

Some Thermodynamic Properties of Calcium Chromate

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Solubilities of CaCrO_4 in water from 110 °C to 160 °C and aqueous sodium chromate solution from 25 °C to 80 °C were measured. From these data, activity coefficients were calculated and compared with Bromley's method. The results agree. The standard enthalpy of formation and standard Gibbs free energy of formation of CaCrO_4 calculated through thermodynamic laws were compared with literature values. Recalculated values are $\Delta_f H(\text{CaCrO}_4, 298 \text{ K}) = -1401.2 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f G(\text{CaCrO}_4, 298 \text{ K}) = -1299.4 \text{ kJ}\cdot\text{mol}^{-1}$.

1. Introduction

CaCrO_4 has long been used as a cathode material in thermally activated electrochemical cells.¹ It is also an intermediate compound formed in the system of Ca–Cr–O, which is involved in many industrial processes.² Therefore, reliable thermodynamic information such as the enthalpy, Gibbs free energy, and solubility product is needed to better understand systems involving CaCrO_4 . Unfortunately, the values in the literature^{3–7} are rather scattered; some are even contradictory and inaccurate. The purpose of this work is to determine some solubility data of CaCrO_4 . Its standard enthalpy of formation and standard Gibbs free energy of formation in the literature are also checked through thermodynamic relationships.

2. Experimental Section

Solubilities of CaCrO_4 in water from 110 °C to 160 °C and in aqueous sodium chromate solution from 25 °C to 80 °C were measured. Literature data exist for the solubility of CaCrO_4 in water below 100 °C, and a few solubility data exist for CaCrO_4 in aqueous sodium chromate solution.

Reagents. Analytical-grade CaCO_3 (purity ≥ 99.0 mass %), $\text{Na}_2\text{CrO}_4\cdot 4\text{H}_2\text{O}$ (purity ≥ 99.5 mass %), and $\text{Na}_2\text{Cr}_2\text{O}_7\cdot 2\text{H}_2\text{O}$ (purity ≥ 99.5 mass %) were purchased from the Beijing Chemical Plant. CaCrO_4 (purity ≥ 99.5 mass %, mean size 5 μm) was prepared from CaCO_3 and $\text{Na}_2\text{Cr}_2\text{O}_7\cdot 2\text{H}_2\text{O}$ according to the method of Wang et al.⁸

Apparatus and Procedure. CaCrO_4 (20 g) and distilled water (1500 mL) were put into a 2-L autoclave (model WHFK-2, Weihai Automation Control Autoclave Co. Ltd., China) with a temperature control unit. The slurry was heated and kept at a predetermined temperature. Samples were taken in a given time interval and filtered with a 0.22- μm membrane filter. Cr^{6+} in the filtrates was titrated with ammonium ferrous sulfate with *N*-phenylanthranilic acid as the indicator⁹ (uncertainty of 0.08 mass %), and the amount of dissolved CaCrO_4 was calculated. When the

Table 1. Solubility of CaCrO_4 s₁ in Water between 110 °C and 160 °C

| $t/^\circ\text{C}$ | 110 | 120 | 130 | 140 | 150 | 160 |
|--|--------|--------|--------|--------|--------|-------|
| $10^3 s_1/\text{mol}\cdot\text{kg}^{-1}$ | 22.244 | 19.167 | 15.192 | 11.923 | 10.385 | 9.487 |

composition reached a constant (in about 12 h), the value was recorded as the solubility at that temperature.

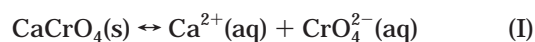
Sodium chromate solution (100 mL), with a composition ranging from about (2 to 30)g/100 g of H_2O prepared from $\text{Na}_2\text{CrO}_4\cdot 4\text{H}_2\text{O}$ and distilled water, and (2 to 5) g of CaCrO_4 were placed into 150-mL conical flasks. For comparison, 100 mL of H_2O without sodium chromate was also used. The mixtures were kept in a shaker bath (model HZS-H, Haerbin Donglian Electronic Development Co., China) to attain the desired temperature with an uncertainty of ± 0.1 °C. Samples were taken at time intervals and filtered with a 0.22- μm membrane filter. The amounts of Cr^{6+} and Ca^{2+} in the filtrates were determined by the above-mentioned method, and EDTA titration was carried out according to the method in ref 10 (uncertainty of 0.1 mass %). When the compositions became constant (at 25 °C, it took 4 weeks; at 80 °C, it took 2 days), the results were recorded. The same procedure was used to analyze all of the filtrates. By means of the electrically neutral condition, the amounts of Na_2CrO_4 and CaCrO_4 in the solutions were calculated. The densities of the equilibrium solutions were measured using a 5-mL pycnometer.

