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Chromium, Molybdenum, and Tungsten: Thermodynamic Properties, Chemical Equilibria, and Standard Potentials

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Contents

I. Introduction

In this review we are primarily concerned with the thermodynamic properties of compounds and aqueous ions of chromium, molybdenum, and tungsten. Thermodynamic data for all of these have long been known to be useful in electrochemistry, analytical chemistry, metallurgy, and many applications of chemical principles. Because many of these thermodynamic quantities are most useful when presented in the form of equilibrium constants or standard potentials, we have listed a large number of these quantities.

We have been critical in our tabulations of data and have recalculated many of the published results cited here. When data from several sources are not in good agreement, we have attempted to justify our choices. In general, we have been explicit about the sources of data and also our treatment of data so that interested readers can check the steps leading to our tabulated values of thermodynamic properties (also related equilibrium constants and standard potentials) and form their own opinions about reliability and accuracy.

In several cases we have combined experimental data from a cited source with an estimate of some thermodynamic property. *Numerical values of estimates are given in parentheses.* We have used auxiliary thermodynamic data [such as $\Delta H_f°$ of Cl^-(aq)] from the National Bureau of Standards Technical Notes 270-3,[3] 270-4,[4] and 270-6,[5] which are the most comprehensive sources of such data available to us.

In spite of considerable discussion in recent years, general agreement is still lacking on "sign conventions" for potentials. Much of the confusion arises because "sign" can be either electrical or algebraic, as previously discussed.[6] All potentials listed in this review are reduction potentials with algebraic signs and may also be taken to be electrode potentials with electrical signs relative to the potential of the standard hydrogen electrode.

The symbols $E°$ and K are used for potentials and equilibrium constants that have been determined in very dilute solutions or in such ways that activity coefficients could be considered in treating the experimental data. Similarly, we use $\Delta G°$, $\Delta H°$, and $\Delta S°$ to indicate data that refer to the usual standard states.[3-5,7] Other useful investigations have been carried out in solutions maintained at some constant ionic strength by means of some "inert" supporting electrolyte. In some cases it has been possible to make reasonable estimates of adjustments to the usual infinite dilution standard states. In other cases we adopt properties based on "uncorrected" data and call attention to the fact that the cited properties refer to solutions having some stated ionic strength.

Except where explicitly stated otherwise, all thermodynamic properties cited in this review refer to 298.15 K (25 °C).

II. Chromium

A. Descriptive Chemistry

In addition to the familiar +2, +3, and +6 oxidation states, compounds and ions containing chromium in the − 2, −1, 0, +4, and +5 oxidation states have been reported. In this section we present brief qualitative descriptions of some compounds and ions characteristic of the various oxidation states and then turn to detailed discussion of thermodynamic properties, equilibrium constants, and standard potentials in following sections.

The best known compound containing chromium in the zero oxidation state is the hexacarbonyl, $Cr(CO)_6$. Reaction of $Cr(CO)_6$ with alkaline solutions yields compounds containing chromium in the −1 and −2 oxidation states. Representative compounds of this sort are $Na_2[Cr(CO)_5]$ and $Na_2[Cr_2(CO)_{10}]$. Although it is well established that these and similar compounds are easily oxidized, we have no relevant quantitative data to cite later in this review.

Reduction of $K_3Cr(CN)_6$ in liquid NH_3 yields $K_6Cr(CN)_6$, which may be described as containing chromium in the zero oxidation state.[8]

Nash, Campbell, and Block[9] have studied the preparation of chromium by thermal decomposition of bis(benzene)chromium.

Electron spin resonance and optical measurements have shown[10] that it is reasonable to describe $K_3[Cr(CN)_5NO]\cdot H_2O$ as containing "effective" Cr^+ and NO^+ ions. Petrakis[11] has made lattice energy calculations that lead to estimates of enthalpies of formation of the hypothetical Cr^+ halides. These calculated $\Delta H_f°$ values show that the hypothetical solid CrX compounds are quite unstable with respect to disproportionation.

Reasonably common compounds containing chromium in the +2 oxidation state are the halides, the sulfate, and the acetate. Such hydrated salts as $CrCl_2\cdot 4H_2O$, $CrSO_4\cdot 7H_2O$, and $[Cr(Ac)_2]_2\cdot 2H_2O$ have been obtained from aqueous solutions. Because of its low solubility in aqueous solution, dimeric chromous acetate is one of the most easily prepared compounds of Cr(II). This interesting red compound has an unusually short Cr–Cr distance and is diamagnetic at room temperature, presumably because of considerable interaction between the metal ions. Deyrup[12] has described preparation of some air-stable Cr(II) compounds: Na_2CrF_4 and $CrXOH\cdot HBO_3$ (X = Cl, Br, or I). Beauchamp and Sullivan[13] have developed procedures for large-scale preparation of $CrCl_2$.

Under most conditions the +3 oxidation state is the most stable state for chromium. The oxide, halides, sulfate, and nitrate are all common compounds. Many octahedral complexes of Cr(III) are known in solution and in the solid state. One indication of the number and variety of such complexes is afforded by the work of Kyuno, Kamada, and Tanaka,[14] who have applied a systematic synthetic procedure to preparation of a series of 25 ammine complexes of Cr(III). Because of the slow substitution reactions of many complexes of Cr(III), these species may persist for long times under conditions where they are thermodynamically unstable. In this review our attention is largely limited to "inorganic" complexes for which fairly complete thermodynamic data are available.

Swaddle et al.[15] have recently discussed the aqueous chemistry of Cr(III) above 100 °C, with particular emphasis on various spinels, which have also been prepared by direct reaction of Cr_2O_3 with various other oxides.

A few solid and gaseous compounds of Cr(IV) and Cr(V) have been prepared.[16] Some of these are the following: Ba_2CrO_4, Cr_2O_5, CrO_2, CrF_4, and oxyfluorides of Cr(V). Solute species containing Cr(IV) and Cr(V) are unstable with respect to disproportionation or reaction with solvent under most conditions. Several aqueous species of Cr(IV) and Cr(V) have been postulated as intermediates in oxidation–reduction reactions, and it is possible to make reasonable estimates of standard potentials for half-reactions involving these species. Evidence for moderately stable Cr(V) species in sulfuric acid solutions[17] and in strong base[18] has been reported.

Peroxo complexes of Cr(III, IV, V, and VI) have been reviewed by Connor and Ebsworth[19] and more recently by Cotton and Wilkinson.[20] We also call attention to a recent equilibrium investigation of peroxo species of Cr(V and VI) by Bartlett and Quane.[21] Among the peroxo compounds and ions that have been identified or postulated are the following: K_3CrO_8, $CrO(O_2)_2$ and related salts, $CrO_5\cdot A$ (A = ether, pyridine, etc.), $Cr_2(O_2)^{4+}$, and $Cr_3(O_2)_2{}^{5+}$.

