Thermodynamics of Aqueous Hydrochloric Acid from E.M.F.'s of Hydrogen-Chlorine Cells

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Activity coefficients for 1.0 to 11.1 molal HCl in aqueous solution have been obtained from e.m.f. measurements of the cell H_2 (1 atm.)/HCl (m)/Cl_2 (0.1 atm.) over the temperature range 25° to 80° C. Partial molal thermodynamic functions for HCl at various molalities have been derived, under the standard conditions: 25° C. and p = 1 atm. Standard molal potentials for the chlorine-chloride electrode have been determined over the range 25° to 80° C.

SILVER–silver chloride electrodes were used extensively by many authors in cells of the type H_2 (1 atm.)/HCl (m)/AgCl/Ag to determine activity coefficients for HCl with related thermodynamic functions (*2, 3, 11*). However, a meaningful interpretation of data may be complicated if one uses HCl molalities greater than 4.0, due to solubility of AgCl in HCl (*2, 18, 19, 21, 25*) to form $[\mathrm{AgCl}_{n+1}]^{n-}$ complexes, a solubility which strongly increases with increasing temperature at constant HCl molality (*7*). In fact, AgCl solubility data at temperatures higher than 25° C. are unavailable in HCl molalities greater than 5.5. The use of the calomel electrode in the place of the silver–silver chloride electrode, with concentrated HCl solutions, would not be recommended because of an identical trend as above—i.e., the solubility of Hg_2Cl_2 in HCl (*29*). Moreover, the calomel electrode would be unsuitable for use at high temperatures as it is notoriously subject to thermal hystereses and to noticeable instability of potential (*14–16*).

These limitations can be removed by using a low-Cl_2-pressure chlorine electrode of the type recently described (*8*). This electrode coupled with a capillary-imbibition hydrogen electrode (*4–6*) to form the cell

$$\mathrm{Pt/H_2\ (1\ atm.)/HCl\ (}m\mathrm{)/N_2\text{-}Cl_2\ 10\%/Pt\text{-}Ir\ 45\%/Ta/Pt} \qquad (1)$$

was used in the context of the present work to determine activity coefficients, with related thermodynamic functions, for 1.0 to 11.1 molal hydrochloric acid over the temperature range 25° to 80° C. In addition, the e.m.f.'s of the cell

$$\mathrm{Pt/H_2\ (1\ atm.)/HCl\ (1\ }m\mathrm{)/AgCl/Ag/Pt} \qquad (2)$$

were also measured, over the same temperature range, to obtain activity coefficients for 1 molal HCl as reference data.

EXPERIMENTAL

Both in Cells 1 and 2, the hydrogen electrodes were of the capillary-imbibition type, as recently described by Bianchi (*4–6*). The low-pressure chlorine electrodes in Cell 1 were prepared as described (*8*), and gave a bias potential of 0.01 mv. The silver–silver chloride electrodes in Cell 2 were prepared according to the electrolytic type (*17*), and their bias potential was 0.01 mv. after aging. All Cells 1 were run in duplicate, and Cells 2 in quadruplicate.

E.m.f.'s were measured by means of a Type K-3 Leeds & Northrup potentiometer having a Type 610-B Keithley electrometer as null-point detector. The input impedance of the latter was greater than 10^{14} ohms, thus permitting one to work with appropriate stopcocks continuously closed between the half-cells to prevent interdiffusion. The e.m.f. readings were taken after appropriate times of equilibration when e.m.f.'s remained constant within ±0.01 mv. for 3 hours.

Solutions were made up with triply distilled water and certified Carlo Erba hydrochloric acid. Concentrations of HCl solutions were determined by the potentiometric titration method (*22, 23*).

Temperatures of cells were regulated to ±0.02° C. by means of a specially designed air-thermostat.

