

Standard Electrode Potential of $\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$ from 5–35°C

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Standard electrode potentials were determined for $\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$ in perchlorate solutions at pH 1.48 and ionic strengths of 0.0824 to 0.0840 from 5–35°C. E° values were corrected for FeOH^{2+} and $\text{Fe}_2(\text{OH})_2^{4+}$ complexes. At 25°C, $E^\circ = 0.770 \pm 0.002$ V. The empirical equation

$$E_T^\circ = -1.23 \times 10^{-2} + 4.147 \times 10^{-3} T - 5.111 \times 10^{-6} T^2$$

where T is in K degrees, fits smoothed E_T° values well within the measurement precision of ± 0.001 V. Smoothed E_T° values from the experimental data are within ± 0.001 V of E_T° 's computed from published enthalpy data at 25°C, assuming (1) $\Delta C_p^\circ = 0$, and (2) $\Delta C_p^\circ = -28$ cal/deg mol. Other thermodynamic properties of the ferric-ferrous cell at 25°C calculated from the above equation were $\Delta G^\circ = -17.75 \pm 0.04$ kcal/mol, $\Delta H^\circ = 10.2 \pm 0.4$ kcal/mol, and $\Delta S^\circ = 25.4 \pm 1.5$ cal/deg mol.

In calculating the solubility of suspended iron oxyhydroxides in groundwater (10), values of E° (standard electrode potential) for the half cell reaction



were required at temperatures below 25°C. Accordingly, E° values have been determined from 5–35°C. These are compared with E° values calculated from published thermodynamic data.

EXPERIMENTAL SECTION

A measured volume of mixed ferrous-ferric perchlorate solution of approximately equal ferrous and ferric ion activities was prepared with reagent-grade salts and distilled deionized water, and acidified to about pH 1.5, using a known amount of perchloric acid. The low pH was desired to decrease Fe^{3+} hydrolysis products including FeOH^{2+} and $\text{Fe}_2(\text{OH})_2^{4+}$ complexes and to prevent Fe^{2+} oxidation during the run. The prepared solution was placed in a pyrex beaker fitted with an airtight lucite cover which had holes to accommodate stopper-fitted indicator and reference electrodes, and a thermometer. Measurements of E (electrode potential) and pH were recorded after holding the solution at a particular temperature in a constant temperature bath for about a half day. Values were obtained from 5–35°C in approximately 5°C intervals.

A combination glass, silver-silver chloride reference electrode was used for pH measurement, and a platinum thimble electrode and silver-silver chloride reference electrode with a saturated KCl internal solution were used for E measurement. Potential values for the reference electrode were from Langmuir (9). The error in these values caused by a residual liquid-junction potential at the low pH's of the study solutions is probably less than +0.001 V (2) (assuming a Debye-Hückel effective ion diameter of 3 Å for the chloride ion). The pH measuring assembly was calibrated with fresh potassium tetroxalate buffer (pH = 1.68 \pm 0.01 at 25°C).

E measurements were checked against Zobell solution (a solution both 0.003M in potassium ferrocyanide and in potassium ferricyanide, and 0.1M in potassium chloride) and are probably accurate to within ± 0.001 V (9). In addition, the reference electrode was checked against a second reference electrode of the same type and differed by only

0.0001 V. Accordingly, pH and Eh (oxidation potential) measurements are probably accurate to ± 0.02 pH unit and 0.002 V, respectively. Temperature measurements were made with a 0–50°C thermometer graduated in divisions of 0.1°C and calibrated at the ice point, and are probably accurate to $\pm 0.2^\circ\text{C}$. Total dissolved iron and total dissolved ferrous iron concentrations were determined by $\text{K}_2\text{Cr}_2\text{O}_7$ titration, and total dissolved ferric iron by difference (8).

RESULTS AND DISCUSSION

Total concentrations of dissolved Fe(II) and Fe(III) species (average of values determined before and after the measurements listed in Table I) were $(3.01 \pm 0.02) \times 10^{-3}M$ and $(6.67 \pm 0.04) \times 10^{-3}M$, respectively, where \pm refers to the range of measured values. The total perchlorate concentration was $5.69 \times 10^{-2}M$. Measured pH ranged from 1.470–1.490 (precision ± 0.005 pH unit) and averaged 1.477, the value used in calculations of E° .