Many solid compounds and aqueous ions containing Cr(VI) are known and have been investigated enough that we can later quote reliable data. Several of these compounds and ions are useful oxidizing agents in acidic solution. The most common Cr(VI) compounds and aqueous ions are CrO_3, $K_2Cr_2O_7$, K_2CrO_4, $Cr_2O_7{}^{2-}$(aq), $HCrO_4{}^-$(aq), and $CrO_4{}^{2-}$(aq). There are several slightly soluble chromates that are of some importance, including Ag_2CrO_4, $PbCrO_4$, $BaCrO_4$, etc.

B. Element and Oxides

The best general sources of thermodynamic data for chromium and its compounds are the National Bureau of Standards Technical Notes 270-4[4] and 270-6,[5] to which we hereafter refer as NBS 270-4 and NBS 270-6.

We follow NBS 270-4 in taking $\Delta H_f° = 0$, $\Delta G_f° = 0$, and $S° = 5.68$ cal K^{-1} mol^{-1} for Cr(c) at 298 K. Kelley and King[22] have reviewed earlier C_p measurements that lead to this $S° = 5.68$ cal K^{-1} mol^{-1}. Two more recent investigations[23,24] have led to $S° = 5.64$ and 5.72 cal K^{-1} mol^{-1}. We also note that Bonilla and Garland[25] have made C_p measurements on Cr(c) at various pressures near the Néel transition.

We accept $S° = 41.68$ cal K^{-1} mol^{-1} for Cr(g) as listed in NBS 270-4, based on statistical thermodynamic calculations. Stull and Sinke[26] and more recently Storms[27] have reviewed results of high-temperature vapor pressure studies and have calculated $\Delta H_f° = 95.0$ and 94.89 ± 0.31 kcal mol^{-1} for Cr(g). Dickson, Myers, and Saxer[28] have made measurements (not considered above[26,27]) that lead to $\Delta H_f° = 95.3$ kcal mol^{-1} for Cr(g) at 298 K. On the basis of all these results, we adopt $\Delta H_f° = 95.0$ kcal mol^{-1} for Cr(g) and combine with the $S°$ to obtain $\Delta G_f° = 84.3$ kcal mol^{-1}.

For the Cr^{n+}(g) ions we adopt the $\Delta H_f°$ values from NBS 270-4 after adjustment for the change in $\Delta H_f°$ for Cr(g) from the NBS 270-4 value (94.8 kcal mol^{-1}) to our value (95.0 kcal mol^{-1}).

For CrO(g) we adopt $\Delta H_f° \simeq 53$ kcal mol^{-1} from Grimley, Burns, and Inghram[29] and $S° = 53.0$ cal K^{-1} mol^{-1} from Kelley and King.[22] These values lead to $\Delta G_f° = 46$ kcal mol^{-1} for CrO(g).

The NBS 270-4 lists $\Delta H_f°$ (at 0 K) = −14 kcal mol^{-1} for CrO_2(g). This value is consistent with the results of Grimley et al.[29] More recent investigations[30,31] have led to less exothermic values. On the basis of all three investigations,[29–31] we adopt $\Delta H_f° \simeq -3$ kcal mol^{-1} and combine with the $S° = 62.0$ cal K^{-1} mol^{-1} from Nagarajan[32] to obtain $\Delta G_f°$ for this compound.

The NBS 270-4 lists $\Delta H_f° = -143$ kcal mol^{-1} for CrO_2(c). Although the only calorimetric investigation we know of for CrO_2(c) (by Ariya et al.[33]) has led to a less exothermic value, we tentatively accept the value from NBS 270-4 and combine with an estimated $S°$ to obtain its $\Delta G_f°$.

For Cr_2O_3(c) we have a well-established $S° = 19.4$ cal K^{-1} mol^{-1}, based on work reviewed by Kelley and King,[22] and as adopted in NBS 270-4. Unfortunately, the situation is not so clear for $\Delta H_f°$ and $\Delta G_f°$ for this important compound.

Combustion calorimetry by Mah[34,35] gives $\Delta H_f° = -272.6 \pm 0.6$ kcal mol^{-1} for Cr_2O_3(c). High-temperature equilibrium measurements of the reduction of Cr_2O_3(c) by H_2(g) have led Novokhatskii and Lenev[36] to report $\Delta H_f°$ (at 298 K) = -272.8 ± 0.8 kcal mol^{-1} for Cr_2O_3(c). Our own second law calculation with their results leads to a slightly more negative value, while our third law calculation with the same results leads to a slightly less negative value, with both calculations making use of high-temperature data from Kelley.[37] All of these values are in agreement with $\Delta H_f° = -272.4$ kcal mol^{-1} for Cr_2O_3(c) as listed in NBS 270-4.

But there is also evidence in favor of a significantly less negative $\Delta H_f°$ for Cr_2O_3(c). For example, high-temperature equilibrium results have led Ramsey, Caplan, and Burr[38] to report $\Delta H_f° = -268.5$ kcal mol^{-1}. High-temperature emf measurements by Tretjakow and Schmalzried[39] have led to results that permit us to calculate (second law) $\Delta H_f^\circ = -261$ kcal mol^{-1} and (third law) $\Delta H_f^\circ = -268$ kcal mol^{-1} for Cr_2O_3(c). More recent high-temperature emf measurements by Mazandarany and Pehlke[40] and also high-temperature equilibrium measurements by Jeannin, Mannerskantz, and Richardson[41] have yielded results that we have used for calculation of ΔH_f° (at 298 K) $= -270.0$ kcal mol^{-1} for Cr_2O_3(c), again making use of auxiliary data from Kelley.[37]

It is obvious from the discussion in the two paragraphs above that there are substantial and unexplained discrepancies between the results of high-quality investigations. Kulkarni and Worrell[42] have selected $\Delta H_f^\circ = -270.0$ kcal mol^{-1} for Cr_2O_3(c), partly on the basis of the work of Richardson et al.[41] and partly to achieve consistency with some results for chromium carbides that we discuss later. But it should also be pointed out that consistency with some other results for chromium carbides is best achieved by way of $\Delta H_f^\circ = -272.6$ kcal mol^{-1} for Cr_2O_3(c) as found by Mah[34,35] or $\Delta H_f^\circ = -272.4$ kcal mol^{-1} as listed in NBS 270-4.