RESULTS AND DISCUSSION

Activity Coefficients of Hydrochloric Acid. In the compartment of the chlorine electrode in Cell 1 the following reaction occurs:

$$\mathrm{Cl_2\ (gas,\ }p\mathrm{\ atm.) + Cl^-\ (aq.) = Cl_3^-\ (aq.)} \qquad (3)$$

Therefore the molality of Cl^- ion, m_{Cl^-}, varies from m_{HCl} because some Cl^- are converted into Cl_3^- ions, whereas in the hydrogen electrode compartment $m_{H^+} = m_{Cl^-} = m_{HCl}$. Of course, the ionic strength of the solution remains unchanged, whereby one can assume that the activity coefficient for the Cl^- ion, γ_{Cl^-}, remains unchanged in the two half-cell compartments. The formation constant of Reaction 3 being $K = 1.0 \times 10^{-2}$ atm.$^{-1}$ at 25° C. (*31*), and the chlorine pressure being 0.1 atm., the amount of Cl_3^- ions is so small that it does not affect the e.m.f. by more than about 0.01 mv. and can be neglected.

The e.m.f. of Cell 1 is given by

$$E_1 = E^\circ_{Cl_2/Cl^-} + (k/2)\log(p_{Cl_2}p_{H_2}) - 2k\log(m\gamma_\pm) \qquad (4)$$

where: $E^\circ_{Cl_2/Cl^-}$ is the standard molal potential of the chlorine electrode; $\gamma_\pm = (\gamma_{H^+}\gamma_{Cl^-})^{1/2}$ is the mean molal activity coefficient of HCl; and $k = (RT/F)\ln 10$. Equation 4 could be used to determine activity coefficients of HCl. However, taking into account that $E^\circ_{Cl_2/Cl^-}$ is known to about ±0.1 mv. (*8*), it is convenient to turn Equation 4 into a more useful form. Let E_1' and E_1'' denote the e.m.f.'s corresponding to two different HCl molalities, m' and m'', the respective activity coefficients being $\gamma_\pm'$ and $\gamma_\pm''$. Working with p_{Cl_2} and p_{H_2} constant (p_{Cl_2} = 0.1 atm., p_{H_2} = 1 atm.), from Equation 4 one obtains

$$E_1'' - E_1' = 2k\log\left(\frac{m'\gamma_\pm'}{m''\gamma_\pm''}\right) \qquad (5)$$

Thus $\gamma_\pm''$ can be calculated from E_1 values by means of Equation 5 provided that at the reference molality m' (which has been chosen as m' = 1.000 for convenience) the activity coefficient $\gamma'_\pm$ is known over the required range of temperatures. This has been achieved by measuring e.m.f. of Cell 2, which can be expressed as

$$E_2 = E^\circ_{Ag/AgCl/Cl^-} - 2k\log(m\gamma_\pm) + (k/2)\log p_{H_2} \qquad (6)$$

working with m = 1.000 and p_{H_2} = 1 atm., and taking the required $E^\circ_{Ag/AgCl/Cl^-}$ values from those recently redetermined critically by Bates and Bower (*3*). The E_2 values, in volts, corrected to 1 atm. pressure of H_2, were 0.23340, 0.23067, 0.22516, 0.21898, 0.21265, 0.20552, 0.19799 at 25°, 30°, 40°, 50°, 60°, 70°, 80° C., respectively. Each E_2 value quoted above is the average of four independent cells, the mean deviation being 0.01 mv. at 25° to 60° C. and 0.02 mv. at 70° to 80° C.

In Table I the values of $\gamma_\pm$ at $m_{HCl} = 1.000$ available in the literature, over the temperature range 25° to 90° C., are compared with the present unsmoothed values, whose estimated errors are ± 0.0005 at 25° C., ± 0.0006 at 30° C., ± 0.0008 at 40°, 50°, and 60° C., ± 0.0009 at 70° C., and ± 0.0013 at 80° C., respectively.

Table II shows E_1 values, corrected to 1 atm. pressure of H_2 and to 0.1 atm. pressure of Cl_2, at various HCl molalities and temperatures. Each E_1 value is the average of two values, obtained from independent cells, rarely differing by more than 0.01 mv.