Results. The solubilities of CaCrO_4 in water from 110 °C to 160 °C determined in this study are shown in Table 1 and compared with those in the literature and shown in Figure 1. It can be found that the values obtained in this study are in very close agreement with those of ref 11. The values of ref 12 are slightly higher.

The solubilities of CaCrO_4 in aqueous sodium chromate solution from 25 °C to 80 °C are shown in Table 2.

3. Thermodynamic Analysis and Discussion

CaCrO_4 dissolves in water and dissociates as follows:



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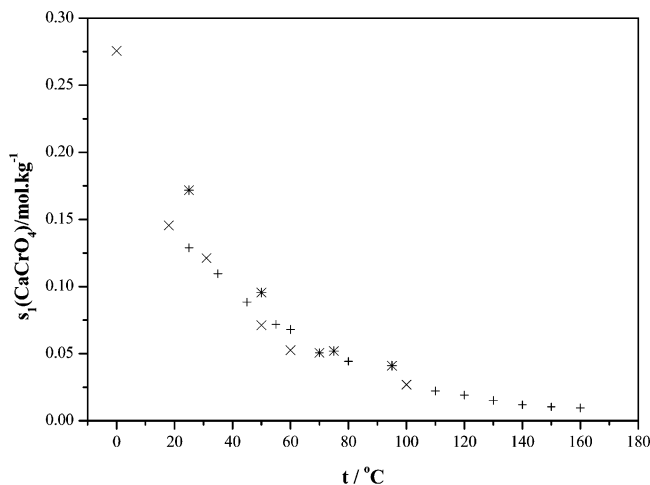


Figure 1. Solubilities of CaCrO_4 in water: +, this work; \times , Linke;¹¹ *, Silcock.¹²

Table 2. Solubility of CaCrO_4 s_1 and Density ρ in an Aqueous Sodium Chromate Solution of m_2

| t | $10^3 s_1$ | m_2 | ρ | t | $10^3 s_1$ | m_2 | ρ |
|------------------|---------------------------------|---------------------------------|--------------------------------|------------------|---------------------------------|---------------------------------|--------------------------------|
| $^\circ\text{C}$ | $\text{mol}\cdot\text{kg}^{-1}$ | $\text{mol}\cdot\text{kg}^{-1}$ | $\text{kg}\cdot\text{dm}^{-3}$ | $^\circ\text{C}$ | $\text{mol}\cdot\text{kg}^{-1}$ | $\text{mol}\cdot\text{kg}^{-1}$ | $\text{kg}\cdot\text{dm}^{-3}$ |
| 25 | 131.310 | 0 | 1.0091 | 55 | 72.310 | 0 | 1.0024 |
| | 114.942 | 0.123 | 1.0181 | | 59.658 | 0.138 | 1.0197 |
| | 112.413 | 0.234 | 1.0386 | | 58.472 | 0.257 | 1.0317 |
| | 109.711 | 0.394 | 1.0576 | | 57.002 | 0.421 | 1.0531 |
| | 104.431 | 0.530 | 1.0697 | | 55.276 | 0.514 | 1.0648 |
| | 103.531 | 0.636 | 1.0936 | | 55.337 | 0.682 | 1.0873 |
| | 105.007 | 0.791 | 1.1033 | | 44.549 | 1.553 | 1.1814 |
| | 105.433 | 0.997 | 1.1252 | | 30.476 | 2.620 | 1.2904 |
| | 105.502 | 1.342 | 1.1714 | 60 | 68.728 | 0 | 0.9969 |
| 35 | 109.173 | 0 | 1.0189 | | 47.566 | 0.130 | 1.0097 |
| | 96.901 | 0.126 | 1.0256 | | 53.284 | 0.289 | 1.0375 |
| | 94.219 | 0.253 | 1.0461 | | 53.192 | 0.652 | 1.0766 |
| | 94.179 | 0.405 | 1.0645 | | 47.866 | 1.261 | 1.1159 |
| | 94.235 | 0.526 | 1.0794 | 70 | 51.131 | 0 | 0.9960 |
| | 92.003 | 0.673 | 1.0987 | | 40.011 | 0.142 | 1.0118 |
| | 76.810 | 1.425 | 1.1865 | | 39.299 | 0.422 | 1.0509 |
| | 49.966 | 2.791 | 1.2950 | | 38.657 | 0.613 | 1.0721 |
| 45 | 89.431 | 0 | 1.0073 | | 39.036 | 0.754 | 1.0931 |
| | 73.878 | 0.143 | 1.0249 | | 34.327 | 1.620 | 1.1857 |
| | 72.005 | 0.261 | 1.0382 | 80 | 44.101 | 0 | 0.9956 |
| | 71.261 | 0.421 | 1.0589 | | 31.881 | 0.140 | 1.0116 |
| | 69.596 | 0.531 | 1.0695 | | 31.79 | 0.278 | 1.0279 |
| | 68.953 | 0.727 | 1.0939 | | 31.949 | 0.414 | 1.047 |
| | 56.368 | 1.579 | 1.1831 | | 32.512 | 0.576 | 1.0643 |
| | 33.868 | 2.644 | 1.2923 | | 32.367 | 0.715 | 1.0842 |
| 50 | 78.473 | 0 | 0.9979 | | 29.529 | 1.672 | 1.1887 |
| | 63.858 | 0.124 | 1.0161 | | 21.175 | 2.759 | 1.2888 |
| | 62.125 | 0.240 | 1.0341 | | | | |
| | 63.398 | 0.399 | 1.0532 | | | | |
| | 62.819 | 0.511 | 1.0707 | | | | |
| | 58.772 | 0.648 | 1.0869 | | | | |

