that both form 1:1 and 1:2 solid compounds with dioxane (*14*). It is possible, however, that the bonding in these compounds is quite different from that in the analogous CCl_4 system. The very much greater stability of the former as evidenced by their high heats of reaction and high melting points suggests a different type of bonding. The relatively large size of the Sn atom may allow it to assume a coordination number of five or six, in which case either one or two dioxane molecules might conceivably be bonded directly to the Sn atom.

ACKNOWLEDGMENT

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Thermodynamic Functions of Aqueous Hydrochloric Acid at Various Concentrations and Temperatures

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The values of the mean molal activity coefficients of aqueous hydrochloric acid have been calculated from e.m.f. measurements of the cell:

$$Pt/H_2/HCl/AgCl/Ag/Pt$$

over a HCl concentration range that includes the highest concentrations (from 0.00555 to 9.251 molal), and covering a temperature range from 20° to 50° C. Moreover the values of the thermodynamic functions of aqueous hydrochloric acid at 25° C. have been obtained over the same concentration range as stated above, and the values of the potential of the saturated calomel electrode for a temperature range from 20° to 50° C. have been redetermined.

THIS INVESTIGATION has been carried out as a preliminary contribution to researches on the electrochemical processes concerning the Cl_2/Cl^- redox system. Redetermination of the mean molal activity coefficients and the thermodynamic functions of aqueous hydrochloric acid over a wide range of concentrations and temperatures, on the basis of electromotive force measurements is reported.

Bates and Kirschman (*3*), Harned and Ehlers (*7*), and Akerlöf and Teare (*2*) have calculated such coefficients and functions over different HCl concentration ranges.

Study of the lowest HCl concentrations have been reconsidered recently by Hills and Ives (*8*) and Gupta, Hills, and Ives (*5*).

EXPERIMENTAL

The measurement apparatus included a Type K3 Leeds and Northrup potentiometer and a high-impedance electronic millivoltmeter, Type Philips GM 6010, as a null-point detector.

The silver-silver chloride electrode was prepared according to Gordon (*10*) and the hydrogen electrode according to Hills and Ives (*9*): characteristics and performances of both of them are described in detail and discussed in the recent book by Ives and Janz on reference electrodes (*11*).

The temperature of the cell was regulated to ±0.01° C. by means of an air-thermostat. All e.m.f. values were corrected to 760 mm. Hg pressure of hydrogen.

The solutions were made up with doubly distilled water and Merck reagents, reagent grade. Analysis and checking of solutions and of other substances involved in the cell were carried out according to commonly used techniques.

RESULTS AND DISCUSSION

Mean Molal Activity Coefficients of Aqueous HCl. The measurements of the e.m.f. E of the cell:

$$-\,Pt/H_2/(1\ atm.)/HCl(m)/AgCl/Ag/Pt\,+ \qquad (1)$$

allowed us to calculate the mean molal activity coefficients

$\gamma_{\pm}$ of HCl at various temperatures and concentrations, because $\gamma_{\pm}$ relates to E according to the equation:

$$E = E^{\circ}_{\mathrm{Ag/AgCl/Cl^-}} - \frac{2RT}{F} \ln(m\gamma_{\pm})_{\mathrm{HCl}} \qquad (2)$$

where $E^{\circ}_{\mathrm{Ag/AgCl/Cl^-}}$ is the standard potential of the silver-silver chloride half cell, and m is the molality of aqueous HCl. The values we used for the term $E^{\circ}_{\mathrm{Ag/AgCl/Cl}}$ appearing in Equation 2 are summarized below and correspond to the average of the values cited in the Ives and Janz' book (*12*), which refers to the previous works of Harned and Ehlers (*7*), Bates and Bower (*4*), and Harned and Paxton (*6*).