In the absence of further definitive measurements involving Cr_2O_3(c), we must make a somewhat arbitrary choice of a best ΔH_f° and then make as many other values as possible be consistent with this chosen value. Partly for convenience in relating our Tables to NBS 270-4 and 270-6 and partly because of our respect for the work of Mah[34,35] and prejudice in favor of calorimetry, we adopt $\Delta H_f^\circ = -272.4$ kcal mol^{-1} for Cr_2O_3(c) as listed in NBS 270-4. Therefore we also adopt $\Delta G_f^\circ = -252.9$ kcal mol^{-1} as listed in NBS 270-4.

Combination of enthalpies of solution[43] of CrO_3(c) and $(NH_4)_2Cr_2O_7$(c) with the enthalpy of decomposition[44] of $(NH_4)_2Cr_2O_7$(c) and the ΔH_f° of Cr_2O_3(c) adopted above leads to $\Delta H_f^\circ = -140.9$ kcal mol^{-1} for CrO_3(c), which is the value listed in NBS 270-4 and is also the value we adopt for this compound. We note, however, that there are other paths to this ΔH_f°. Bichowsky and Rossini[45] have quoted (from Roth and Becker) a ΔH for decomposition of CrO_3(c) to Cr_2O_3(c) and O_2(g) that leads us to $\Delta H_f^\circ = -139.7$ kcal mol^{-1} for CrO_3(c), based on our adopted ΔH_f° for Cr_2O_3(c). More recent measurements by Richelmi and Laffitte[46] of the enthalpy of decomposition of CrO_3(c) lead to $\Delta H_f^\circ = -137.0$ kcal mol^{-1} for CrO_3(c). Because of the disagreements between these values, it must be concluded that at least one of the three kinds of measurements [enthalpies of solution, enthalpy of decomposition of CrO_3, enthalpy of decomposition of $(NH_4)_2Cr_2O_7$] is in error. We combine an estimated S° with our adopted ΔH_f° to obtain the ΔG_f° of CrO_3(c).

For CrO_3(g) we adopt $\Delta H_f^\circ \simeq -65$ kcal mol^{-1} from the results of Grimley et al.[29] and the more recent results of Farber and Srivastava.[31] We combine this value, which is considerably less negative than the value listed in NBS 270-4, with $S^\circ = 63.6$ cal K^{-1} mol^{-1} from Nagarajan[32] to obtain $\Delta G_f^\circ \simeq -60$ kcal mol^{-1} for this compound.

McDonald and Margrave[47] have investigated vaporization of CrO_3 to form various $(CrO_3)_n$(g) species.

The investigation by Richelmi and Laffitte[46] of the decomposition of CrO_3(c) to Cr_2O_3(c) indicates that the reaction proceeds via Cr_5O_{12}(c) and Cr_8O_{21}(c). Their results lead to ΔH_f° values for these compounds, which we list as $\Delta H_f^\circ = -140.3$ kcal mol^{-1} for $CrO_{2.40}$(c) and $\Delta H_f^\circ = -139.1$ kcal mol^{-1} for $CrO_{2.62}$(c). Because the ΔH_f° of CrO_3(c) from these workers[46] differs from the value we have adopted, the ΔH_f° values quoted above for the intermediate oxides may not bear the right relationship to our ΔH_f° values for CrO_3(c) and Cr_2O_3(c).

C. Cr(VI): Compounds and Aqueous Ions

Bomb calorimetric measurements by Neugebauer and Margrave[44] have led to ΔH° of decomposition of $(NH_4)_2Cr_2O_7$(c) to Cr_2O_3(c). Combination of this result with our selected ΔH_f° of Cr_2O_3(c) leads to $\Delta H_f^\circ = -431.8$ kcal mol^{-1} for $(NH_4)_2Cr_2O_7$(c), which is the same as the value listed in NBS 270-4 for this compound. As noted in the preceding section, we have used this result with enthalpies of solution[43] in establishing the ΔH_f° of CrO_3(c).

The most direct route to the ΔH_f° of CrO_4^{2-}(aq) is by way of the calorimetrically measured[43] enthalpy of solution of CrO_3(c) in excess OH^-(aq). Combination of the resulting ΔH° of solution with our adopted ΔH_f° of CrO_3(c) leads to $\Delta H_f^\circ = -210.60$ kcal mol^{-1} for CrO_4^{2-}(aq), which is the value we adopt and is also the value listed in NBS 270-4.

The entropy of CrO_4^{2-}(aq) can be obtained by way of Ag_2CrO_4(c) as follows. Smith, Pitzer, and Latimer[48] have reported $S^\circ = 51.82$ cal K^{-1} mol^{-1} for Ag_2CrO_4(c), based on their C_p measurements. Subsequent recalculation[22] has led to $S^\circ = 52.0$ cal K^{-1} mol^{-1}, which is the value listed in NBS 270-4 and adopted here. Smith, Pitzer, and Latimer[48] have also made calorimetric measurements leading to $\Delta H^\circ = 14.45$ kcal mol^{-1} for

$$Ag_2CrO_4(c) = 2Ag^+(aq) + CrO_4^{2-}(aq) \qquad (1)$$

Subsequent emf measurements and the derived d ln K_{sp}/dT from Pan[49] lead to $\Delta H^\circ = 14.49$ kcal mol^{-1} for this reaction, in good agreement with the calorimetric result.[48] Smith, Pitzer, and Latimer[48] chose $K_{sp} = 1.1 \times 10^{-12}$ from the work of Cann and Mueller.[50] We combine the ΔG° of solution from this K_{sp} with their[48] enthalpy of solution and entropies of Ag^+(aq) and Ag_2CrO_4(c) to obtain $S^\circ = 11.1$ cal K^{-1} mol^{-1} for CrO_4^{2-}(aq). There are, however, two other K_{sp} values worth consideration in connection with this calculation. Pan's measurements[49] led to $K_{sp} = 1.3 \times 10^{-12}$ at 25 °C, while conductance measurements by Howard and Nancollas[51] have led to $K_{sp} = 2.5 \times 10^{-12}$ for Ag_2CrO_4(c). Use of this latter K_{sp} in the calculation described above leads to $S^\circ = 12.6$ cal K^{-1} mol^{-1} for CrO_4^{2-}(aq), while Pan's results lead to a value intermediate between 11.1 and 12.6 cal K^{-1} mol^{-1} for this ion. It is also possible to calculate S° for CrO_4^{2-}(aq) from the solubility, enthalpy of solution, activity coefficient in saturated solution, and the third law entropy of K_2CrO_4(c), but the result is not accurate enough to help us choose between the entropies cited above. In the absence of another reliable path or new data for silver chromate, the best we can do is adopt $S^\circ = 12$ cal K^{-1} mol^{-1} for CrO_4^{2-}(aq). The NBS 270-4 lists $S^\circ = 12.00$ cal K^{-1} mol^{-1} for this ion, but we are unable to justify the last two figures in this value.

