state value 1046 cm.$^{-1}$.[13] The observed transitions fit the following formula, derived by a least squares fit.

$$\nu = 80{,}995 + 1278v_2 - 19.0v_2^2 + 975v_3 + 3.8v_3^2 - 21.2v_2v_3$$
$$v_2 = 1..5,\ v_3 = 1..3$$

Analysis of the vibrational structure of the corresponding (σa_1) state of CF_3H, shown in Table III, utilizes ν_2 = 1191 cm.$^{-1}$ and ν_3 = 446 cm.$^{-1}$. The former is interpreted as a symmetrical C–F stretching mode with normal state value of 1209 cm.$^{-1}$, while ν_3 is interpreted as a CF_3 symmetrical deformation mode with normal state value 699 cm.$^{-1}$.[14] The frequencies of Table III fit a formula, derived by least squares fit

$$\nu = 83.015 + 1191v_2 + 3.4v_2^2 + 446v_3 - 18.2v_3^2 - 9.8v_2v_3$$
$$v_2 = 1..5,\ v_3 = 1,2$$

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ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Thermodynamics of Aqueous Hydrogen Chromate and Dichromate Ions. Heats of Formation of Chromates and Dichromates

BY LOREN G. HEPLER[1]

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New thermodynamic calculations based on results of earlier calorimetric investigations have been carried out and heats of the reactions $HCrO_4^-(aq) = H^+(aq) + CrO_4^{=}(aq)$ and $Cr_2O_7^{=}(aq) + H_2O = 2HCrO_4^-(aq)$ have been obtained from these calculations. These reaction heats have been combined with entropies and free energies from the literature to obtain new values for the entropies of $Cr_2O_7^{=}(aq)$ and $HCrO_4^-(aq)$. Also, from the heats of the above reactions, the heat of solution of $(NH_4)_2Cr_2O_7(c)$ and the heat of reaction of $CrO_3(c)$ with $OH^-(aq)$, it has been shown that the heats of formation of $CrO_3(c)$ and $(NH_4)_2Cr_2O_7(c)$ are consistent. Heats of formation of $HCrO_4^-(aq)$, $Cr_2O_7^{=}(aq)$, $CrO_4^{=}(aq)$, $K_2Cr_2O_7(c)$ and $K_2CrO_4(c)$ and free energies of formation of $HCrO_4^-(aq)$, $Cr_2O_7^{=}(aq)$ and $CrO_4^{=}(aq)$ have been calculated. The relation between calorimetric and equilibrium investigations of various Cr(IV) species in aqueous solution has been discussed.

As a result of calculations made to determine the optimum conditions for a reasonably direct calorimetric investigation of the aqueous hydrogen chromate ion, $HCrO_4^-$, it became apparent that results of heat of solution and reaction experiments already reported[2] from this Laboratory were sufficient to give the desired information about $HCrO_4^-(aq)$. Some of the calculations of heats of formation and entropies given in the earlier paper[2] are incorrect because of the unjustified neglect of $HCrO_4^-(aq)$. Results of correct and more complete calculations, reported in this paper, yield directly the desired information about $HCrO_4^-(aq)$ and also bring the heats of formation of $CrO_3(c)$ and $(NH_4)_2Cr_2O_7$ into accord,[3] thus making possible reliable calculations of a number of heats and free energies of formation.

The important species in a weakly acidic aqueous solution of Cr(VI) can be deduced from the equilibrium constants[4-6] for equilibria 1, 2, 3 and 4, all at 25°

$$HCrO_4^-(aq) = CrO_4^{=}(aq) + H^+(aq) \quad (1)$$
$$H_2CrO_4(aq) = H^+(aq) + HCrO_4^-(aq) \quad (2)$$
$$Cr_2O_7^{=}(aq) + H_2O = 2HCrO_4^-(aq) \quad (3)$$
$$HCr_2O_7^-(aq) = H^+(aq) + Cr_2O_7^{=}(aq) \quad (4)$$

In solutions in which the total Cr(VI) concentration is between about 10^{-3} and 5×10^{-2} *M* and the *p*H is about 3, the important Cr(VI) species are $HCrO_4^-(aq)$ and $Cr_2O_7^{=}(aq)$. These conditions of Cr(VI) and H$^+$ concentration are pertinent to the calculations that follow.