Temp., ° C.	$E^{\circ}_{\mathrm{Ag/AgCl/Cl}}$ (volts)
20	0.22555
25	0.22240
30	0.21911
35	0.21569
40	0.21207
45	0.20832
50	0.20448

The measured values of the e.m.f. E of the aforementioned cell are given in Table I, with an estimated error not exceeding ±0.00001v. The values of the mean molal activity coefficients, that we computed by means of Equation 2 on the basis of the experimental data collected in Table I, are summarized in Table II. The effect of increasing solubility of silver chloride with the hydrochloric acid concentration needs consideration, as to whether it might cause an uncertainty in the calculated $\gamma_{\pm}$ values. However, as we computed from solubility data of Akerlöf and Teare (*1*), in correspondence with 9.251, 6.938, and 5.551 molal HCl this uncertainty affects the $\gamma_{\pm}$ values only by 9, 3, and 1 units, respectively, in the last sighificant figure. At lower HCl molalities the effect of AgCl solubility is quite negligible.

Thermodynamic Functions of Aqueous HCl. Using the experimental data in Table I it is possible to calculate the values of the thermodynamic functions of aqueous hydrochloric acid at 25° C. and 1 atm. as a function of the HCl molalities. This calculation is based on the following treatment. The e.m.f. E of cell 1 is characterized by this overall reaction:

$$\mathrm{AgCl} + \tfrac{1}{2}\mathrm{H_2(1\ atm.)} \rightarrow \mathrm{Ag} + \mathrm{HCl}\ (m) \qquad (3)$$

The free energy change ΔG_3 and the corresponding entropy change ΔS_3 for this reaction are related to the e.m.f. E of the aforementioned cell 1 and to the temperature coefficient $\mathrm{d}E/\mathrm{d}T$ of such e.m.f., according to the following equations (where F is the Faraday constant):

$$\Delta G_3 = G_{\mathrm{HCl},\,m} - G_{\mathrm{AgCl}} = -EF \qquad (4)$$

$$\Delta S_3 = S_{\mathrm{HCl},\,m} + S_{\mathrm{Ag}} - \tfrac{1}{2}S_{\mathrm{H_2\,1\,atm}} - S_{\mathrm{AgCl}} = F\mathrm{d}E/\mathrm{d}T \qquad (5)$$

$$\Delta H_3 = \Delta G_3 + T\Delta S_3 = -EF + TF\mathrm{d}E/\mathrm{d}T = H_{\mathrm{HCl},\,m} - H_{\mathrm{AgCl}} \qquad (6)$$

Table I. E.M.F. of the Cell –Pt/H_2 (1 atm.)/HCl(m)/AgCl/Ag/Pt+, in Volts, at Various Temperatures

Molality of HCl	20° C.	25° C.	30° C.	35° C.	40° C.	45° C.	50° C.
9.251[a]	–0.01045	–0.01450	–0.01845	–0.02245	–0.02665	–0.03078	–0.03497
6.938	0.03891	0.03511	0.03131	0.02751	0.02363	0.01974	0.01677
5.551	0.08063	0.07693	0.07324	0.06954	0.06581	0.06244	0.05895
3.700	0.13316	0.12956	0.12595	0.12236	0.11901	0.11524	0.11145
2.775	0.16501	0.16150	0.15801	0.15451	0.15131	0.14820	0.14487
2.220	0.18236	0.17895	0.17556	0.17214	0.16903	0.16592	0.16297
1.850	0.19708	0.19368	0.19026	0.18697	0.18387	0.18076	0.17775
1.388	0.21637	0.21316	0.20998	0.20682	0.20379	0.20070	0.19781
1.110	0.23042	0.22730	0.22419	0.22113	0.21829	0.21534	0.21259
0.740	0.25405	0.25130	0.24854	0.24584	0.24327	0.24098	0.23847
0.555	0.26984	0.26729	0.26473	0.26223	0.25967	0.25748	0.25495
0.277	0.30456	0.30254	0.30054	0.29872	0.29675	0.29492	0.29281
0.185	0.32482	0.32313	0.32144	0.31979	0.31817	0.31648	0.31463
0.139	0.33842	0.33692	0.33540	0.33393	0.33253	0.33086	0.32943
0.111	0.34867	0.34733	0.34598	0.34465	0.34335	0.34206	0.34100
0.0555	0.38174	0.38096	0.38015	0.37939	0.37857	0.37788	0.37701
0.00555	0.49195	0.49294	0.49394	0.49497	0.49621	0.49740	0.49863

[a] The negative sign before the e.m.f. values on the first line in correspondence with 9.251 molal HCl, means that the cell polarities in this case are inverse to the ones indicated on the table heading.