Combination of our selected S° and ΔH_f° values leads to $\Delta G_f^\circ = -173.9_6$ kcal mol^{-1} for CrO_4^{2-}(aq), in agreement with the NBS 270-4.

The properties of $HCrO_4^-$(aq) can now be derived from the thermodynamics of the reaction

$$HCrO_4^-(aq) = H^+(aq) + CrO_4^{2-}(aq) \qquad (2)$$

The equilibrium results of several sets of investigators[52-57] are in agreement with $K = 3.3 \times 10^{-7}$ for this reaction at 298 K. We therefore adopt the corresponding $\Delta G_f^\circ = -182.8$ kcal mol^{-1} for $HCrO_4^-$(aq), which is also the value listed in NBS 270-4. We also adopt $\Delta H_f^\circ = -209.9$ kcal mol^{-1} for this ion as derived from a calorimetric[43] ΔH° for reaction 2 and as listed in NBS 270-4. This ΔH_f° is in good agreement with the d ln K/dT results of Linge and Jones.[52] Combination of the ΔG_f° and ΔH_f° values above leads to $S^\circ = 44$ cal K^{-1} mol^{-1} for $HCrO_4^-$(aq).

We also note that there have been several investigations[56-58] of reaction 2 in 3 M ClO_4^- medium, with the best results probably being those of Arnek and Johansson.[58]

For the reaction

$$2HCrO_4^-(aq) = Cr_2O_7^{2-}(aq) + H_2O(liq) \qquad (3)$$

we choose $K = 33.9$ from the results of several investigators[59-61] and the corresponding $\Delta G_f^\circ = -311.0$ kcal mol^{-1} for $Cr_2O_7^{2-}$(aq), with this same ΔG_f° being listed in NBS 270-4. This K is in only fair agreement with the results of other investigators.[53,62] We also adopt $\Delta H_f^\circ = -356.2$ kcal mol^{-1} for $Cr_2O_7^{2-}$(aq) from the results of calorimetric investigation[43] of reaction 3 and as listed in NBS 270-4. This ΔH_f° is in good agreement with the d ln K/dT results of Linge and Jones[59] and Davies and Prue[60] but in poorer agreement with the results of other investigators.[62] Combination of ΔG_f° and ΔH_f° values leads to $S^\circ = 62.6$ cal K^{-1} mol^{-1} for $Cr_2O_7^{2-}$(aq), as in NBS 270-4.

Several investigations[56-58,61,63,64] have yielded results for reaction 3 in various constant ionic strength media.

Results of two investigations[65,66] are in reasonable agreement with the following:

$$H_2CrO_4(aq) = H^+(aq) + HCrO_4^-(aq) \qquad K(3\text{ M}) \simeq 5$$

We use this K with the ΔG_f° of $HCrO_4^-$(aq) to calculate $\Delta G_f^\circ = -181._8$ kcal mol^{-1} for H_2CrO_4(aq). The d ln K/dT results of Tong and Johnson[65] permit calculation of $\Delta H_f^\circ = -201$ kcal mol^{-1} and $S^\circ = 70$ cal K^{-1} mol^{-1} for H_2CrO_4(aq). Their investigations[65] have also led to the following:

$$HCrO_4^-(aq) + H^+(aq) + Cl^-(aq) = CrO_3Cl^-(aq) + H_2O(liq)$$

$$K(1\text{ M}) = 11$$

This K is in agreement with results of an earlier investigation.[66] We use the above[65] K and also d ln K/dT to calculate $\Delta G_f^\circ = -158._9$ kcal mol^{-1}, $\Delta H_f^\circ = -180._4$ kcal mol^{-1}, and $S^\circ = 49$ cal K^{-1} mol^{-1} for CrO_3Cl^-(aq).

We also have the following equilibrium constants[66,67] for other reactions of $HCrO_4^-$(aq):

$$HCrO_4^-(aq) + HSO_4^-(aq) = CrSO_7^{2-}(aq) + H_2O(liq)$$

$$K(3\text{ M}) = 4$$

$$HCrO_4^-(aq) + H_2PO_4^-(aq) = HCrPO_7^{2-}(aq) + H_2O(liq)$$

$$K(0.25\text{ M}) = 3$$

$$HCrO_4^-(aq) + H_3PO_4(aq) = H_2CrPO_7^-(aq) + H_2O(liq)$$

$$K(0.25\text{ M}) = 9$$

We combine the second and third of these equilibrium constants with ΔG_f° values for $H_2PO_4^-$(aq) and H_3PO_4(aq) from NBS 270-3 to obtain our tabulated ΔG_f° values for the Cr–P species. We do not do this same calculation for $CrSO_7^{2-}$(aq) because of the high ionic strength of the medium to which the K applies.

We also have

$$HCrO_4^-(aq) + Fe^{3+}(aq) = FeCrO_4^+(aq) + H^+(aq)$$
$$K(1\text{ M}) = 0.43$$

from the work of Espenson and Helzer.[68]

Two high-temperature investigations[31,69] are in good agreement with $\Delta H_f^\circ = -176$ kcal mol^{-1} for H_2CrO_4(g), as compared with -174 kcal mol^{-1} listed in NBS 270-4.

We now consider the properties of various chromates and dichromates, beginning with Ag_2CrO_4(c). As previously stated, we have[22,48] $S^\circ = 52.0$ cal K^{-1} mol^{-1} from C_p measurements and the third law. We combined the calorimetric enthalpy of solution from Smith, Pitzer, and Latimer[48] with ΔH_f° Values for Ag^+(aq) and CrO_4^{2-}(aq) to obtain $\Delta H_f^\circ = -174.58$ kcal mol^{-1} for Ag_2CrO_4(c). Further combination of ΔH_f° and S° leads to $\Delta G_f^\circ = -153.11$ kcal mol^{-1} for this compound and thence to a calculated $K_{sp} = 1.8 \times 10^{-12}$ for Ag_2CrO_4(c).

Ferrante, Stuve, and Krug[70] have made C_p measurements leading to $S^\circ = 42.212$ cal K^{-1} mol^{-1} for Na_2CrO_4(c) at 298 K. They[70] have also made high-temperature measurements leading to values of $(H_T - H_{298})$ and related thermodynamic quantities. The enthalpy of solution[71] leads to $\Delta H_f^\circ = -320.8$ kcal mol^{-1}, which we combine with the entropy to obtain $\Delta G_f^\circ = -295.2$ kcal mol^{-1} for Na_2CrO_4(c).

