**Special Issue dedicated to Peter Williams**

**Evaluation for internal consistency in the thermodynamic network involving fluorite, cryolite and villiaumite solubilities and aqueous species at 25°C and 1 bar**

D. Kirk Nordstrom

United States Geological Survey, Boulder, CO 80303, USA

**Appendix.** Variations in molal concentrations and activities for the data of Roberson and Hem (1968) by Method 1: using the measured concentrations and using *PHREEQC* to calculate free ion activities and Method 2: changing the measured concentrations until the free-ion activities matched those measured with ion-selective electrodes. The reported results of Roberson and Hem (1968) are shown for comparison.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Constituent  | Roberson and Hem (1968) | Revised, Method 1 with PHREEQC | Revised, Method 2 with PHREEQC |
| I | Na, *m* | 0.104 | 0.104 | 0.1036 |
| I | Na+, activity | 0.0810 | 0.0812 | 0.0810 |
| I | Al, *m* | 0.00759 | 0.00759 | 0.00759 |
| I | Al3+, activity | 5.01 × 10–9 | 8.31 × 10–11  | 7.82 × 10–9 |
| I | F, *m* | 0.0260 | 0.0260 | 0.02122 |
| I | F–, activity | 0.000214 | 0.000971 | 0.000214 |
| I | ClO4, *m* | 0.105 | 0.105 | 0.105 |
|  | Charge balance |  | –1.98% | +0.07% |
| II | Na, *m* | 0.0909 | 0.0909 | 0.0940 |
| II | Na+, activity | 0.0758 | 0.0707 | 0.0734 |
| II | Al, *m* | 0.0272 | 0.0272 | 0.0272 |
| II | Al3+, activity | 1.20 × 10–7 | 3.703 × 10–6 | 1.76 × 10–7 |
| II | F, *m* | 56.9 | 56.9 | 68.6 |
| II | F–, activity | 0.107 | 0.02834 | 0.107 |
| II | ClO4, *m* | 0.105 | 0.105 | 0.105 |
|  | Charge balance |  | +4.81% | 0.91% |
| III | Na, *m* | 0.111 | 0.111 | 0.111 |
| III | Na+, activity | 0.0890 | 0.0862 | 0.0863 |
| III | Al, *m* | 1.12 × 10–4 | 1.12 × 10–4 | 1.12 × 10–4 |
| III | Al3+, activity | 1.25 × 10–13 | 4.585 × 10–13 | 5.07 × 10–13  |
| III | F, *m* | 8.21 | 8.21 | 0.00693 |
| III | F–, activity | 0.0050 | 0.00590 | 0.0050 |
| III | ClO4, *m* | 0.105 | 0.105 | 0.105 |
|  | Charge balance |  | –1.00% | –0.44% |
| IV | Na, *m* | 0.111 | 0.111 | 0.111 |
| IV | Na+, activity | 0.0890 | 0.0864 | 0.0890 |
| IV | Al, *m* | 1.11 × 10–5  | 1.11 × 10–5 | 1.11 × 10–5 |
| IV | Al3+, activity | 1.36 × 10–14 | 3.01 × 10–14 | 2.71 × 10–14 |
| IV | F, *m* | 0.00205 | 0.00205 | 0.00210 |
| IV | F–, activity | 0.00151 | 0.00146 | 0.00151 |
| IV | ClO4, *m* | 0.109 | 0.109 | 0.109 |
|  | Charge balance |  | –0.01% | –0.04% |
| V | Na, *m* | 0.0974 | 0.0974 | 0.100 |
| V | Na+, activity | 0.085 | 0.0759 | 0.0782 |
| V | Al, *m* | 0.0259 | 0.0259 | 0.0259 |
| V | Al3+, activity | 1.22 × 10–7 | 1.23 × 10–7 | 1.77 × 10–7 |
| V | F, *m* | 0.0665 | 0.0665 | 0.0652 |
| V | F–, activity | 1.04 × 10–4 | 1.04 × 10–4 | 1.04 × 10–4 |
| V | ClO4, *m* | 0.109 | 0.109 | 0.109 |
|  | Charge balance |  | –0.11% | +1.81% |