Table II. Mean Molal Activity Coefficients of Aqueous HCl at Various Molalities and Temperatures

Molality of HCl	20° C.	25° C.	30° C.	35° C.	40° C.	45° C.	50° C.
9.251	11.544	10.864	10.196	9.572	9.009	8.462	7.960
6.938	5.795	5.516	5.245	4.982	4.731	4.491	4.191
5.551	3.171	3.053	2.938	2.822	2.707	2.577	2.457
3.700	1.682	1.641	1.607	1.566	1.516	1.476	1.436
2.775	1.194	1.179	1.160	1.140	1.111	1.079	1.051
2.220	1.059	1.049	1.036	1.022	1.000	0.976	0.949
1.850	0.949	0.944	0.938	0.927	0.911	0.893	0.873
1.388	0.864	0.862	0.858	0.851	0.840	0.828	0.812
1.110	0.818	0.819	0.817	0.813	0.803	0.793	0.779
0.740	0.769	0.770	0.769	0.766	0.758	0.745	0.734
0.555	0.750	0.752	0.752	0.750	0.746	0.735	0.728
0.277	0.756	0.759	0.759	0.756	0.752	0.744	0.739
0.185	0.758	0.761	0.762	0.761	0.757	0.752	0.748
0.139	0.770	0.775	0.777	0.776	0.772	0.770	0.763
0.111	0.788	0.792	0.794	0.794	0.791	0.786	0.776
0.0555	0.819	0.823	0.826	0.826	0.824	0.818	0.813
0.00555	0.924	0.932	0.936	0.937	0.932	0.925	0.916

Table III. Thermodynamic Functions of Aqueous HCl at 25° C. and 1 Atm.

Molality of HCl	Moles HCl per mole H_2O[a]	dE/dT (mV/° C.)	G Cal./Mole	H[b] Cal./Mole	S Cal./° C. Mole
9.251	1/6	−0.80	−25890	−35528	9.92
6.938	1/8	−0.76	−27034	−36397	10.84
5.551	1/10	−0.74	−27998	−37224	11.31
3.700	1/15	−0.72	−29218	−38300	11.77
2.775	1/20	−0.70	−30040	−38899	12.23
2.220	1/25	−0.68	−30351	−39164	12.69
1.850	1/30	−0.68	−30690	−39504	12.69
1.388	1/40	−0.64	−31139	−39678	13.61
1.110	1/50	−0.62	−31465	−39866	14.07
0.740	1/75	−0.55	−32019	−39938	15.69
0.555	1/100	−0.51	−32388	−40032	16.61
0.277	1/200	−0.40	−33201	−40089	19.15
0.185	1/300	−0.34	−33675	−40151	20.53
0.139	1/400	−0.30	−33993	−40194	21.45
0.111	1/500	−0.27	−34233	−40228	22.14
0.0555	1/1000	−0.16	−35009	−40247	24.68
0.00555	1/10000	+0.20	−37591	−40354	32.98

[a] The column "moles HCl per mole H_2O" has been included to facilitate the comparison with the values of thermodynamic functions of HCl that are available in literature. [b] The single H values collected in Table III and the corresponding N.B.S. data (*15*) differ less than ±0.90%, excepting the first four terms, a maximum deviation about −6.04% being observed for the term corresponding to 9.251m HCl. An analogous comparison for the G and S values is impossible because the corresponding N.B.S. data are missing.

