−0.00009	0.02688	0.09561	0.00015	0.02521	0.08534	+0.00013
0.04758	0.08499	0.00018	0.03763	0.08122	0.00000	0.03918	0.06599	−0.00049
0.05125	0.08165	−0.00023	0.04891	0.07033	−0.00021	0.05116	0.05538	−0.00007
0.06678	0.07167	0.00005	0.05670	0.06474	0.00011	0.06230	0.04733	−0.00008
0.08404	0.06269	−0.00003	0.08404	0.04900	−0.00011	0.08272	0.03655	0.00041
0.08658	0.06197	0.00008				0.08411	0.03538	−0.00038
				100% CH_3OH				
0.00533	0.14702	−0.00002	0.00567	0.13311	−0.00007	0.00434	0.13509	−0.00059
0.00919	0.12248	0.00014	0.01062	0.10410	0.00015	0.00808	0.10540	−0.00018
0.01676	0.09521	−0.00001	0.01311	0.09430	0.00000	0.01552	0.07477	−0.00004
0.01762	0.09350	0.00004	0.01902	0.07759	0.00004	0.02585	0.05195	0.00050
0.02505	0.07816	0.00005	0.02602	0.06373	0.00011	0.02808	0.04785	−0.00001
0.03480	0.06392	−0.00027	0.03651	0.04847	−0.00023	0.05595	0.01687	0.00002
0.05085	0.04804	−0.00009	0.06391	0.02463	−0.00030	0.07389	0.00499	0.00028
0.08357	0.02762	0.00016	0.08474	0.01321	0.00019			

and the difference, $E_{\text{exptl}} - E_{\text{calcd}}$, to show how the data fit the theory used to determine the constants and standard molal potential of the cell. E_{exptl} is the measured potential of cell 1 over a range of HBr molality, solvent composition, and temperature, and E_{calcd} is the calculated potential of cell 1 over the same range based on the equation

$$E_{\text{calcd}} = E^{\circ *}_{m} + E_{\text{ext}} - 2K \log m + 2KS_f c^{1/2}/(1 + A'c^{1/2}) + 2K \log (1 + 0.002 M_{xy} m) \qquad (2)$$

This equation allows the determination of a potential for any molality of HBr in any given solvent and temperature, providing the $E^{\circ *}_{m}$ and other constants have been determined from experimental data.

Equation 3, based on an equation given by Harned and Owen (*14*, *15*), was used to determine the standard potential of cell 1 from the experimental data. This equation is

$$E^{\circ \prime} = E + 2K \log m - 2KS_f c^{1/2}/(1 + A'c^{1/2}) - 2K \log (1 + 0.002 M_{xy} m) = E^{\circ *}_{m} + E_{\text{ext}} + 2KBc \qquad (3)$$

where E is the measured electromotive force of cell 1, S_f and A' are Debye-Hückel constants, K is given by 2.3026 RT/F, c is the molarity of hydrobromic acid, m is the molality of the acid, M_{xy} is the mean molecular weight of the solvent, B is the salting out coefficient, and E_{ext} may be found by

$$E_{\text{ext}} = 2\kappa \left[\left(\frac{e^2 z^2}{DkTa} \right)^3 \left[\tfrac{1}{2} X_3 (\kappa\alpha) - 2 Y_3 (\kappa\alpha) \right] + \left(\frac{e^2 z^2}{DkTa} \right)^5 \left[\tfrac{1}{2} X_5 (\kappa\alpha) - 4 Y_5 (\kappa\alpha) \right] \right] \qquad (4)$$

where D is the dielectric constant, T is the temperature, z is the valence of the ion, e is the electronic charge, α is the ion size parameter, and κ may be found from the equation $1/\kappa = 2.812 \times 10^{-10} (DT/\Gamma)^{1/2}$. Γ = ional concentration =

$$\sum_{i}^{s} c_i z_i^2.$$

S_f applies when molar concentration, c, is used.