Table III shows mean molal activity coefficients for HCl at various molalities and temperatures. Those at $m_{HCl} = 1$ have, of course, been obtained from the E_2's through Equation 6, and their limits of error have been already quoted above. The $\gamma_\pm$'s at the other nine molalities were obtained through Equation 5 from the E_1's combined with the $\gamma_\pm$'s at $m_{HCl} = 1$ previously determined. The limits of error for the $\gamma_\pm$'s at these nine molalities are $\pm 0.11\%$ at 25° and 30° C., $\pm 0.14\%$ at 40° and 50° C., $\pm 0.15\%$ at 60° and 70° C., and $\pm 0.20\%$ at 80° C.

In Figure 1, curve *A*, comparison is made of the present activity coefficients of HCl with those of Randall and Young (*26*), which were derived from vapor pressure measurements at 25° C. Data of Harned and Ehlers (*11*) are also included. The interagreement is excellent.

To provide another indirect check of the present values of $\gamma_\pm$'s, the relative partial molal enthalpies of HCl at 25° C. were computed with the following equation (*12, 27*)

$$\bar{L} = \bar{H} - \bar{H}^* = \bar{H} - \bar{H}^\circ = -2RT^2\left(\frac{\delta \ln \gamma_\pm}{\delta T}\right)_{p,m} \qquad (7)$$

In Figure 1, curve *B*, these $\bar{L}$ values are compared with the corresponding calorimetric data of Sturtevant (*32*) and with the e.m.f.-based data of Harned and Ehlers (*11*) as well as with others interpolated at 25° C. from the results of Akerlöf and Teare (*2*). The interagreement of data is again satisfactory. The $(\delta \ln \gamma_\pm / \delta T)$ value required by Equation 7 was obtained from the first derivative of the least-squares polynomial

$$\log \gamma_\pm = a + bT + cT^2 \qquad (8)$$

whose constants *a*, *b*, and *c* are collected in Table IV. The mean deviation between observed and calculated log $\gamma_\pm$ values is 0.5%.

Standard Molal Potentials of the Cl_2/Cl^- Electrode. Combining the e.m.f.'s of Cells 1 and 2 measured in 1 molal HCl at $p_{H_2} = 1$ atm., one can determine accurate values for the standard molal potentials of the Cl_2/Cl^- electrode over the temperature range 25° to 80° C. In fact, from Equations 4 and 6 one gets

Table I. Comparison of Activity Coefficients for Aqueous 1 Molal HCl at Various Temperatures

	Temperature, ° C.							
	25	30	40	50	60	70	80	90
Ref. (*11, 13*)	0.8090	0.8018	0.7865	0.7697	0.7541	. . .	. . .	. . .
Ref. (*9*)	0.8062	. . .	. . .	. . .	0.7621	. . .	. . .	0.7138
Ref. (*10*)	0.8101	0.8029	0.7892	. . .	. . .	. . .	. . .	. . .
This work	0.8063	0.8004	0.7848	0.7709	0.7547	0.7413	0.7287	. . .

Table II. E.M.F.'s of Cell 1, in Volts, at Various HCl Molalities and Temperatures, with $p_{H_2} = 1$ atm. and $p_{Cl_2} = 0.1$ atm.

	Temperature, ° C.						
m_{HCl}	25	30	40	50	60	70	80
1.000	1.34000	1.33380	1.32120	1.30817	1.29455	1.28045	1.26576
3.084	1.25535	1.24934	1.23529	1.22001	1.20582	1.19046	1.17495
3.701	1.23776	1.23142	1.21725	1.20201	1.18753	1.17194	1.15610
4.626	1.21240	1.20566	1.19136	1.17618	1.16137	1.14555	1.12940
5.551	1.18827	1.18121	1.16683	1.15171	1.13671	1.12081	1.10456
6.938	1.15437	1.14700	1.13266	1.11756	1.10257	1.08678	1.07080
7.930	1.13183	1.12435	1.11011	1.09503	1.08025	1.06472	1.04922
9.251	1.10397	1.09652	1.08255	1.06745	1.05321	1.03825	1.02380
10.092	1.08754	1.08020	1.06646	1.05134	1.03760	1.02315	1.00960
11.102	1.06915	1.06202	1.04866	1.03348	1.02050	1.00679	0.99457