The heat of solution of $K_2Cr_2O_7(c)$ in dilute $HClO_4$ has been measured at a number of total Cr(VI) concentrations[2] denoted by $\Sigma(Cr)$. The two important reactions that occur in this process are given by equations 5 and 6 and equation 7 gives the

$$K_2Cr_2O_7(c) + H_2O = 2K^+(aq) + 2HCrO_4^-(aq) \quad \Delta H_5 \quad (5)$$
$$K_2Cr_2O_7(c) = 2K^+(aq) + Cr_2O_7^{=}(aq) \quad \Delta H_6 \quad (6)$$
$$(x + y)K_2Cr_2O_7(c) + xH_2O = 2(x + y)K^+(aq) + 2xHCrO_4^-(aq) + yCr_2O_7^{=}(aq) \quad (x + y)\Delta H_7 \quad (7)$$

total calorimetric reaction where *x* and *y* represent the number of moles of $K_2Cr_2O_7(c)$ that dissolve to give $HCrO_4^-(aq)$ and $Cr_2O_7^{=}(aq)$, respectively. ΔH_7 represents the calorimetrically determined heat content change per mole of $K_2Cr_2O_7$ and ΔH_5 and ΔH_6 represent the heat content changes of reactions 5 and 6 per mole of $K_2Cr_2O_7(c)$. Equation 8 gives ΔH_7 in terms of *x*, *y*, ΔH_5 and ΔH_6. This equation has been rearranged to equation 9 where

$$x\Delta H_5 + y\Delta H_6 = (x + y)\Delta H_7 \quad (8)$$
$$(X/\Delta H_7) = -(Y/\Delta H_7) \quad (\Delta H_6/\Delta H_5) + (1/\Delta H_5) \quad (9)$$

X and *Y* represent $x/(x + y)$ and $y/(x + y)$, respectively.

From the equilibrium constant (at zero ionic strength) for reaction 3 given by Tong and King[5] and a known value of $\Sigma(Cr)$, a first approximation was made to the concentrations of $HCrO_4^-(aq)$ and $Cr_2O_7^{=}(aq)$. These calculations were based on relations 10 and 11. The $(HCrO_4^-)$ and $(Cr_2O_7^{=})$

$$\Sigma(Cr) = 2(Cr_2O_7^{=}) + (HCrO_4^-) \quad (10)$$
$$\Sigma(Cr) = 2(HCrO_4^-)^2/K_3 + (HCrO_4^-) \quad (11)$$

so obtained were used to calculate to a first approximation the ionic strength of the solution under con-

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sideration. Tong and King's[5] equation for the dependence of K_3 on ionic strength then was used to obtain a value for K_3 applicable at the approximate ionic strength of the solution. This value for K_3 now was used with equations 10 and 11 to obtain better values for ($HCrO_4^-$) and ($Cr_2O_7^{=}$) and these calculations were repeated until consistent values of ($HCrO_4^-$) and ($Cr_2O_7^{=}$) were obtained which then were used to evaluate X and Y. From the intercept and slope of the straight line in a plot of $X/\Delta H_7$ *vs.* $Y/\Delta H_7$, ΔH_5 and ΔH_6 have been found to be 20.7 and 15.8 kcal./mole of $K_2Cr_2O_7$, respectively.

Heats of solution of $(NH_4)_2Cr_2O_7$(c) analogous to the heats of solution of $K_2Cr_2O_7$(c) represented by equations 5 and 6 may be denoted by $\Delta H_5'$ and $\Delta H_6'$. Similar treatment of the experimentally determined heats[2] leads to $\Delta H_5' = 16.7$ and $\Delta H_6' = 12.4$ kcal./mole $(NH_4)_2Cr_2O_7$(c).