A' of Equation 2 is a constant which depends upon this ion-size parameter. To determine the standard molal potential, $E^{\circ *}_{m}$, initially as in the study on HCl by Oiwa (*20*), the value of α in each solvent was evaluated so as to make the value of $E^{\circ \prime} - E_{\text{ext}}$ as constant as possible over the molality range studied when the salting-out coefficient term in Equation 3 was assumed to be zero.

Figure 1 is a plot of data for cell 1 at 25° C. in 100% methanol based on the equation, $E + 2K \log m - 2KS_f c^{1/2} = E^{\circ *}_{m} - 2KB'm$ (*14*). Below molality of 0.035 the plot is a straight line which can be extrapolated with high precision to a $E^{\circ *}_{m} = -0.1350$. This value corresponds to −0.1349, determined by Equation 3, and shows that the accuracy of the method used to determine $E^{\circ *}_{m}$ for all solvents and temperatures is within 0.1 mv., since 100% methanol is the solvent of lowest dielectric constant studied. The deviation of the plot from linearity above 0.035 molal probably arises from ion pairing.

Table IV is a summary of the constants of Equation 3, the values of α for hydrobromic acid with varied content of methanol when the salting-out coefficient was assumed to be zero, and the most probable value of $E^{\circ *}_{m}$ obtained by averaging the values was calculated over the range of electrolyte concentrations studied.

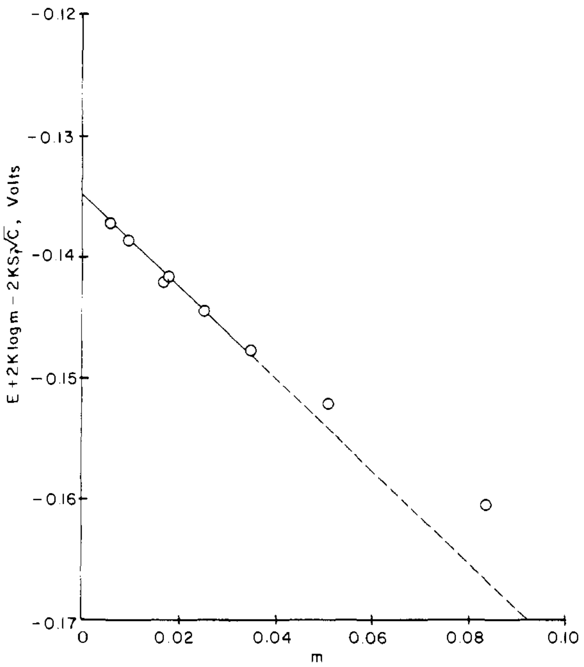

Figure 1. Graphic determination of $E^{\circ *}_{m}$ for 100 weight % methanol at 25° C.

Table IV. Constants of Equation 2 and Standard Molal Potential of Cell 1

MeOH, Wt. %	T, ° C.	M_{XY}	$2kS_f$	A'	$\mathring{a}$	$E^{\circ *}_{m}$
0	25	18.02	0.07790	2.2346	6.8	0.0712
30	25	20.74	0.08028	2.3598	6.5	0.0582
	35		0.08630	2.3820	6.5	0.0499
	45		0.09173	2.4088	6.5	0.0411
60	25	24.53	0.11899	2.5569	6.2	0.0436
	35		0.12814	2.5920	6.2	0.0316
	45		0.13773	2.6271	6.2	0.0191
90	25	29.71	0.19664	3.8938	8.0	−0.0226
	35		0.21144	3.9522	8.0	−0.0399
	45		0.22868	4.0138	8.0	−0.0582
99	25	31.75	0.23205	2.1638	4.2	−0.1046
	35		0.24798	2.1882	4.2	−0.1254
	45		0.26688	2.2186	4.2	−0.1463
100	25	32.01	0.23705	3.1131	6.0	−0.1349
	35		0.25271	3.1457	6.0	−0.1556
	45		0.27057	3.1840	6.0	−0.1760