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

	Temperature, ° C.						
m_{HCl}	25	30	40	50	60	70	80
1.000	0.8063	0.8004	0.7848	0.7709	0.7547	0.7413	0.7287
3.084	1.358	1.307	1.250	1.217	1.148	1.101	1.051
3.701	1.594	1.535	1.455	1.401	1.315	1.255	1.193
4.626	2.088	2.011	1.881	1.783	1.659	1.569	1.481
5.551	2.784	2.676	2.470	2.306	2.125	1.986	1.856
6.938	4.308	4.120	3.722	3.406	3.081	2.825	2.586
7.930	5.844	5.561	4.945	4.466	3.977	3.589	3.225
9.251	8.616	8.121	7.064	6.281	5.459	4.814	4.197
10.092	10.87	10.17	8.73	7.69	6.57	5.70	4.86
11.102	14.14	13.10	11.03	9.63	8.04	6.83	5.65

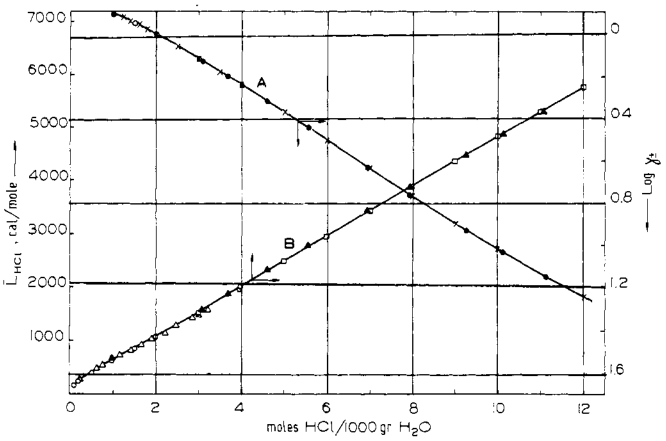

Figure 1. Comparison of values obtained by different methods, at 25° C., for the activity coefficients (curve *A*) and the relative partial molal enthalpies (curve *B*) as functions of the molalities of aqueous HCl

●, ▲ Present work; Harned and Ehlers, (*11*)
× Randall and Young, (*26*); Sturtevant, (*32*)
☐ Interpolated from Akerlöf and Teare's data, (*2*)

Table V. Standard Molal Potentials, in Volts, for the Cl_2/Cl^- Electrode at Various Temperatures

Temp., ° C.	$E^\circ_{Cl_2/Cl^-}$, This Work	$E^\circ_{Cl_2/Cl^-}$, Ref. (*8*)
25	1.35852	1.35830
30	1.35224	1.35213
40	1.33919	1.33919
50	1.32574	1.32559
60	1.31144	1.31114
70	1.29679	1.29651
80	1.28153	1.28104

$$E^\circ_{Cl_2/Cl^-} = E_1 - E_2 + E^\circ_{Ag/AgCl/Cl^-} - (k/2)\log p_{Cl_2} \qquad (9)$$

The $E^\circ_{Cl_2/Cl^-}$ values calculated through Equation 9 using Bates and Bower's values for $E^\circ_{Ag/AgCl/Cl^-}$ (*3*) are given in Table V. The limits of error, in millivolts, for these $E^\circ_{Cl_2/Cl^-}$ values are ±0.11, ±0.12, ±0.13, ±0.13, ±0.14, ±0.16, and ±0.19 at 25°, 30°, 40°, 50°, 60°, 70°, and 80° C., respectively. The $E^\circ_{Cl_2/Cl^-}$'s can be expressed within the limits of error quoted above, by the expression