Table I gives the experimental data in the order of measurement. Values of Eh were taken from a smoothed plot of measured Eh vs. temperature. E° values at five-degree intervals were calculated from

$$E^\circ = Eh + \frac{RT}{nF} \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad (2)$$

where R is the gas constant, 1.9872×10^{-3} kcal/deg mol, T the temperature in K degrees, n the number of electrons in the cell reaction, F the Faraday, 23.061 kcal/V equiv, and $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$ the activities of Fe^{2+} and Fe^{3+} , respectively.

Activity coefficients of Fe^{2+} and Fe^{3+} at the different temperatures were calculated from the Debye-Hückel equation using A and B coefficients on a volume basis (5), and taking into account the FeOH^{2+} complex, and the $\text{Fe}_2(\text{OH})_2^{4+}$ dimer. The equilibrium constants

$$K_1 = \frac{[\text{FeOH}^{2+}][\text{H}^+]}{[\text{Fe}^{3+}]} \quad (3)$$

and

$$K_{22} = \frac{[\text{Fe}_2(\text{OH})_2^{4+}]}{[\text{FeOH}^{2+}]^2} \quad (4)$$

as a function of temperature were determined from the data of

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Table I. Experimental Data in Order of Measurement

| T, °C | pH | E, V | Eh, V | $\gamma_{\text{Fe}^{2+}}$ | $\gamma_{\text{Fe}^{3+}}$ | $[\text{Fe}^{2+}] \times 10^3$ | $[\text{Fe}^{3+}] \times 10^3$ | E° |
|-------|-------|--------|--------|---------------------------|---------------------------|--------------------------------|--------------------------------|-----------|
| 25.0 | 1.475 | 0.5695 | 0.7680 | 0.421 | 0.193 | 1.268 | 1.171 | 0.7700 |
| 19.3 | 1.49 | 0.5587 | 0.7633 | 0.424 | 0.194 | 1.275 | 1.217 | 0.7645 |
| 5.4 | 1.47 | 0.5282 | 0.7463 | 0.430 | 0.200 | 1.293 | 1.295 | 0.7462 |
| 10.0 | 1.48 | 0.5381 | 0.7519 | 0.428 | 0.198 | 1.287 | 1.272 | 0.7522 |
| 15.0 | 1.48 | 0.5485 | 0.7574 | 0.426 | 0.196 | 1.281 | 1.245 | 0.7581 |
| 25.0 | 1.48 | 0.5688 | 0.7673 | 0.421 | 0.193 | 1.268 | 1.171 | 0.7693 |
| 30.0 | 1.475 | 0.5787 | 0.7722 | 0.419 | 0.191 | 1.262 | 1.127 | 0.7752 |
| 35.0 | 1.475 | 0.5876 | 0.7760 | 0.417 | 0.189 | 1.254 | 1.071 | 0.7802 |
| 20.0 | 1.48 | 0.5581 | 0.7620 | 0.423 | 0.194 | 1.274 | 1.212 | 0.7633 |

Milburn (15). At 25°C for the monomer, $K_1 = (6.7 \pm 0.4) \times 10^{-3}$ and $\Delta H^\circ = 10.4 \pm 0.2$ kcal/mol, and for the dimer, $K_{22} = 30 \pm 10$, and $\Delta H^\circ = -7.3 \pm 1.0$ kcal/mol. ΔH° for the monomer is in good agreement with Arnek's (1) calorimetric value of 11.0 ± 1.8 kcal/mol. The equality $\gamma_{\text{FeOH}^{2+}} = \gamma_{\text{Fe}^{2+}}$ was used as a good approximation based on the assumption that the ions would have similar hydration envelopes and thus a similar Debye-Hückel effective ion diameter (\tilde{a}) of 6 Å. A measure of the maximum uncertainty in this assumption was determined by choosing $\tilde{a} = 8$ Å in the $\gamma_{\text{FeOH}^{2+}}$ calculation, which lowered the 35°C value of E° by 0.0004 V. For the calculation of $\gamma_{\text{Fe}_2(\text{OH})_2^{4+}}$, $\tilde{a} = 11$ Å was used, based on the assumption that the complex's hydration sphere resembles that of Zn^{4+} ion (7).

Ionic strength (μ) values used in the Debye-Hückel equation were calculated from the concentrations of the following species: perchlorate from ferrous and ferric perchlorates and added perchloric acid, free Fe^{3+} , FeOH^{2+} and $\text{Fe}_2(\text{OH})_2^{4+}$ complexes, Fe^{2+} , and H^+ . The calculation was made by iteration, first ignoring FeOH^{2+} and $\text{Fe}_2(\text{OH})_2^{4+}$, then recalculating to include the effect of these complexes until μ remained constant. Values of μ ranged from 0.0840 at 5°C to 0.0824 at 35°C.