The value at 25° C. of $E^{\circ *}_{m}$ in 100% methanol is 0.7 mv. greater in absolute value than the value $E^{\circ *}_{m}$ (−0.1342) calculated from the data of Kanning and Campbell (*17*) by Equation 2. This difference is probably due to the fact that in our study a drier methanol was used. Hartley and coworkers (*19*) found that the addition of 0.01% by weight of water to a 0.01 molal methanol solution of hydrochloric acid caused an increase in the cell potential of about 1 mv. and that the effect of moisture was greater than for the more dilute solution. Kanning and Campbell (*17*) noted a similar effect in moisture in their work on the potential of the silver–silver bromide electrode in methanol.

In Figure 2 the standard molal potential is plotted against the reciprocal of the dielectric constant of the methanol-water system for both the HBr and HCl cell at 25° C. The data for the HCl were taken from Oiwa (*20*) and the two dark circles on the curve for HBr were taken from Feakins and Watson (*7*).

The upward curvature of the plots at the lower values of $1/D$ may be explained as being due to the selective solvation of, or the selective solvent binding by the ions of the higher dielectric, more polar component of the solvent, in this case, water.

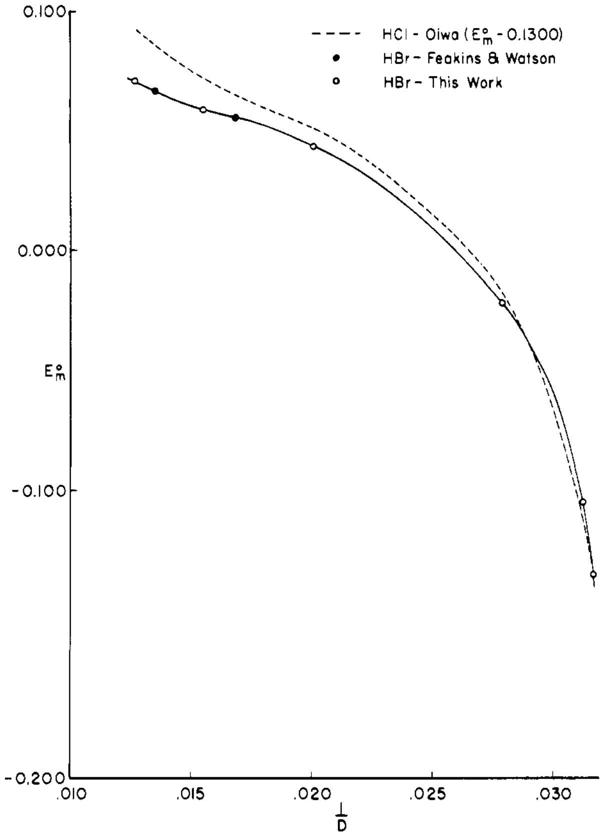

Figure 2. Standard molar potentials of Ag–AgX electrode (X = Cl or Br) in water–methanol system at 25° C. vs. reciprocal dielectric constant

Harned and Owen (*14*) explained the very rapid decrease of the standard potential with $1/D$ after this upward curvature on the basis that as the water content of the mixture becomes small, the oxonium ion, H_3O^+, is being replaced by (solvent) H^+ according to the reaction:

$$H_3O^+ + (\text{solvent}) \rightleftharpoons H_2O + (\text{solvent})\,H^+$$

THERMODYNAMIC FUNCTIONS OF CELL PROCESS

The free energy changes, ΔG°, when the activities of all reacting and resulting species are unity in each solvent and at each temperature, were calculated from $E^{\circ *}_m$.

The change in enthalpies, ΔH°, was obtained from;

$$\Delta H^\circ = \frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial\left(\frac{1}{T}\right)} \tag{5}$$

by plotting $(\Delta G^\circ)/T$ *vs.* $1/T$ and taking the slope. The change in entropies was calculated from ΔG° and ΔH°. The results are tabulated in Table V. The data for pure water at 25° and 45° C. are calculated from $E^{\circ *}_m$ values reported by Harned *et al* (*13*).