$$E^\circ_{Cl_2/Cl^-} = 1.479874 + (4.315277 \times 10^{-4})T - (2.812217 \times 10^{-6})T^2 \qquad (10)$$

whose constants have been determined by the least-squares method; the *T*'s are absolute temperatures. The mean deviation between observed and calculated $E^\circ_{Cl_2/Cl^-}$ values is 0.02 mv. For comparison purposes, values of $E^\circ_{Cl_2/Cl^-}$ recently determined (*8*) over the same temperature range but using a different cell are also quoted in Table V. Taking into account the cumulative uncertainties, the two sets of $E^\circ_{Cl_2/Cl^-}$ values are in good agreement.

Partial Molal Thermodynamic Functions for HCl. The e.m.f.'s of E_1 have been measured working with $p_{H_2} = 1$ atm. and $p_{Cl_2} = 0.1$ atm. If E_1^* denotes the e.m.f.'s of Cell 1 at $p_{H_2} = 1$ atm. and $p_{Cl_2} = 1$ atm., the E_1^*'s can be obtained from the corresponding E_1's by simply adding the term $(k/2)$, as shown by inspection of Equation 4. The E_1^* values correspond to the cell reaction

$$\tfrac{1}{2}H_2 \text{ (gas, 1 atm.)} + \tfrac{1}{2}Cl_2 \text{ (gas, 1 atm.)} = HCl \text{ (aq., } m) \qquad (11)$$

Thus, from E_1^* and dE_1^*/dT data, accurate values can be obtained for the partial molal free energies, enthalpies, and entropies of HCl at various molalities, starting from hydrogen and chlorine under standard conditions of pressure and temperature. The required dE_1^*/dT values at each HCl molality considered were obtained from the first derivatives of polynomials of the type

$$E_1^* = A + BT + CT^2 \qquad (12)$$

whose constants *A*, *B*, and *C* were determined with the least-squares method and are collected in Table IV. Equation 12 reproduces the observed E_1^*'s with an average deviation of 0.18 mv.

The $E^\circ_{Cl_2/Cl^-}$ values correspond to the reaction

$$\tfrac{1}{2}H_2 \text{ (gas, 1 atm.)} + \tfrac{1}{2}Cl_2 \text{ (gas, 1 atm.)} = HCl \text{ (aq., hyp. } m = 1) \qquad (13)$$

Thus also the standard values, $\bar{G}^\circ$, $\bar{H}^\circ$, and $\bar{S}^\circ$, for HCl can be determined from $E^\circ_{Cl_2/Cl^-}$ and $dE^\circ_{Cl_2/Cl^-}/dT$ data, the latter quantity being taken from the first derivative of Equation 10.

The partial molal functions $\bar{G}$ and $\bar{H}$ (referred to zero for the free energies and the enthalpies of H_2 and Cl_2 at 25° C. and 1 atm.) and $\bar{S}$ (referred to $S^\circ_{H_2} = 31.211$ and to $S^\circ_{Cl_2} = 53.286$ cal. deg.$^{-1}$ mole^{-1} at 25° C. and 1 atm.) for HCl at 25° C. at various molalities are collected in Table VI. The limits of error are ±2 cal. mole^{-1}, ±5 cal. mole^{-1}, and ±0.009 cal. deg.$^{-1}$ mole^{-1}, for $\bar{G}$, $\bar{H}$, and $\bar{S}$ respectively.