The enthalpy of reaction[71] of $Na_2Cr_2O_7$(c) with excess OH^-(aq) leads to its $\Delta H_f^\circ = -473.0$ kcal mol^{-1}, which we combine with our estimated $S^\circ = (64)$ cal K^{-1} mol^{-1} to obtain $\Delta G_f^\circ = -430._3$ kcal mol^{-1} for $Na_2Cr_2O_7$(c).

We use the calorimetric enthalpy[43] of solution of K_2CrO_4(c) to obtain its $\Delta H_f^\circ = -335.4$ kcal mol^{-1} and combine with the entropy[22] ($S^\circ = 47.8$ cal K^{-1} mol^{-1}) to obtain $\Delta G_f^\circ = -309.6$ kcal mol^{-1} for K_2CrO_4(c).

Measurements by Farber and Srivastava[31] lead to $\Delta H_f^\circ = -249$ kcal mol^{-1} for K_2CrO_4(g) and to $\Delta H_f^\circ = -217$ kcal mol^{-1} for $KHCrO_4$(g).

The enthalpy of reaction[71] of $K_2Cr_2O_7$(c) with excess OH^-(aq) leads to its $\Delta H_f^\circ = -492.9$ kcal mol^{-1}. We combine this quantity with the $S^\circ = 69.6$ cal K^{-1} mol^{-1} from Kelley and King[22] to obtain $\Delta G_f^\circ = -450.0$ kcal mol^{-1} for $K_2Cr_2O_7$(c). We also note that Shmagin and Shidlovskii[72] have measured enthalpies of dilution of supersaturated solutions of $K_2Cr_2O_7$(aq).

For $(NH_4)_2CrO_4$(c) we adopt $\Delta H_f^\circ = -279.0$ kcal mol^{-1} as listed in NBS 270-4, consistent with an old enthalpy of solution.[45]

We also adopt $\Delta H_f^\circ = -321.1$ kcal mol^{-1} for $MgCrO_4$(c) as listed in NBS 270-6, based on results of older investigations that are cited in NBS Circular 500.[73]

Shidlovskii, Voskresenskii, and Balakireva[74] have measured the enthalpy of solution of $SrCrO_4$(c) in acid with results that lead us to $\Delta H_f^\circ = -341.6$ kcal mol^{-1} for this compound. Sillén[75] has listed $K_{sp} = 2 \times 10^{-5}$ for $SrCrO_4$(c), which leads us to its $\Delta G_f^\circ = -314.0$ kcal mol^{-1}. Combination of this ΔG_f° with the ΔH_f° gives $S^\circ = 23._6$ cal K^{-1} mol^{-1} for $SrCrO_4$(c). This calculated entropy is smaller than seems reasonable. Combination of the ΔH_f° above with a "more reasonable" larger entropy leads to a calculated K_{sp} that is smaller than the listed[75] value. Further measurements are needed.

Shidlovskii et al.[74] have also measured the enthalpy of precipitation of $BaCrO_4$(c), which leads us to $\Delta H_f^\circ = -345.3$ kcal mol^{-1} for this compound. Taking $K_{sp} = 1.2 \times 10^{-10}$ from Beyer and Rieman,[76] we calculate $\Delta G_f^\circ = -321.53$ kcal mol^{-1} for $BaCrO_4$(c), which is the value listed in NBS 270-6. Combination of ΔH_f° and ΔG_f° values leads to $S^\circ = 38.9$ cal K^{-1} mol^{-1} for $BaCrO_4$(c). Our values for the ΔH_f° and S° of $BaCrO_4$(c) differ slightly from those listed in NBS 270-6, possibly because we have used an enthalpy of precipitation that appeared too late for consideration there. A third law entropy would be a useful check on the other results.

Old (somewhat uncertain) calorimetric results[45] lead us to $\Delta H^\circ = -11$ kcal mol^{-1} for the enthalpy of precipitation of $PbCrO_4$(c) and thence to $\Delta H_f^\circ = -222$ kcal mol^{-1} for this compound. Taking $K_{sp} = 2.5 \times 10^{-13}$ from Kolthoff, Perlich, and Weiblen,[77] we calculate $\Delta G_f^\circ = -197.0$ kcal mol^{-1} for $PbCrO_4$(c) and combine this value with the ΔH_f° above to obtain $S^\circ = 35$ cal K^{-1} mol^{-1} for this compound. On the basis of apparently reliably known entropies for other compounds of lead and barium, it seems safe to predict that the entropy (at 298 K) of $PbCrO_4$(c) should be larger than that of $BaCrO_4$(c). Because the S° we have calculated here for $PbCrO_4$(c) is *smaller* than that calculated in the preceding paragraph for $BaCrO_4$(c), we suggest that there is at least one error in the various properties listed above for these compounds. Further measurements are needed.

Sillén[75] has listed $K_{sp} = 9.77 \times 10^{-13}$ for Tl_2CrO_4(c), with reference to Suzuki.[78] We use this K_{sp} to calculate ΔG_f° = −205.82 kcal mol^{-1} for Tl_2CrO_4(c), in close agreement with the value listed in NBS 270-4. The abstract[78] of Suzuki's paper quotes ΔH° = −50.74 kcal mol^{-1} [Neither ΔG° nor ΔS° is given in the abstract.] for the reaction

$$Ag_2CrO_4(c) + 2Tl(c) = Tl_2CrO_4(c) + 2Ag(c)$$

from which we calculate ΔH_f° = −225.3 kcal mol^{-1} for Tl_2CrO_4(c). About half of the difference between this value and the value (−225.8 kcal mol^{-1}) listed in NBS 270-4 is due to the difference between our ΔH_f° for Ag_2CrO_4(c) and that listed in NBS 270-4. Combination of our ΔH_f° and ΔG_f° values leads to a calculated S° = 69.2 cal K^{-1} mol^{-1} for Tl_2CrO_4(c), as compared to S° = 67.5 cal K^{-1} mol^{-1} listed in NBS 270-4. Because entropies of various other compounds of silver and thallium lead us to estimate S° = (61) cal K^{-1} mol^{-1} for Tl_2CrO_4(c), we suspect some error in the reported[78] data. We adopt ΔH_f° and S° values that are averages of the values we have quoted above and the values listed in NBS 270.4.

Gaultier and Pannetier[79] have investigated the thermodynamics of solid-state transitions and melting of Tl_2CrO_4, while Natarajan and Secco[79] have investigated enthalpies of phase transitions of Tl_2CrO_4(c) and Ag_2CrO_4(c).