Table IV. Measured E.M.F. (E') of Cell (*10*), in Volts, at Various Temperatures

Molality of HCl	20° C.	25° C.	30° C.	35° C.	40° C.	45° C.	50° C.
9.251	0.14007	0.14036	0.14068	0.14089	0.14140	0.14182	0.14222
6.938	0.11538	0.11558	0.11580	0.11589	0.11628	0.11658	0.11636
5.551	0.09455	0.09470	0.09485	0.09489	0.09518	0.09522	0.09527
3.700	0.06828	0.06839	0.06848	0.06852	0.06858	0.06881	0.06901
2.775	0.05235	0.05240	0.05245	0.05246	0.05247	0.05238	0.05231
2.220	0.04368	0.04369	0.04369	0.04364	0.04363	0.04357	0.04330
1.850	0.03630	0.03632	0.03634	0.03624	0.03621	0.03614	0.03592
1.388	0.02667	0.02658	0.02647	0.02629	0.02626	0.02618	0.02590
1.110	0.01965	0.01950	0.01937	0.01915	0.01900	0.01884	0.01852
0.740	0.00783	0.00748	0.00718	0.00672	0.00648	0.00594	0.00558
0.555[a]	−0.00005	−0.00048	−0.00091	−0.00146	−0.00174	−0.00227	−0.00266
0.277	−0.01741	−0.01812	−0.01881	−0.01965	−0.02023	−0.02094	−0.02159
0.185	−0.02755	−0.02840	−0.02925	−0.03020	−0.03095	−0.03171	−0.03252
0.139	−0.03434	−0.03529	−0.03624	−0.03725	−0.03811	−0.03890	−0.03988
0.111	−0.03943	−0.04050	−0.04158	−0.04269	−0.04356	−0.04460	−0.04572
0.0555	−0.05596	−0.05731	−0.05861	−0.05998	−0.06113	−0.06241	−0.06374
0.00555	−0.11107	−0.11331	−0.11550	−0.11777	−0.11995	−0.12221	−0.12452

[a] The negative sign before the e.m.f. values in correspondence with the range from 0.555 to 0.00555 molal HCl, means that the cell polarities in these cases are inverse to the ones indicated on the text.

From equations 4, 5, and 6, respectively, it follows that:

$$G_{\mathrm{HCl},\,m} = G_{\mathrm{AgCl}} - EF \tag{7}$$

$$S_{\mathrm{HCl},\,m} = F\,\mathrm{d}E/\mathrm{d}T + S_{\mathrm{AgCl}} + \tfrac{1}{2}S_{\mathrm{H_2,\,1\,atm.}} - S_{\mathrm{Ag}} \tag{8}$$

$$H_{\mathrm{HCl},\,m} = H_{\mathrm{AgCl}} + \Delta H_3 = H_{\mathrm{AgCl}} - EF + TF\,\mathrm{d}E/\mathrm{d}T \tag{9}$$

The values of E at 25° C. are collected in Table I. The temperature coefficient $\mathrm{d}E/\mathrm{d}T$ can be computed by plotting E against temperature: this plot shows that $\mathrm{d}E/\mathrm{d}T$ in the range from 20° to 30° C. varies less than ±0.01mv. deg.$^{-1}$ Consequently we assume the mean $\mathrm{d}E/\mathrm{d}T$ value calculated over the range from 20° to 30° C. as the $\mathrm{d}E/\mathrm{d}T$ value at 25° C. Table III collects such $\mathrm{d}E/\mathrm{d}T$ values at 25° C. as a function of the corresponding HCl molalities. For G_{AgCl}, H_{AgCl}, S_{AgCl}, S_{Ag}, and $S_{\mathrm{H_2}}$ under the standard conditions, we used N.B.S. data (*14*). Table III summarizes also the values of the thermodynamic functions of HCl computed from equations 7, 8, and 9. The estimated errors for G_{HCl}, H_{HCl}, and S_{HCl} do not exceed ±2 cal. mole^{-1}, ±70 cal. mole^{-1} and ±0.25 cal. deg.$^{-1}$ mole^{-1}, respectively.

Redetermination of the Potential of the Saturated-Calomel Electrode at Various Temperatures. The potential E_{sc} of the saturated-calomel electrode may be computed from potentiometric measurements of the e.m.f. E' of the cell:

$$- \mathrm{Pt/Ag/AgCl/HCl}(m)//\mathrm{KCl\ salt\ bridge}//\ \mathrm{sat.\ KCl/Hg_2Cl_2/Hg/Pt} + \tag{10}$$

where the molalities of HCl are the same as for cell (1). In fact the e.m.f. E' is expressed by the following equation:

$$E' = E_{\mathrm{sc}} - E^{\circ}_{\mathrm{Ag/AgCl/Cl^-}} + \frac{RT}{F}\ln(m\gamma_{\pm})_{\mathrm{HCl}} \tag{11}$$

