

# Spectrophotometric Determination of the Chromate-Dichromate Equilibrium Constant

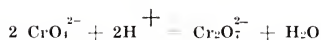
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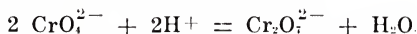
## Abstract

Using conventional spectrophotometric techniques, the concentration equilibrium constant for the reaction



was determined. For seven solutions with constant ionic strength of 0.375 molar, the average value is  $1.3 \times 10^{16}$  and the estimate of the standard deviation is  $0.97 \times 10^{16}$ . Calculations concerning total Cr(VI) content of the mixtures indicate that the concentration of the proposed intermediate  $\text{HCrO}_4^-$  is nearly 3 per cent of the content in the slightly acidic solutions studied.

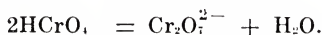
If a Beer's law plot is made for either the chromate or dichromate ion, the resulting curve of absorbance,  $A$ , plotted against the logarithm of the concentration is not a straight-line relationship as predicted by theory. This failure of the Bouger-Beer relationship is the result of the chemical equilibrium existing between the ions and the solvent. The overall reaction in acid or neutral media is



where the  $\text{H}^+$  could originate from the dissociation of the water or from an added source. The concentration equilibrium constant for this reaction,  $K_1$ , is given by

$$K_1 = [\text{Cr}_2\text{O}_7^{2-}] / [\text{CrO}_4^{2-}]^2 [\text{H}^+]^2$$

Previous work on this system by Sherrill (12) and Spitalsky (13) has shown that the probable mechanism for the reaction involves  $\text{HCrO}_4^-$  as an intermediate ion in a two step process which can be written as



Associated with each step is an equilibrium constant given by

$$K_2 = [\text{HCrO}_4^-] / [\text{CrO}_4^{2-}] [\text{H}^+]$$

$$K_3 = [\text{Cr}_2\text{O}_7^{2-}] / [\text{HCrO}_4^-]^2$$

where  $K_1 = K_2^2 K_3$ .

For solutions that are slightly acidic, the relative concentration of the intermediate ion is in the order of 1-10% of the total Cr(VI) concentration based on previous measurements of  $K_2$  and  $K_3$  reported by several investigators (2-6, 8, 9-14). For the purpose of determining

$K_1$ , the exact value of  $[\text{HCrO}_4^-]$  is not important, but by comparing the calculated value for the concentration of  $\text{Cr(VI)}$  from experimental values of  $[\text{Cr}_2\text{O}_7^{2-}]$  and  $[\text{CrO}_4^{2-}]$  to the known stoichiometric total of  $\text{Cr(VI)}$ , an estimate of  $[\text{HCrO}_4^-]$  can be made.

### Experimental

All spectrophotometric measurements were made using a Beckman DB-G recording spectrophotometer. The insulating jacket of the cell compartment was thermostated at  $25^\circ\text{C}$  by circulating water through it from a constant temperature bath. The pH measurements were made using a Leeds and Northrup Model 7401 pH meter. All solutions were prepared using normal quantitative laboratory techniques using Class A volumetric glassware. Once prepared, the solutions were allowed to sit for a period of a few hours in a constant temperature bath to come to equilibrium.

Spectra were taken for  $6 \times 10^{-5}\text{M}$  solutions of  $\text{Na}_2\text{CrO}_4$  containing 0.01 M HCl, 0.1 M HCl, 0.01 M NaOH and 0.1 M NaOH. There were no differences in the two acid spectra nor in the two base spectra indicating that complete separation of the  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions was achieved. A four-fold increase in concentration was desired to obtain spectra in the optimum range of 20-60% transmittance. From the spectra of an  $8 \times 10^{-5}\text{M}$   $\text{Na}_2\text{CrO}_4$  solution containing 0.4 M NaOH and  $2.4 \times 10^{-4}\text{M}$   $\text{Na}_2\text{CrO}_4$  containing 0.4 M HCl ( $[\text{Cr}_2\text{O}_7^{2-}] = 1.2 \times 10^{-4}\text{M}$ ) the working wavelengths of 352 and 373 nm were chosen.