Activity coefficients of CaCrO_4 in saturated water solution and in aqueous sodium chromate solution can be calculated through the following equation:

$$\gamma_{\pm}^2 = \frac{K_{\text{sp}}(\text{CaCrO}_4)}{m(\text{Ca}^{2+}) m(\text{CrO}_4^{2-})} \quad (1)$$

$m(\text{Ca}^{2+})$ and $m(\text{CrO}_4^{2-})$ are the molalities of Ca^{2+} and CrO_4^{2-} in solution. However, only the value of $K_{\text{sp}}(\text{CaCrO}_4, 298 \text{ K})$ is available. Thermodynamically, the solubility product of CaCrO_4 , $K_{\text{sp}}(\text{CaCrO}_4)$, and the standard Gibbs free energy change, ΔG_1 , for reaction I have the following relationship:

$$\Delta G_1 = -RT \ln K_{\text{sp}}(\text{CaCrO}_4) \quad (2)$$

where $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and T is the absolute

Table 3. Standard Gibbs Free Energies of Formation, Enthalpies of Formation, and Entropies of CaCrO_4 , $\text{Ca}^{2+}(\text{aq})$, and $\text{CrO}_4^{2-}(\text{aq})$

| | $\text{CaCrO}_4(\text{s})$ | $\text{Ca}^{2+}(\text{aq})$ | $\text{CrO}_4^{2-}(\text{aq})$ |
|--|----------------------------|-----------------------------|--------------------------------|
| $-\Delta G/\text{kJ}\cdot\text{mol}^{-1}$ | 1277.4 ^a | 1299.4 ^a | 553.5 ^a |
| $-\Delta H/\text{kJ}\cdot\text{mol}^{-1}$ | 1379.1 ^a | 1401.2 ^a | 542.8 ^a |
| $S/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ | 133.9 ^a | -53.1 ^a | 50.2 ^a |

^a Values from this work.