For the very reactive chromyl fluoride (CrO_2F_2) we have only vapor pressure data[80] from which we calculate ΔS° = 18 cal K^{-1} mol^{-1} for melting and ΔS° = 27 cal K^{-1} mol^{-1} for vaporization at the normal boiling point. Edwards, Falconer, and Sunder[81] have reported a new synthesis of $CrOF_4$. Their vapor pressure measurements show that there is a solid-state transition at 24.1 °C (ΔH° = 3.7 kcal mol^{-1} and ΔS° = 12 cal K^{-1} mol^{-1}) and have also led to ΔS° = 8 cal K^{-1} mol^{-1} for melting (55 °C) and to ΔS° = 27 cal K^{-1} mol^{-1} for vaporization at the normal boiling point (95 °C). It is interesting to note that the sum of the entropies of transition and melting for $CrOF_4$ is close to the entropy of melting of CrO_2F_2 and that entropies of vaporization of both compounds suggest that both liquids are associated.

The properties listed in NBS 270-4 for CrO_2Cl_2(liq and g) are consistent with enthalpies of reaction,[73,82,83] vapor pressures,[73,82] and an entropy of CrO_2Cl_2(g) calculated from estimated molecular constants.

D. Cr(II) and Cr(III): Compounds and Aqueous Ions

The NBS 270-4 lists S° = 22.44 cal K^{-1} mol^{-1} for CrF_3(c), which is the value obtained by Hansen and Griffel[84] from their C_p measurements. Old results cited by Bichowsky and Rossini,[45] NBS Circular 500,[73] Brewer et al.,[85] and more recent high-temperature emf results from Tanaka, Yamaguchi, and Moriyama[86] lead to various values of the thermodynamic properties of CrF_2(c) and CrF_3(c). Weighting the recent results[86] most heavily leads us to values for the thermodynamic properties of these compounds that are consistent with those listed in NBS 270-4, which we adopt here. High-temperature measurements by Kent and Margrave[87] lead to ΔH_f° = −99 kcal mol^{-1} for CrF_2(g), as also listed in NBS 270-4, and to ΔH_f° = 5 kcal mol^{-1} for CrF(g). The enthalpy of sublimation of CrF_3(c) from Zmbov and Margrave[88] leads to ΔH_f° = −217 kcal mol^{-1} for CrF_3(g).

For $CrCl_2$(c) we adopt S° = 27.56 cal K^{-1} mol^{-1} from the C_p measurements of Stout and Chisholm,[89] whose review of earlier high-temperature equilibrium investigations has led to ΔH_f° = −94.52 kcal mol^{-1} and ΔG_f° = −85.1 kcal mol^{-1} for this compound. All of these values are the same as those listed in NBS 270-4. It might be noted that these values are not consistent with the recent high-temperature equilibrium results of Papapietro and Monnier.[90]

The ΔH_f° = −30.7 kcal mol^{-1} for $CrCl_2$(g) that is listed in NBS 270-4 is consistent with the work of Maier,[91] who has also calculated S° = 74.2 cal K^{-1} mol^{-1} for this compound. A more recent calculation[92] leads to S° = 74.8 cal K^{-1} mol^{-1}, which we adopt and use with the ΔH_f° above to obtain ΔG_f° = −35.4 kcal mol^{-1} for $CrCl_2$(g).

The NBS 270-4 lists ΔH_f° = −111 kcal mol^{-1} for $(CrCl_2)_2$(g), consistent with the high-temperature mass spectroscopic results of Schoonmaker, Friedman, and Porter.[93] Results from these investigators might also be used to calculate approximate ΔG_f° and S° values for $(CrCl_2)_2$(g).

The NBS 270-4 lists S° = 29.38 cal K^{-1} mol^{-1} for $CrCl_3$(c), which is the value derived by Hansen and Griffel[84] from their C_p measurements. A weighted average of results cited in NBS Circular 500[73] and by Sano[94] is consistent with ΔH_f° = −133.0 kcal mol^{-1} for $CrCl_3$(c) as listed in NBS 270-4 and as adopted here. These values lead to ΔG_f° = −116.2 kcal mol^{-1} for $CrCl_3$(c).

There are also two other routes to the ΔH_f° of $CrCl_3$(c). Vasil'kova et al.[95] have made calorimetric measurements with results that we combine with our tabulated ΔH_f° of CrO_3(c) to obtain ΔH_f° = −124 kcal mol^{-1} for $CrCl_3$(c). Or we may combine some of the results of Vasil'kova et al.[95] with the enthalpy of solution of $CrCl_3$(c) reported by Gregory and Burton[96] to obtain ΔH_f° = −130 kcal mol^{-1} for $CrCl_3$(c). Because it is not certain that the same Cr(III) species were formed in all of these experiments,[95,96] this last calculation that involves combination of results obtained under different conditions may be unjustified.

Maier's[91] work leads to ΔH_f° = −71 kcal mol^{-1}, S° = 84 cal K^{-1} mol^{-1}, and ΔG_f° = −71 kcal mol^{-1} for $CrCl_3$(g).

The NBS 270-4 lists ΔH_f° = −72.2 kcal mol^{-1} for $CrBr_2$(c), a value that is consistent with our calculations (±1 or 2 kcal mol^{-1}) based on the high-temperature equilibrium results of Shchukarev et al.[97] We estimate S° = (32) cal K^{-1} mol^{-1} and combine with the ΔH_f° above to obtain ΔG_f° = −69 kcal mol^{-1} for $CrBr_2$(c). The high-temperature vaporization measurements of Sime and Gregory[98] and the mass spectral investigations of Schoonmaker et al.[93] lead to ΔH_f° = −17 kcal mol^{-1} for $CrBr_2$(g) and ΔH_f° = −84 kcal mol^{-1} for $(CrBr_2)_2$(g) as listed in NBS 270-4. We also have S° = 80.62 cal K^{-1} mol^{-1} for $CrBr_2$(g) from Shaw and Porter[92] and thence ΔG_f° = $-28._5$ kcal mol^{-1} for $CrBr_2$(g).

It is possible to use quantities reported by Rupcheva et al.[99] to calculate ΔH_f° = −97.4 and −76.6 kcal mol^{-1} for $CrBr_3$(c), with no clear indication as to the reliability of either value. We therefore omit $CrBr_3$(c) from our Table I. It might also be noted that the properties listed by Rupcheva et al.[99] for $CrBr_2$(c) are much different from those cited above.

Combination of the calorimetric results of Gregory and Burton[96] with our tabulated ΔH_f° of $CrCl_2$(c) leads to ΔH_f° = −37.5 kcal mol^{-1} for CrI_2(c), which is also the value listed in NBS 270-4 for this compound. We estimate S° = (37) cal K^{-1} mol^{-1} and combine with the ΔH_f° to obtain ΔG_f° = −39 kcal mol^{-1} for CrI_2(c).