To provide comparison with the available data of enthalpies of HCl in the standard literature, which essentially are apparent molal enthalpies (*24*, *30*), denoted as Φ_H, the present values of partial molal enthalpies were converted to Φ_H by means of the relationship

$$\Phi_H = \bar{H}_2 + \frac{n_1}{n_2}\bar{L}_1 \qquad (14)$$

where subscripts 1 and 2, and numbers of moles n_1 and n_2, refer to water and to HCl, respectively, and $\bar{L}_1 = \bar{H}_1 - \bar{H}_1^\circ$ is the relative partial molal enthalpy of water. The

Table IV. Constants for the Least-Squares Equations 8 and 12 for Each HCl Molality

m_{HCl}	*a*	$b \times 10^3$	$c \times 10^6$	*A*	$B \times 10^3$	$C \times 10^6$
1.000	0.1657880	−0.914167	0.154591	1.5026385	0.231120	−2.271342
3.084	0.7420574	−2.132787	0.264109	1.5166297	−0.273058	−1.684489
3.701	1.0527337	−3.382851	1.754100	1.4804588	−0.142399	−1.915537
4.626	1.5209277	−5.155563	3.768049	1.4368558	−0.013126	−2.146197
5.551	1.8852368	−6.203840	4.600284	1.4389590	−0.167180	−1.925352
6.938	2.2618434	−6.643943	3.982436	1.4444310	−0.414708	−1.539197
7.930	2.3866888	−6.035489	2.029575	1.4604024	−0.667704	−1.124499
9.251	2.3755620	−4.112926	−2.402170	1.5204351	−1.246094	−0.172672
10.092	2.2475267	−2.140841	−6.445822	1.5872915	−1.792346	0.723880
11.102	2.0118531	0.726249	−12.138705	1.6758528	−2.500476	1.897585

Table VI. Thermodynamic Functions for HCl at Various Molalities, at 25° C.[a]

m_{HCl}	(n_{HCl}/n_{H_2O})	$\bar{G}$	$\bar{H}$	$\bar{S}$	ϕ_H, This Work	ϕ_H, Ref. *(30)*
Std. state, (hyp. $m = 1$)	...	−31331 −31372[b]	−39895 −39952[b]	13.526 13.5[b] 13.51[c]	−39895	−39952
1.000	1/55.51	−31586	−39315	16.342	−39543	...
3.084	1/18	−29634	−38424	12.786	−39135	...
3.701	1/15	−29228	−38067	12.621	−38927	−38964
4.626	1/12	−28643	−37539	12.430	−38590	−38762
5.551	1/10	−28087	−37136	11.915	−38371	−38556
6.938	1/8	−27305	−36473	11.517	−38051	−38242
7.930	1/7	−26785	−35992	11.385	−37837	...
9.251	1/6	−26143	−35425	11.136	−37582	−37687
10.092	1/5.5	−25764	−35125	10.868	−37447	...
11.102	1/5	−25340	−34758	10.679	−37318	−37231

[a] The second column, moles of HCl per mole of H_2O, has been included to facilitate the comparison with the corresponding N.B.S. data *(30)*. $\bar{G}$, $\bar{H}$, and ϕ_H are given in cal. mole^{-1}; $\bar{S}$ in cal. deg.$^{-1}$ mole^{-1}. [b] From Ref. *(30)*. [c] From Ref. *(1, 34)*.

values of $\bar{L}_1$ have been obtained by graphical integration according to the equation *(20, 33)*:

$$\bar{L}_1 = \int d\bar{L}_1 = -\int \frac{x_2}{x_1}\, d\bar{L}_2 \qquad (15)$$

where x_1 and x_2 are the mole fractions of water and of HCl, respectively, and $\bar{L}_2$ is the relative partial molal enthalpy of HCl, a quantity which is known over the range 0 to 4 molal HCl from Harned and Ehlers' work *(11)* and over the range 1 to 11 molal HCl from the present work. To facilitate the comparison, both the Φ_H values from Wagman *et al.* *(30)* and from the present results are quoted in Table VI. The greatest difference observed is 0.50%, at 6.938 molal HCl.

As Table VI shows, the present $\bar{S}^{\circ}_{HCl}$ value, the corresponding N.B.S. value *(30)*, and that found by independent methods by Ahluwalia and Cobble *(1)* and by Vanderzee and Nutter *(34)*, are in good agreement. For the sake of simplicity, the $\bar{L}_1$ and $\bar{L}_2$ values were not quoted in Table VI as they can be easily recalculated from the quoted data.

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