Table 4. Activity Coefficients of CaCrO_4 in Aqueous Sodium Chromate Solution^a

| $t/^\circ\text{C}$ | $\text{mol}\cdot\text{kg}^{-1}$ | γ_{\pm} | γ_{\pm}^* | $\gamma_{\pm}/\gamma_{\pm}^*$ | $t/^\circ\text{C}$ | $\text{mol}\cdot\text{kg}^{-1}$ | γ_{\pm} | γ_{\pm}^* | $\gamma_{\pm}/\gamma_{\pm}^*$ |
|--------------------|---------------------------------|----------------|------------------|-------------------------------|--------------------|---------------------------------|----------------|------------------|-------------------------------|
| 25 | 0.516 | 0.205 | 0.181 | 1.132 | 55 | 0.290 | 0.244 | 0.227 | 1.074 |
| | 0.829 | 0.164 | 0.148 | 1.111 | | 0.653 | 0.163 | 0.162 | 1.004 |
| | 1.153 | 0.137 | 0.128 | 1.069 | | 1.004 | 0.131 | 0.135 | 0.971 |
| | 1.620 | 0.116 | 0.110 | 1.052 | | 1.49 | 0.108 | 0.114 | 0.955 |
| | 2.008 | 0.107 | 0.100 | 1.070 | | 1.763 | 0.101 | 0.105 | 0.961 |
| | 2.324 | 0.099 | 0.093 | 1.059 | | 2.266 | 0.089 | 0.094 | 0.952 |
| | 2.792 | 0.09 | 0.085 | 1.056 | | 4.836 | 0.070 | 0.066 | 1.051 |
| | 3.414 | 0.082 | 0.078 | 1.053 | | 7.981 | 0.068 | 0.056 | 1.215 |
| | 4.449 | 0.072 | 0.069 | 1.040 | 60 | 0.275 | 0.243 | 0.232 | 1.046 |
| 35 | 0.445 | 0.207 | 0.191 | 1.085 | | 0.580 | 0.182 | 0.170 | 1.071 |
| | 0.766 | 0.158 | 0.153 | 1.034 | | 1.08 | 0.124 | 0.131 | 0.946 |
| | 1.136 | 0.128 | 0.129 | 0.994 | | 2.17 | 0.088 | 0.096 | 0.919 |
| | 1.592 | 0.107 | 0.111 | 0.970 | | 3.976 | 0.071 | 0.072 | 0.986 |
| | 1.955 | 0.097 | 0.101 | 0.960 | 70 | 0.204 | 0.287 | 0.261 | 1.101 |
| | 2.387 | 0.088 | 0.092 | 0.964 | | 0.586 | 0.174 | 0.169 | 1.028 |
| | 4.583 | 0.071 | 0.068 | 1.040 | | 1.423 | 0.111 | 0.116 | 0.958 |
| | 8.573 | 0.069 | 0.055 | 1.244 | | 1.992 | 0.095 | 0.099 | 0.956 |
| 45 | 0.358 | 0.225 | 0.209 | 1.076 | | 2.418 | 0.086 | 0.091 | 0.944 |
| | 0.725 | 0.159 | 0.156 | 1.022 | | 4.998 | 0.065 | 0.066 | 0.999 |
| | 1.07 | 0.131 | 0.132 | 0.993 | 80 | 0.176 | 0.298 | 0.277 | 1.077 |
| | 1.548 | 0.109 | 0.112 | 0.971 | | 0.546 | 0.179 | 0.174 | 1.026 |
| | 1.871 | 0.100 | 0.103 | 0.976 | | 0.962 | 0.134 | 0.137 | 0.975 |
| | 2.457 | 0.088 | 0.090 | 0.973 | | 1.371 | 0.111 | 0.117 | 0.949 |
| | 4.962 | 0.070 | 0.066 | 1.067 | | 1.858 | 0.095 | 0.102 | 0.932 |
| | 8.066 | 0.074 | 0.056 | 1.313 | | 2.275 | 0.086 | 0.093 | 0.927 |
| 50 | 0.32 | 0.239 | 0.218 | 1.094 | | 5.135 | 0.062 | 0.065 | 0.960 |
| | 0.626 | 0.173 | 0.165 | 1.048 | | 8.363 | 0.060 | 0.055 | 1.087 |
| | 0.968 | 0.138 | 0.137 | 1.007 | | | | | |
| | 1.451 | 0.111 | 0.115 | 0.968 | | | | | |
| | 1.783 | 0.1 | 0.105 | 0.959 | | | | | |
| | 2.179 | 0.094 | 0.095 | 0.985 | | | | | |

^a γ_{\pm} was calculated from equation 1 and γ_{\pm}^* was calculated using Bromley's method and the ionic strength I .