Allen[100] has made vapor pressure measurements on CrI_2(c) and has used a second law method to calculate ΔH° of vaporization at 298 K, which we combine with the ΔH_f° of CrI_2(c) to obtain ΔH_f° = 34 kcal mol^{-1} for CrI_2(g), as compared with ΔH_f° = 24 kcal mol^{-1} listed in NBS 270-4. Our third law treatment of Allen's[100] results leads to somewhat smaller values for ΔH° of vaporization and ΔH_f°. We adopt ΔH_f° = 32 kcal mol^{-1} for CrI_2(g) and combine with S° = 84.15 cal K^{-1} from Shaw and Porter[92] (whose results were also used in our third law calculations) to obtain ΔG_f° = 17 kcal mol^{-1} for CrI_2(g).

Combination of the calorimetric results of Gregory and Burton[96] with our tabulated ΔH_f° of $CrCl_3$(c) leads to ΔH_f° = −45.8 kcal mol^{-1} for CrI_3(c). We also use the results of de-

TABLE I.[a] **Thermodynamic Properties of Chromium Compounds at 298 K**

Substance	$\Delta H_f°$ kcal mol^{-1}	$\Delta G_f°$ kcal mol^{-1}	$S°$ cal K^{-1} mol^{-1}
Cr(c)	*0*	*0*	*5.68*$^{22-24}$
Cr(g)	95.0$^{26-28}$	84.3	*41.68*
Cr^{+}(g)	*252.5*^{b}		
Cr^{2+}(g)	634.4^{b}		
Cr^{3+}(g)	*1350*		
Cr^{4+}(g)	*2495*		
Cr^{5+}(g)	*4182*		
Cr^{6+}(g)	*6273*		
Cr^{7+}(g)	*9991*		
CrO(g)	$\sim$*53*^{29}	~ 46	53.0^{22}
CrO_2(c)	*−143*	−131	(13)
CrO_2(g)	$\sim -3^{29-31}$	~ -5	62.0^{32}
Cr_2O_3(c)	*−272.4*	*−252.9*	*19.4*^{22}
$CrO_{2.40}$(c)	−140.3^{46}		
$CrO_{2.62}$(c)	−139.1^{46}		
CrO_3(c)	*−140.9*^{43,44}	−122	(16)
CrO_3(g)	$\sim -65^{29,31}$	~ -60	63.6^{32}
$CrO_4{}^{2-}$(aq)	*−210.60*^{43}	*−173.9*$_{6}$	12$^{46-51}$
$HCrO_4{}^{-}$(aq)	*−209.9*^{43}	*−182.8*$^{52-57}$	*44.*$_{0}$
H_2CrO_4(aq)	−201^{65}	−181.$_{8}{}^{65,66}$	70^{65}
H_2CrO_4(g)	−176^{31,69}		
$Cr_2O_7{}^{2-}$(aq)	*−356.2*^{43}	*−311.0*$^{59-61}$	*62.*$_{6}$
$CrO_4{}^{3-}$(aq)		−176.$_{3}{}^{18}$	
CrO_3Cl^{-}(aq)	−180.$_{4}{}^{65}$	−158.$_{9}{}^{65,66}$	49^{65}
$HCrPO_7{}^{2-}$(aq)		−396.$_{9}{}^{67}$	
$H_2CrPO_7{}^{-}$(aq)		−400.5^{67}	
Ag_2CrO_4(c)	−174.58^{48}	−153.11	*52.0*^{22,48}
Na_2CrO_4(c)	−320.8^{71}	−295.2	42.212^{70}
$Na_2Cr_2O_7$(c)	−473.0^{71}	−430.$_{3}$	(64)
K_2CrO_4(c)	−335.4^{43}	−309.6	47.8^{22}
K_2CrO_4(g)	−249^{31}		
$KHCrO_4$(g)	−217^{31}		
$K_2Cr_2O_7$(c)	−492.9^{71}	−450.0	69.6^{22}
$(NH_4)_2CrO_4$(c)	*−279.0*^{45}		
$(NH_4)_2Cr_2O_7$(c)	*−431.8*^{44}		
$MgCrO_4$(c)	*−321.1*^{73}		
$SrCrO_4$(c)	−341.6^{74}	−314.0^{75}	23.6 (?)
$BaCrO_4$(c)	−345.3^{74}	*−321.52*^{76}	38.9 (?)
$PbCrO_4$(c)	−222^{45}	−197.0^{77}	35 (?)
Tl_2CrO_4(c)	−225.6^{78}	−205.8$_{2}$	68 (?)
CrO_2Cl_2(liq)	*−138.5*^{73,82,83}	*−122.1*^{73,82}	*53.0*
CrO_2Cl_2(g)	*−128.6*^{73,82}	*−119.9*^{73,82}	*78.8*
CrF(g)	5^{87}		
CrF_2(c)	*−186*	−176	(20)
CrF_2(g)	*−99*^{87}		
CrF_3(c)	*−277*^{45,73,85,86}	*−260*	*22.44*^{84}
CrF_3(g)	−217^{88}		
CrF_4(c)	*−298*^{153}	−277	(33)
$CrCl_2$(c)	*−94.5*$_{2}{}^{89}$	*−85.1*^{89}	*27.56*^{89}
$CrCl_2$(g)	*−30.7*^{91}	−35.4	*74.8*^{92}
$(CrCl_2)_2$(g)	*−111*^{93}		
$CrCl_3$(c)	*−133.0*^{73,94}	*−116.2*	*29.38*^{84}
$CrCl_3$(g)	−71^{91}	−71^{91}	84^{91}
$CrCl_4$(g)	*−102*^{91,154,155}	−97.$_{5}$	87.$_{5}{}^{91}$
$CrBr_2$(c)	*−72.2*^{97}	−69	(32)
$CrBr_2$(g)	*−17*^{93,98}	−28.$_{5}$	80.62^{92}
$(CrBr_2)_2$(g)	*−84*^{93,98}		
CrI_2(c)	*−37.5*^{96}	−39	(37)
CrI_2(g)	32^{100}	17	84.15^{92}
CrI_3(c)	*−49*^{96,101,102}	−49	47^{101,102}
CrI_4(g)	3^{102}	−12	112^{102}
$CrICl_2$(c)	*−100*^{103}		
$CrIBr_2$(c)	*−79*^{103}		
Cr^{2+}(aq)	*−34.*$_{3}{}^{45,96}$	−35	(−24)
$Cr(H_2O)_6{}^{3+}$(aq)	~ -467	$\sim -386.{}_{6}$	~ 24
Cr^{3+}(aq)	~ -57	$\sim -46.{}_{5}$	~ -76
$Cr(H_2O)_5(OH)^{2+}$ (aq)	−457$^{114-116}$	−381.$_{4}{}^{75,114,115}$	~ 42
$Cr(OH)^{2+}$ (aq, i.s.^{c})	−115$^{114-116}$	−98.$_{0}{}^{75,114,115}$	~ -42
$Cr(H_2O)_4(OH)_2{}^{+}$ (aq)	−449^{73,75,114}	−372^{75,114}	~ 35
$Cr(OH)_2{}^{+}$(aq, i.s.)	−176^{73,75,114}	−145^{75,114}	~ -32
$Cr(OH)_3$(ppt)		−200.$_{2}{}^{75,114}$	
$Cr(OH)_4{}^{-}$(aq)	−298^{117}	$\sim -236^{75}$	−26^{117}
$Cr(H_2O)_5Cl^{2+}$(aq)	−434$^{120-122}$	−360.3$^{119-123}$	35
$CrCl^{2+}$(aq, i.s.)	−92$^{120-122}$	−76.9$^{119-123}$	−49
$Cr(H_2O)_6Cl^{2+}$ (aq, o.s.^{d})		−417.$_{9}{}^{123}$	
$CrCl^{2+}$(aq, o.s.)		−77.$_{8}{}^{123}$	
$Cr(H_2O)_4Cl_2{}^{+}$(aq)	−401^{117,122}	−336.$_{3}{}^{75,112}$	~ 52
$CrCl_2{}^{+}$(aq, i.s.)	−127^{117,122}	−109.$_{6}{}^{75,112}$	~ -15
$Cr(H_2O)_3(OH)Cl_2$ (aq)		−328.$_{5}{}^{124}$	
$Cr(OH)Cl_2$(aq, i.s.)		−158.$_{4}{}^{124}$	
$Cr(H_2O)_5Br^{2+}$(aq)	−422.7^{126}	−351.1^{126}	41.$_{5}{}^{126}$
$CrBr^{2+}$(aq, i.s.)	−81.1^{126}	−67.7^{126}	−42.$_{0}{}^{126}$
$Cr(H_2O)_4Br_2{}^{+}$(aq)	−377.$_{1}{}^{45}$		
$CrBr_2{}^{+}$(aq, i.s.)	−103.$_{8}{}^{45}$		
$Cr(H_2O)_5SCN^{2+}$ (aq)	−382.$_{5}{}^{116}$	−312.$_{0}{}^{116}$	$\sim 49^{116}$
$CrSCN^{2+}$(aq, i.s.)	−40.$_{9}{}^{116}$	−28.$_{6}{}^{116}$	$\sim -35^{116}$
$FeCr_2O_4$(c)	*−345.3*$^{39,145-147}$	*−321.2*	*34.9*^{22}
$MgCr_2O_4$(c)	−426.9^{148}	−399.5	*25.34*^{22}
$NiCr_2O_4$(c)	−330.6^{148}	−305.$_{3}$	(31.5)
$ZnCr_2O_4$(c)	−370.9^{148}	−344.$_{4}$	(30.5)
$CdCr_2O_4$(c)	−344.3^{148}	−318.$_{1}$	(34)
$CuCr_2O_4$(c)	−307.3^{148}	−282.$_{2}$	(33)
$NaCrO_2$(c)	−210^{110}		
$NH_4Cr(SO_4)_2 \cdot 12H_2O$(c)			*170.9*^{22}
$CrH_{0.84}$(c)			8.98^{158}
$CrH_{0.91}$(c)			8.06^{158}
$CrH_{0.94}$(c)			8.20^{158}
Cr_7H_2(c)	*−3.8*^{159}		
Cr_3C_2(c)	*−19.3*	*−19.5*	*20.42*^{22}
Cr_7C_3(c)	*−38.7*	*−39.9*	*48.0*^{22}
$Cr_{23}C_6$(c)	*−87.2*	*−89.3*	*145.8*^{22}
CrC_2(g)	$\sim 184^{163}$		
CrN(c)	−29^{45,73,164,165}	−22	(6)
Cr_2N(c)	−30^{45,73,164,165}	−18	(12)
CrSi(c)	−12.7^{166}	−12.9	10.5^{166}
$CrSi_2$(c)	−19.1^{166}	−18.7	13.3^{24,166,167}
Cr_3Si(c)	−22.0^{166}	−21.8	20.6^{166}
Cr_5Si_3(c)	−50.4^{166}	−50.9	43.5^{166}
CrGe(c)			14.6^{168}
Cr_5Ge_3(c)			56.6^{168}
$Cr_{11}Ge_{19}$(c)			227.3^{168}
CrS(c)	−32^{169}	−33^{169}	17
CrS(g)	$\sim 83^{170}$	~ 69	(60)
Cr_2Te_3(c)			*49.86*^{171}
Cr_3Te_4(c)			*70.05*^{171}
Cr_5Te_6(c)			*112.49*^{171}
$Cr(CO)_6$(c)	−234(?)^{175}	−207	72^{173,176}
$Cr(CO)_6$(g)	−217^{173,176}	−202	111.6^{178}
$Cr(PF_3)_6$(c)	−1446.4^{179}		