The free energy change increases positively with decreasing dielectric constant at the same temperature. As the dielectric constant decreases, more work is required to keep the ions apart, and therefore, less work is produced by the electrode reaction and more positive free energy changes result. There is less spontaneity, because of decreased dissociation at lower dielectric constants.

For any one solvent as the temperature increases the dielectric constant decreases, and the forces among the ions are greater. There is less spontaneity at higher temperature than at low, since a greater portion of the work available for electrode reaction has been used in keeping the ions apart.

Table V. Thermodynamic Functions of Cell 1

MeOH, Wt. %	T, °C.	$\Delta G^\circ \pm 2$, Cal. per Mole per Degree	$\Delta H^\circ \pm 125$, Cal. per Mole per Degree	$\Delta S^\circ \pm 0.4$, Cal. per Mole per Degree
0	25	−1642	−5366	−12.5
	35	−1517	−5501	−12.9
	45	−1383	−5646	−13.4
30	25	−1342	−7096	−19.2
	35	−1150	−7228	−19.7
	45	−947	−7380	−20.3
60	25	−1005	−9320	−27.6
	35	−724	−9640	−28.2
	45	−440	−9572	−28.7
90	25	521	−11338	−39.9
	35	920	−11699	−40.9
	45	1342	−12084	−42.2
99	25	2412	−11894	−48.0
	35	2892	−11941	−48.1
	45	3374	−11992	−48.2
100	25	3111	−11135	−47.7
	35	3588	−11384	−47.3
	45	4059	−10894	−47.1

The enthalpy change in general decreases with decreasing dielectric constant at the same temperature. The data for ΔH° and ΔS° as a function of temperature in the various solvents are given, though the change of these functions with temperature may not be significant. One referee has suggested that in water and pure methanol, ΔG° can be represented by the respective equations

$$\Delta G^\circ = 13T - 5520 \tag{6}$$

$$\Delta G^\circ = 47.2T - 11{,}020 \tag{7}$$

within the limits indicated in Table V. These would result in best values for ΔH° for the cell process in water and pure methanol of −5520 and −11,020 cal. per mole, respectively.

The changes of both ΔH° and ΔS° with solvent composition at constant temperature are marked; however, these values show that something unusual is happening in the region of high percentage of methanol where the values of ΔH° are lower than that of 100%. Feakins and Watson (*8*) in a theoretical paper on solvents and their aqueous mixtures stated that the region of 90 to 100 weight % methanol is a critical one structurally and that for the study of acid solutions in this region some "uncompensated" structural effect clearly becomes important. They further stated that this phenomenon is an entropic effect due to increased structure making by the ions as the water content of the mixture decreases, and that although the data in this region are not very reliable, there seems to be little doubt about the large effect for the proton. This fact ties in with the data from the Hammett acidity function, which indicate that although methanol is a stronger base than water, it is weaker than a 90 or 99% mixture of methanol and water (*22*).

From the influence of small amounts of water on the conductivity of acids in methanol or ethanol, this effect for the proton may also be observed. Goldenberg and Amis (*11*) noted a sharp decrease in the equivalent conductance of perchloric acid in the methanol-ethanol-water system when only 0.3 weight % water was added.

Strehlow (*22*) in a detailed study of the influence of small amounts of water on the conductivity of HCl in methanol found that this sharp decrease continued until 1 weight % water had been added and then gradually flattened out as the water content approached 10 weight %. He based an explanation for this phenomenon on the fact that the equilibrium of the reaction

$$CH_3OH_2^+ + H_2O \rightleftharpoons H_3O^+ + CH_3OH$$

was shifted toward the right by a small concentration of water. He derived values from the conductivity measurements for the equilibrium constant of the Hammett acidity equation with water acting as a base and HCl behaving as an acid in both methanol and ethanol, and calculated the ratio of Hammett acidity functions for methanol to ethanol. This value was of the same magnitude as the value determined from spectrophotometric studies using *p*-nitroaniline as the base. Goldenberg and Amis used this same type of explanation, except that they postulated the formation of not only H_3O^+ but also $H_9O_4^+$ ions.