Because of the overlap of the absorption curves at these wavelengths, it was necessary to measure the molar absorptancies for each ion at both wavelengths and to use the following equations to determine the individual ionic concentrations

$$[\text{CrO}_4^{2-}] = \frac{a_{2D}A_2 - a_{1D}A_1}{a_{1C}a_{2D} - a_{1D}a_{2C}}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = \frac{a_{1C}a_{2D} - a_{2C}A_1}{a_{1C}a_{2D} - a_{1D}a_{2C}}$$

where  $a$  is the molar absorptancy,  $A$  is the absorbance of the mixture, the subscripts 1 and 2 refer to the two chosen wavelengths, and the subscripts C and D stand for chromate and dichromate ion, respectively.

Duplicate trials were made on solutions of  $1.2 \times 10^{-4}\text{M}$   $\text{CrO}_4^{2-}$ , 0.125 M  $\text{Na}_2\text{HPO}_4$  and 0.03 M citric acid;  $2 \times 10^{-4}\text{M}$   $\text{CrO}_4^{2-}$ , 0.125 M  $\text{Na}_2\text{HPO}_4$  and 0.03 M citric acid;  $1.6 \times 10^{-4}\text{M}$   $\text{CrO}_4^{2-}$ , 0.125 M  $\text{Na}_2\text{HPO}_4$  and 0.045 M citric acid; and  $2.4 \times 10^{-4}\text{M}$   $\text{CrO}_4^{2-}$ , 0.125 M  $\text{Na}_2\text{HPO}_4$  and 0.045 M citric acid. The buffering components of these solutions gave a constant ionic strength of 0.375 M. Spectra were taken for one set of these solutions after sitting a week to assure the establishment of equilibrium.

## Results

The data and results of the spectra and pH measurements are given in Table 1. The second set of data taken for the second set of solutions showed a 22% decrease in  $K_1$  which is well within the experimental error present in this investigation. Thus, the results reflect equilibrium conditions.

TABLE 1. *Data and results of the spectra and pH measurements.*

| %T <sub>1</sub> | %T <sub>2</sub> | pH   | a <sub>1</sub> | a <sub>2</sub> | [CrO <sub>4</sub> <sup>2-</sup> ]<br>x 10 <sup>5</sup> | [Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> ]<br>x 10 <sup>5</sup> | [H <sup>+</sup> ]<br>x 10 <sup>7</sup> | K <sup>1</sup><br>x 10 <sup>-16</sup> |
|-----------------|-----------------|------|----------------|----------------|--------------------------------------------------------|----------------------------------------------------------------------|----------------------------------------|---------------------------------------|
| 56.0            | 37.8            |      | 3145           | 5275           | (8.01)                                                 | —                                                                    |                                        |                                       |
| 43.6            | 53.0            |      | 3002           | 2296           | —                                                      | (12.01)                                                              |                                        |                                       |
| 55.0            | 46.5            | 6.32 |                |                | 4.66                                                   | 3.76                                                                 | 4.79                                   | 7.5 <sup>1</sup>                      |
| 29.9            | 19.0            | 6.22 |                |                | 11.14                                                  | 5.78                                                                 | 6.03                                   | 1.3                                   |
| 49.9            | 50.4            | 5.38 |                |                | 2.32                                                   | 7.62                                                                 | 41.68                                  | 0.8                                   |
| 35.1            | 36.0            | 5.43 |                |                | 3.34                                                   | 11.63                                                                | 37.15                                  | 0.8                                   |
| 53.5            | 37.0            |      | 3392           | 5393           | (8.01)                                                 |                                                                      |                                        |                                       |
| 44.0            | 55.0            |      | 2969           | 2161           |                                                        | (12.01)                                                              |                                        |                                       |
| 62.2            | 54.0            | 6.14 |                |                | 4.02                                                   | 2.35                                                                 | 7.24                                   | 2.8                                   |
| 31.8            | 18.6            | 6.33 |                |                | 12.58                                                  | 2.36                                                                 | 4.68                                   | 0.6                                   |
| 54.2            | 55.3            | 5.63 |                |                | 2.17                                                   | 6.47                                                                 | 23.44                                  | 2.5                                   |
| 40.5            | 41.6            | 5.26 |                |                | 3.25                                                   | 9.50                                                                 | 54.95                                  | 0.3                                   |

<sup>1</sup> Discarded value of  $K_1$ .