Substituting numerical values for $E^{\circ}_{\mathrm{Ag/AgCl/Cl^-}}$ and E' the logarithmic term $(RT/F)\ln(m\gamma_{\pm})_{\mathrm{HCl}}$ being already known from Equation 2, E_{sc} can be computed in correspondence with each experimental value of HCl molality, at various temperatures. In this way we obtained E_{sc} values that differ among them less than 0.08mv., at each temperature. Table V shows the average of such E_{sc} values, calculated in correspondence with each experimental temperature, comparison being made with the values cited by Ives and Janz (*13*), which are based on Wingfield and Acree's measurements (*16*). The E' values (Table IV) are given with an estimated error not exceeding ±0.00001v.; the limits of error for the E_{sc} values (Table V) are thus estimated not greater than ±0.00005v.

Table V. Comparison of Values of the Potential E_{sc} of the Saturated Calomel Electrode, in Volts, at Various Temperatures

Temp., °C.	E_{sc} This work	E_{sc} Ives and Janz *(13)*
20	0.24764	0.2477
25	0.24435	0.2444
30	0.24101	0.2411
35	0.23752	0.2377
40	0.23416	0.2343
45	0.23064	...
50	0.22702	0.2272

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Thermodynamic Solubility Products of α- and β-SrHPO₄ from 25° to 90° C.

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Thermodynamic solubility products of α-$SrHPO_4$ and β-$SrHPO_4$ were determined in aqueous solutions at 25°, 37°, 50°, 70°, and 90° C. In several cases α-$SrHPO_4$ recrystallized to form β-$SrHPO_4$ during equilibration. At 25° C. the thermodynamic solubility product is 1.07×10^{-7} for the less soluble β-$SrHPO_4$, which is lower than those reported for $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$. Both forms exhibit decreasing solubility with increasing temperature. For the temperature range studied, the following expression for the solubility product of β-$SrHPO_4$ was found to fit the data, using the method of least squares:

$$pK_{sp}(\beta\text{-}SrHPO_4) = 13.364 \log T - 26.130$$

An expression for ΔH° of solution at 298° K. was derived yielding $\Delta H^\circ(\beta\text{-}SrHPO_4) = -7.91$ kcal./mole, from which the heat of formation of β-$SrHPO_4$ was calculated to be −432.87 kcal./mole.

IN A RECENT review *(11)* of the alkaline earth phosphates, the scarcity of thermodynamic data on strontium and barium phosphates compared to the calcium phosphates was noted. A solubility study of $SrHPO_4$ at 38° C. by Holt, Pierce, and Kajdi *(9)* gave a value of 7.06 for pK_{sp} at infinite dilution. However, the variation of solubility with temperature was not investigated. A study of dibasic strontium phosphates conducted in this laboratory *(12, 15)* showed that crystalline $SrHPO_4$ is dimorphic, hence work prior to 1959 including that on solubility referenced above could not take the dimorphism of $SrHPO_4$ into account. Recent Russian work *(4)* gave a value of 6.24 for pK_{sp} of $SrHPO_4$ at 19-20° C., but activities were not used. More recently, Frere *(6)* estimated a value of 6.38 for pK_{sp} of $SrHPO_4$ at 25° C. from his solubility diagram. Again activities were not used and identification of $SrHPO_4$ as the α- or β- form was not made.

The present work was undertaken to determine the thermodynamic solubility products, as a function of temperature, for the crystalline species, α- and β-$SrHPO_4$. The values are compared to published data for $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$.

EXPERIMENTAL

Materials. The dibasic phosphates, β-$SrHPO_4$ and α-$SrHPO_4$, were prepared by the addition of solutions of $(NH_4)_2HPO_4$ to solutions of $Sr(NO_3)_2$ at temperatures of 18° and 80° C., respectively, as previously described *(12)*. The identity of the resulting crystalline precipitates was confirmed by chemical analyses and examination of their characteristic Debye-Scherrer powder patterns *(15)*.

Equilibration Technique. An excess of either α- or β-$SrHPO_4$ was added to 3500 ml. of H_3PO_4 solution in a 5-liter flask at room temperature. The concentration of H_3PO_4, and hence the ionic strength of the solution, was varied from run to run as indicated in Table I. The flask was immersed

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