Calculations based on observed heats of reaction of K_2CrO_4(c) with excess dilute acid must also take proper account of the presence of both $HCrO_4^-$(aq) and $Cr_2O_7^-$(aq) in the final calorimetric solutions. The two important reactions that occur are given by equations 12 and 13 and equation 14 gives

$$K_2CrO_4(c) + H^+(aq) = 2K^+(aq) + HCrO_4^-(aq) \qquad \Delta H_{12} \quad (12)$$

$$K_2CrO_4(c) + H^+(aq) = 2K^+(aq) + (1/2)Cr_2O_7^{=}(aq) + (1/2)H_2O \qquad \Delta H_{13} \quad (13)$$

$$(p+q)K_2CrO_4(c) + (p+q)H^+(aq) = 2(p+q)K^+(aq) + pHCrO_4^-(aq) + (q/2)Cr_2O_7^{=}(aq) + (q/2)H_2O \qquad (p+q)\Delta H_{14} \quad (14)$$

the total calorimetric reaction where p and q represent the number of moles of K_2CrO_4 that give $HCrO_4^-$(aq) and $Cr_2O_7^{=}$(aq), respectively. ΔH_{14} represents the calorimetrically determined heat content change per mole of K_2CrO_4(c) and ΔH_{12} and ΔH_{13} represent the heat content changes of reactions 12 and 13 per mole of K_2CrO_4(c). Equation 15 gives ΔH_{14} in terms of p, q, ΔH_{12} and ΔH_{13}. This

$$p\Delta H_{12} + q\Delta H_{13} = (p+q)\Delta H_{14} \qquad (15)$$

equation has been rearranged to equation 16 where

$$(P/\Delta H_{14}) = -(Q/\Delta H_{14})(\Delta H_{13}/\Delta H_{12}) + (1/\Delta H_{12}) \qquad (16)$$

P and Q represent $p/(p+q)$ and $q/(p+q)$, respectively.

Equations 10 and 11 and Tong and King's[5] equilibrium data were used to obtain p and q and hence P and Q as before. From the intercept and slope of the straight line in a plot of $(P/\Delta H_{14})$ *vs.* $(Q/\Delta H_{14})$, ΔH_{12} and ΔH_{13} have been found to be 5.0 and 2.4 kcal./mole K_2CrO_4, respectively.

For all these calculations based on calorimetrically measured heats of solution and reaction,[2] heats of dilution have been neglected and all calculated heats (ΔH_5, ΔH_6, $\Delta H_5'$, $\Delta H_6'$, ΔH_{12} and ΔH_{13}) are taken equal to the standard heats of the appropriate reactions. The calorimetric experiments were carried out in very dilute solution so all of the neglected heats of dilution are small. Furthermore, in the reaction of K_2CrO_4(c) with H^+(aq), heats of dilution tend to cancel. The best estimate that can be made is that the total uncertainties in ΔH_5^0, ΔH_6^0, $\Delta H_5^{0\prime}$, $\Delta H_6^{0\prime}$, ΔH_{12}^0 and ΔH_{13}^0 are about one-half kcal./mole and are surely less than one kcal./mole.

Davies and Prue[6] have determined K_3 at 20 and 25° and we have calculated from their results that $\Delta H_3^0 = 4.6$ kcal./mole $Cr_2O_7^{=}$. The present values for ΔH_5^0 and ΔH_6^0 have been combined to give $\Delta H_3^0 = 4.9$ kcal./mole $Cr_2O_7^{=}$ from the relation $\Delta H_3^0 = \Delta H_5^0 - \Delta H_6^0$. Similarly, $\Delta H_5^{0\prime}$ and $\Delta H_6^{0\prime}$ and ΔH_{12}^0 and ΔH_{13}^0 have been combined to give $\Delta H_3^0 = \Delta H_5^{0\prime} - \Delta H_6^{0\prime} = 4.3$ kcal./mole $Cr_2O_7^{=}$ and $\Delta H_3^0 = 2(\Delta H_{12}^0 - \Delta H_{13}^0) = 5.2$ kcal./mole $Cr_2O_7^{=}$. On the basis of all four of these somewhat interdependent values we may take $\Delta H_3^0 = 4.7 \pm 0.3$ kcal./mole $Cr_2O_7^{=}$ as the "best" value. The satisfactory agreement of the calorimetric heats with the heat calculated from the temperature coefficient of K_3 confirms the reliability of the equilibrium studies and of the present interpretation of the calorimetric data.