Resultant smoothed values of E° vs. temperature, probably accurate to ± 0.002 V, are listed in Table II. The empirical equation

$$E_T^\circ = -1.23 \times 10^{-2} + 4.147 \times 10^{-3} T - 5.111 \times 10^{-6} T^2 \quad (5)$$

fits the smoothed E_T° values well within the measurement precision of ± 0.001 V. The uncertainty in Milburn's ΔH° and K_1 for FeOH^{2+} at 25°C (15), giving errors in $\log K_1$ of ± 0.03 at 25° and 35°C, and ± 0.04 at 5°C, change E° by less than ± 0.0003 V. The uncertainty in K_{22} has a similar effect on E_T° .

Values of E_T° may also be computed from thermochemical data at 25°C with the two equations

$$-E_T^\circ = \frac{T \Delta G_{298}^\circ}{nF (298.15)} + \frac{\Delta H_{298}^\circ}{nF} \left(1 - \frac{T}{298.15} \right) \quad (6)$$

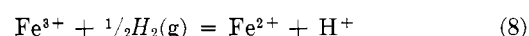
Table II. Experimental and Computed E° Values in Volts as a Function of Temperature

| T, °C | Exptl ^a | Equation 6, $\Delta C_p^\circ = 0$ | Equation 7, $\Delta C_p^\circ = -28$ cal/deg mol |
|-------|--------------------|---------------------------------------|--|
| 0 | (0.7391) | 0.7404 | 0.7393 |
| 5 | 0.7458 | 0.7463 | 0.7454 |
| 10 | 0.7522 | 0.7521 | 0.7517 |
| 15 | 0.7583 | 0.7580 | 0.7578 |
| 20 | 0.7642 | 0.7638 | 0.7638 |
| 25 | 0.7698 | 0.7697 | 0.7697 |
| 30 | 0.7752 | 0.7756 | 0.7755 |
| 35 | 0.7803 | 0.7814 | 0.7812 |
| 50 | (0.7941) | 0.7990 | 0.7977 |

^a Parentheses denote extrapolated values.

$$-E_T^\circ = \frac{T \Delta G_{298}^\circ}{nF (298.15)} + \frac{\Delta H_{298}^\circ}{nF} \left(1 - \frac{T}{298.15} \right) - \frac{\Delta C_{p298}^\circ}{nF} \left[(298.15 - T) - T \ln \frac{298.15}{T} \right] \quad (7)$$

These assume $\Delta C_{p298}^\circ = 0$, and $\Delta C_{p298}^\circ = \text{constant}$, respectively, for



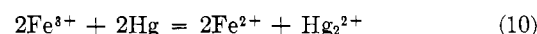
which is equivalent to Reaction 1. Substituting $\Delta G_{298}^\circ = -17.75$ kcal/mol and $\Delta H_{298}^\circ = -9.7$ kcal/mol from data in Wagman et al. (21) into Equation 6 yields

$$E_T^\circ = 0.42062 \pm 0.0011708 T \quad (9)$$

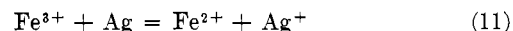
$\Delta C_{p298}^\circ = -28$ cal/deg mol for Reaction 8 based on a conventional $C_{p298}^\circ = 6.889$ cal/deg mol for $\text{H}_2(\text{g})$ (21) and "absolute" ionic heat capacities of 86 cal/deg mol for Fe^{3+} from Criss and Cobble (4) and 61 cal/deg mol for Fe^{2+} (estimated). The use of mixed conventions for the heat capacities is permissible in that each convention is used once on each side of Equation 8.

Computed values of E_T° from 0–50°C based on Equations 6 and 7 are listed with measured values of this quantity in Table II. Experimental and computed values from 5–35°C agree to within about 0.001 V, the measurement precision. E_T° values estimated assuming $\Delta C_p^\circ = 0$ and $\Delta C_p^\circ = -28$ cal/deg mol differ from each other by less than 0.001 V except at 0° and 50°C where the differences are slightly larger. Extrapolation of empirical Equation 5 to 0°C gives 0.7391 V, in good agreement with 0.7393 V estimated from Equation 7. At 50°C, however, the extrapolated value from Equation 5 is 0.0036 V lower than the value from Equation 7.