temperature. The values of ΔG_1 are not available. If the heat capacity change is assumed to be zero, then the following equation holds

$$\ln \frac{K_{\text{sp}2}}{K_{\text{sp}1}} \approx \frac{\Delta H_1(298 \text{ K})}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \quad (3)$$

where $K_{\text{sp}1}$ and $K_{\text{sp}2}$ are the solubility products of CaCrO_4 at temperatures T_1 and T_2 . $\Delta H_1(298 \text{ K})$ is the enthalpy change for reaction I at 298 K and can be calculated from the enthalpies of formation of CaCrO_4 , $\text{Ca}^{2+}(\text{aq})$, and $\text{CrO}_4^{2-}(\text{aq})$, which are listed in Table 3. The result for $\Delta H_1(298 \text{ K})$ is $-44.88 \text{ kJ}\cdot\text{mol}^{-1}$.

When the calculated results of $K_{\text{sp}}(\text{CaCrO}_4)$ were used in our research work, unreasonable results occurred. Therefore, we doubted the accuracy of $\Delta_f H(\text{CaCrO}_4, 298 \text{ K}) = -1379.1 \text{ kJ}\cdot\text{mol}^{-1}$. $\Delta H_1(298 \text{ K})$ was redetermined by the following equation:

$$\Delta H_1(298 \text{ K}) = \Delta G_1(298 \text{ K}) - 298.15 \Delta S_1(298 \text{ K})$$

where $\Delta G_1(298 \text{ K}) = 17.97 \text{ kJ}\cdot\text{mol}^{-1}$ was calculated by means of eq 2 and $K_{\text{sp}}(\text{CaCrO}_4, 298 \text{ K}) = 7.1 \times 10^{-4}$ (ref 4). $\Delta S_1(298 \text{ K}) = -136.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ was calculated from the data of Table 1. Recalculated $\Delta H_1(298 \text{ K})$ is -22.80

$\text{kJ}\cdot\text{mol}^{-1}$. With this value, $K_{\text{sp}}(\text{CaCrO}_4, 298 \text{ K})$, and eq 3, $K_{\text{sp}}(\text{CaCrO}_4)$ values of different temperatures were obtained and used to calculate the mean ionic activity coefficients of CaCrO_4 . The results are shown in Table 4 and compared with those calculated by Bromley's method.¹³

The activity coefficients calculated by eq 1 and those by Bromley's method are consistent with each other. Except for three values at about $I = 8.0 \text{ mol}\cdot\text{kg}^{-1}$, the majority of the differences are less than 10%. However, if $\Delta H_1(298 \text{ K}) = -44.88 \text{ kJ}\cdot\text{mol}^{-1}$ were used instead of $\Delta H_1(298 \text{ K}) = -22.80 \text{ kJ}\cdot\text{mol}^{-1}$, then the differences would be substantial. Although Bromley's method is an empirical correlation and cannot be used to justify $\Delta H_1(298 \text{ K}) = -22.80 \text{ kJ}\cdot\text{mol}^{-1}$ fully, we may consider $\Delta H_1(298 \text{ K}) = -22.80 \text{ kJ}\cdot\text{mol}^{-1}$ to be more reasonable.

With $\Delta H_1(298 \text{ K}) = -22.80 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H(\text{Ca}^{2+}(\text{aq}), 298 \text{ K}) = -542.8 \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_f H(\text{CrO}_4^{2-}(\text{aq}), 298 \text{ K}) = -881.2 \text{ kJ}\cdot\text{mol}^{-1}$, the recalculated formation enthalpy of CaCrO_4 is $-1401.2 \text{ kJ}\cdot\text{mol}^{-1}$ and is also shown in Table 3.

4. Conclusions

The solubilities of CaCrO_4 in water and aqueous sodium chromate solution were measured from experiments, and the activity coefficients were calculated from the thermodynamic relationship and Bromley's method. The results are consistent with each other. The enthalpy of formation and Gibbs free energy of formation of CaCrO_4 calculated through thermodynamic laws were compared with the data in the literature, which indicated that $\Delta_f H(\text{CaCrO}_4, 298$

$\text{K}) = -1401.2 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f G(\text{CaCrO}_4, 298 \text{ K}) = -1299.4 \text{ kJ}\cdot\text{mol}^{-1}$ seem to be more reasonable.

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