The previously reported[2] heat of solution of K_2CrO_4(c) as in equation 17, $\Delta H_{17}^0 = 4.2$ kcal./mole, has been combined with ΔH_{12}^0 to obtain

$$K_2CrO_4(c) = 2K^+(aq) + CrO_4^{=}(aq) \qquad \Delta H_{17}^0 \quad (17)$$

ΔH_1^0 to be -0.8 kcal./mole from the relation $\Delta H_1^0 = \Delta H_{17}^0 - \Delta H_{12}^0$. Similarly, the previously reported[2] heat of reaction of $K_2Cr_2O_7$(c) with OH^-(aq) as in equation 18

$$K_2Cr_2O_7(c) + 2OH^-(aq) = 2K^+(aq) + 2CrO_4^{=}(aq) + H_2O \qquad \Delta H_{18}^0 \quad (18)$$

$\Delta H_{18}^0 = -7.3$ kcal./mole K_2CrO_7, has been combined with ΔH_5^0 and the heat of ionization of water ΔH_w^0, as calculated from Bureau of Standards[7] heats of formation, to obtain ΔH_1^0 to be -0.6 kcal./mole from the relation $\Delta H_1^0 = (1/2)(\Delta H_{18}^0 - \Delta H_5^0) + \Delta H_w^0$. The "best" value for ΔH_1^0 is taken to be -0.7 ± 0.4 kcal./mole.

Heat content changes of reactions 1 and 3 have been combined with free energy changes of reactions (1)[4] and (3)[4-6] to give $\Delta S_1^0 = -32.1$ and $\Delta S_3^0 = 8.7$ cal./mole deg., respectively. These entropies of reaction combined with Bureau of Standards[7] entropies of $CrO_4^{=}$(aq) and H_2O give the standard partial molal entropies of $HCrO_4^-$(aq) and $Cr_2O_7^{=}$(aq) to be 41.3 and 57.2 cal./deg. mole, respectively.

Heats of formation of $CrO_4^{=}$(aq), $HCrO_4^-$(aq) and $Cr_2O_7^{=}$(aq) can be calculated from several heats of solution and reaction. One value for the heat of formation of $CrO_4^{=}$(aq) (−207.6 kcal./mole), based on the heat of reaction of CrO_3(c) with OH^-(aq) and the heat of formation of CrO_3(c), has already been reported.[2] The heat of reaction 5′ with the heats of formation of $(NH_4)_2Cr_2O_7$(c),[3] NH_4^+(aq)[7] and H_2O[7] leads to −208.6 kcal./mole for the heat of formation of $HCrO_4^-$(aq) which gives with ΔH_1^0 the heat of formation of $CrO_4^{=}$(aq) to be −209.3 kcal./mole. Similarly, the heat of reaction 6′ with heats of formation of NH_4^+(aq)[7] and $(NH_4)_2Cr_2O_7$(c)[3] leads to −353.1 kcal./mole for the heat of formation of $Cr_2O_7^{=}$(aq). This heat of formation combined with ΔH_1^0 and ΔH_3^0 gives the heats of formation of $HCrO_4^-$(aq) and $CrO_4^{=}$(aq) to be −208.3 and −209.0 kcal./mole. These heats of formation of $CrO_4^{=}$(aq) indicate that the heats of formation of CrO_3(c)[2] and

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(7) "Selected Values for Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

$(NH_4)_2Cr_2O_7(c)$ are consistent to within about one and one-half kcal./mole. The "best" value for the standard heat of formation of $CrO_4^{=}(aq)$ is taken to be the average of the values based on CrO_3 and $(NH_4)_2Cr_2O_7$, namely, −208.6 kcal./mole.