$E_{298}^\circ = 0.770 \pm 0.002$ V measured in this study agrees well with published values of 0.772 ± 0.001 V (3), 0.771 ± 0.004 V (14), and 0.7701 ± 0.0002 V (19). Bray and Hershey's (3) E_{298}° was an average of 0.7715 and 0.7725 V calculated from data on the reactions



and



respectively. Their approach involved subtraction of the appropriate mercury and silver half-cell standard potentials from the cell potentials of Reactions 10 (18) and 11 (16), which they obtained from equilibrium data and corrected for ferric ion hydrolysis. The measurements on Reaction 10 were made in acidified perchlorate salt solutions at low μ (18); those on Reaction 11 in acidified nitrate salt solutions at high μ (16). ΔG_{298}° data from Wagman et al. (21) permit recalculation of E° values for the mercury and silver half-cells and correction of cell potentials for Reactions 10 and 11 to give 0.7695 and 0.7733 V, respectively.

Mattoo (14) calculated E_{298}° from the measured data of Lapteva (11) on ferrous-ferric sulfate solutions, which he corrected for ferric sulfate complexing.

Table III. Thermodynamic Properties of Ferric-Ferrous Cell, Equation 8, at 25°C^a

| | This work | Wagman et al. (21) | Larson et al. (12) |
|--------------------------------|---------------|--------------------|--------------------|
| E° , V | 0.770 ± 0.002 | 0.770 ± 0.001 | 0.771 ± 0.001 |
| ΔG° , kcal/mol | -17.75 ± 0.04 | -17.75 ± 0.02 | -17.78 ± 0.02 |
| ΔH° , kcal/mol | -10.2 ± 0.4 | -9.7 ± 0.5 | -10 ± 0.5 |
| ΔS° , cal/deg mol | 25.4 ± 1.5 | 27.0 ± 1.5 | 26 ± 1.7 |

^a Uncertainties in Wagman et al. values from V. B. Parker (17).

The E_{298}° value of Schumb et al. (19) was obtained by extrapolation to $\mu = 0$ of E values measured at different ionic strengths in ferrous-ferric perchlorate solutions. The log of K_1 , which they used to correct their E_{298}° value, differed from log K_1 in this study by only -0.05 unit. Their E_{298}° appears to be the best and differs by only +0.0003 V from the smoothed experimental value from Equation 5.

For all of the above values and in this paper, ferric perchlorate and nitrate association was assumed to be negligible. This assumption is valid based on the data of Jones et al. (6) and Zagorets and Bulgakova (22) who found no evidence for ferric perchlorate association in Raman spectra of 3M Fe(ClO₄)₃ and ultraviolet spectra of solutions $3.1 \times 10^{-2}M$ in Fe³⁺ and 0.5 to 3M in perchloric acid, respectively. Changes in the ultraviolet spectra in ferric perchlorate solutions from which Sykes (20) obtained FeClO₄²⁺ association constants do not appear to be caused by association, but by the influence of the electrostatic fields of alkali metal and alkaline earth ions on the hydration shell of the Fe³⁺ ion (22).

Other thermodynamic properties of the ferric-ferrous cell (Reaction 8) may be calculated from empirical Equation 5 using the following expressions:

$$\Delta G_T^\circ = -nFE_T^\circ \quad (12)$$

$$\Delta H_T^\circ = -nF \left[E_T^\circ - T \left(\frac{\partial E_T^\circ}{\partial T} \right)_p \right] \quad (13)$$

$$\Delta S_T^\circ = - \left(\frac{\partial \Delta G_T^\circ}{\partial T} \right)_p = -nF \left(\frac{\partial E_T^\circ}{\partial T} \right)_p \quad (14)$$

where ΔS_T° is the entropy of the reaction. Values at 25°C so obtained are compared with similar published values (12, 21) in Table III. An accuracy of ±0.002 V in E° gives an uncertainty of ±0.04 kcal/mol in ΔG_T° . Uncertainties in ΔH_T° and ΔS_T° were calculated by rotating the experimental curve about its center (20°C), adding the experimental precision of 0.001 V to the 35°C value, and subtracting it from the 5°C value. Although a residual junction-potential could affect the accuracy of the E° values, it would not change the slope of the curve.

The E_{298}° value chosen by Larson et al. (12) is from Latimer (13) who in turn obtained his value as an average from Bray and Hershey (3) and Schumb et al. (19). The ΔH_{298}° of Larson et al. is an estimation of the most probable value from six references in which measurements were made by calorimetric and equilibrium methods. Except for one value, all range from 9.5–10.6 kcal/mol. The ΔS_{298}° value of Larson et al. is derived from

$$\Delta S_T^\circ = \frac{\Delta H_T^\circ - \Delta G_T^\circ}{T} \quad (15)$$

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