The average of all 8 values if  $K_1$  is  $2.1 \times 10^{16}$ , but based on the Range Rejection Test of Moshman and Otta (7), there is a 99% probability that the  $7.5 \times 10^{16}$  value has a systematic error present and should be discarded. The average of the remaining data is  $1.3 \times 10^{16}$  with an estimate of the standard deviation of  $0.97 \times 10^{16}$  which corresponds to a confidence interval for the mean on a 99% probability limit basis of  $\pm 1.4 \times 10^{16}$ .

The experimental value of the Cr(VI) content is found by adding the value found in Column 6 of Table 1 to twice the value found in Column 7. Subtracting the known value gives the amount of Cr(VI) present presumably as  $\text{HCrO}_4^-$ . Doing this calculation on a percentage basis, the average value for the 7 data is 3% of the Cr(VI) present as  $\text{HCrO}_4^-$ .

## Discussion

The overlap of the absorption curves introduces considerable error in calculating the molar absorptivities and concentrations. Although the error in reading the transmittance at the peak of the absorption curve is rather small,  $\pm 0.5\%$ , the error in the %T at the other wavelength is considerably larger,  $\pm 2\%$ . Using these estimates of random error, the predicted errors in the molar absorptivities are  $a_{1c} = \pm 200$ ,  $a_{2c} = \pm 60$ ,  $a_{1D} = \pm 40$  and  $a_{2D} = \pm 140$ . These predicted values are near those observed between the two sets of standard solutions given in Table 1. Using these results and assuming that the error in the pH values is  $\pm 0.02$  and in the %T readings is  $\pm$

2%, the error in  $K_1$  is predicted to be  $1.7 \times 10^{16}$  agreeing with the confidence interval. It can be concluded that the reproducibility of the  $K_1$  values is the result of the limited precision of the technique.

The experimental value of  $K_1$  differs considerably from the value of  $2.4 \times 10^{14}$  which is the thermodynamic equilibrium coefficient calculated from available data (9). The values of the ionic activity coefficients are not available for the solutions of ionic strength equal to 0.375 M, so an exact comparison to the true equilibrium constant cannot be made. The experimental value is valid, however, for a solution for that particular value of ionic strength.

The previously-determined experimental values and those calculated from self-consistent values of  $K_2$  and  $K_3$  cover a wide range, *e.g.*,  $6.7 \times 10^{12}$  reported by Sand and Kaestle (10) who reported "disturbing conditions,"  $1.6 \times 10^{13}$  by Sherrill (12),  $1.95 \times 10^{11}$  reported by Spitalsky (13),  $3.23 \times 10^{14}$  reported by Carriere and Castel (2) at 18°C,  $5 \times 10^{13}$  reported by Mohanty, Ramana-Rao and Pani (6),  $1 \times 10^{14}$  reported by Sasaki (11) for solutions of ionic strength of 3M, and  $1.9 \times 10^{14}$  reported by Jain and Jain (5). Although a rather large scatter in results of this type would normally be expected, the range of  $2 \times 10^{11}$  to  $1 \times 10^{15}$  is rather large and the system should be further investigated to determine the actual effect of ionic strength and to experimentally determine the thermodynamic equilibrium constant.

The experimental value of approximately 3% of the Cr(VI) existing as  $\text{HCrO}_4^-$  in the solution studied does not differ appreciably from the value of 5-10% which appears on the graphs in the paper by Sasaki (11). Thus, it can be concluded that the  $\text{HCrO}_4^-$  concentration does not account for a significant amount of the total Cr(VI) present for the slightly acidic solutions studied.

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