It may be concluded from the conductivity studies that the formation of such ions in these solvents is probably true; however, this one fact may not be the entire answer to the phenomena observed in this study. That increased structure-making by the ions as the water content of the solvent decreases is an entropic effect is indicated by the large negative entropies occurring in 99% methanol (Table V). The formation of the H_3O^+ and $H_9O_4^+$ ions could account for the largest negative enthalpy change in this solvent.

SOLVATION PHENOMENA

Figure 3 shows a plot of the ion-size parameter and the salting-out coefficient *vs.* weight per cent methanol for both HBr and HCl. The salting-out coefficient was calculated from Equation 3 by setting $\mathring{a}$ equal to 4.5, a value adopted by Harned, Keston, and Donelson (*13*) and close to the value used by Feakins and Watson for HBr in 10 and 43.12 weight % methanol (*7*). The shapes of the curves for HBr and HCl are generally the same except for the minimum in the HBr curves at 99 weight %. Hydrogen chloride has not been measured in this particular solvent. The plots further show that the change of B with the change of solvent is similar to that of $\mathring{a}$ when the latter was calculated assuming B equal to zero. This seems to be natural, because the greater the solvation (coordination) sphere the greater the salting-out effect. B has a positive value from 0 to 60% methanol of almost the same magnitude. When methanol is added to the aqueous solution, the proton undergoes preferential solvation by water molecules which, in turn, makes the ratio of methanol to water outside the ionic sphere greater than that of pure solvent, resulting in a low dielectric constant of the bulk solution and giving B a positive value. In 90 weight % methanol both B and $\mathring{a}$ are very large. This may be explained by the fact that at this percentage the ions are solvated not only by water but also by methanol. At 100% methanol, solvation by methanol occurs, but the ion-dipole force is not so great as in water and the force field of the cation is perhaps not transferred throughout the methanol molecules as far as through the water molecules, resulting in a smaller $\mathring{a}$ in methanol that in water, although the methanol molecule is larger than the water molecule. This same type of behavior has been noted by Bezman and Verhoek (*2*).

The minima in both B and $\mathring{a}$ at 99 weight % methanol can be explained on the basis of formation of H_3O^+ ions and the discussion used to explain the minima observed in the changes in enthalpies and entropies in this same solvent composition.

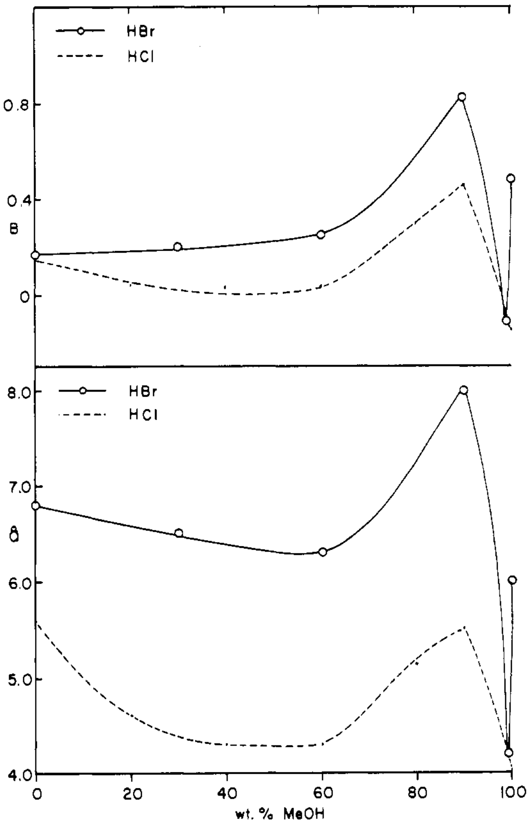

Figure 3. Plots of ion-size parameter, å, and salting-out coefficient for HBr and HCl *vs.* weight per cent MeOH at 25° C.

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