From the "best" heat of formation of $CrO_4^{=}(aq)$ and heats of reactions 1 and 3, the "best" heats of formation of $HCrO_4^-(aq)$ and $Cr_2O_7^{=}(aq)$ have been calculated to be −207.9 and −352.2 kcal./mole, respectively. These heats of formation have been combined with heats of solution and reaction from this and the earlier paper[2] to calculate "best" heats of formation of $K_2CrO_4(c)$ and $K_2Cr_2O_7(c)$ to be −332.8 and −488.3 kcal./mole, respectively. From heats of formation and entropies given in this paper and others tabulated by the Bureau of Standards,[7] free energies of formation of $CrO_4^{=}(aq)$, $HCrO_4^-(aq)$ and $Cr_2O_7^{=}(aq)$ have been calculated to be −171.1, −180.0 and −305.9 kcal./mole, respectively.

Conclusions

Neuss and Rieman,[4] Tong and King[5] and Davies and Prue[6] are in fair agreement as to the value of K_3 at 25°. Their concordant results give us confidence in the reported values for K_3 that is substantiated by the satisfactory agreement between our calorimetric ΔH_3^0 and the ΔH_3^0 calculated from the temperature dependence of K_3. It also seems very likely that the reported values for K_2 and K_4 are at least approximately correct.

The equilibrium constant for reaction 1 has been less adequately investigated than has K_3. It is planned to reinvestigate in this Laboratory this equilibrium at 25° with the aim of checking the results of Neuss and Rieman.[4] It is also intended to investigate this equilibrium at several temperatures in order that an independent value of ΔH_1^0 may be obtained to be compared with the calorimetric ΔH_1^0 reported in this paper.

CHARLOTTESVILLE, VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

The Ionization and Dissociation of Oxygen by Electron Impact[1]

BY D. C. FROST AND C. A. MCDOWELL

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The ionization and dissociation of molecular oxygen has been studied using the retarding potential difference (r.p.d.) method of obtaining essentially mono-energetic electrons. All the spectroscopically known excited states of molecular oxygen, *i.e.*, ${}^2\Pi_g$, ${}^4\Pi_u$, ${}^2\Pi_u$, ${}^4\Sigma_g^-$, and one additional state, have been observed. The vertical ionization potentials here determined are in very good agreement with those calculated from available spectroscopic data. Six different dissociation processes leading to the production of O^+ ions have been observed. These ions arise from either of these two types of processes: $O_2 + e = O^+ + O + 2e$ (a), $O_2 + e = O^+ + O^- + e$ (b). Each particular process has been identified by a careful study of the negative and positive ions formed. Ambiguities in earlier work, which arose largely from the difficulty of calibrating the negative ion energy scale, have been overcome by using sulfur hexafluoride as a calibrating gas.

Oxygen has been the object of many fairly detailed electron impact studies. The most detailed work is perhaps reported by Hagstrum.[2] Besides studying the various ionization and dissociation processes, Hagstrum measured the appearance potentials of the positive and negative oxygen ions. Hagstrum also determined the kinetic energies with which the various ions are formed in the different dissociation processes observed. Later work by Thorburn[3] has, however, shown that some of Hagstrum's observations are perhaps not quite as well founded as they formerly appeared. Examination of Thorburn's results indicates that these more recent observations are still not quite satisfactory.

The main difficulties in all the earlier work arise from the fact that the various workers used electron beams which had quite a large spread in their energy distribution. These experimental methods thus precluded the observation of fine details which are to be expected if the known spectroscopic data on oxygen are studied (see McDowell[4]). Furthermore, in studying negative ion efficiency curves, these workers were unable to observe the true shape of the electron resonance capture peaks, and also they were unable to calibrate accurately the negative ion energy scale. Both these major difficulties recently have been shown to be resolved if one uses essentially mono-energetic electrons.[5-7] It is now possible to calibrate the negative ion energy scale accurately by using the near-zero appearance potential of the SF_6^- ion from sulfur hexafluoride as a standard.[6] Our own previous work[5,8,9] has shown that the retarding potential difference method of obtaining essentially mono-energetic electrons developed by Fox, *et al.*,[7] yields accurate values for the excited states of molecular and atomic ions. It thus seems that the application of this method to oxygen would resolve many of the discrepancies noted in earlier electron impact studies of this molecule.

Experimental

The mass spectrometer used was that described in our earlier publications.[8,9] Krypton served as a calibrating gas for the measurements on the positive ions. Sulfur

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