[a] Italicized values agree with values in NBS 270-4 or NBS 270-6. Values in parentheses are estimates. [b] From NBS 270-4, adjusted for different $\Delta H_f°$ of Cr(g). [c] i.s. = inner sphere. [d] o.s. = outer sphere.

composition studies on CrI_3(c) by Handy and Gregory[101] and by Shieh and Gregory[102] with our tabulated $\Delta H_f°$ for CrI_2(c) to obtain $\Delta H_f° = -50$ kcal mol^{-1} for CrI_3(c). Their results[101,102] are also consistent with $S° = 47$ cal K^{-1} mol^{-1} and thence $\Delta G_f° = -50$ kcal mol^{-1} for CrI_3(c). We adopt $\Delta H_f° = -49$ kcal mol^{-1}, $S° = 47$ cal K^{-1} mol^{-1}, and $\Delta G_f° = -49$ kcal mol^{-1} for CrI_3(c).

Handy and Gregory[103] have made high-temperature equilibrium measurements on decomposition of $CrICl_2(c)$ and $CrIBr_2(c)$, with results that we combine with our tabulated ΔH_f° values for $CrCl_2(c)$ and $CrBr_2(c)$ to obtain $\Delta H_f^\circ = -100$ kcal mol^{-1} for $CrICl_2(c)$ and $\Delta H_f^\circ = -79$ kcal mol^{-1} for $CrIBr_2(c)$. These same values are listed in NBS 270-4. We use the thermodynamic properties to calculate $\Delta H^\circ = -16$ kcal mol^{-1} of $CrI_3(c)$ for

$$3CrICl_2(c) = 2CrCl_3(c) + CrI_3(c)$$

This indication that $CrICl_2(c)$ is unstable with respect to the CrX_3 compounds suggests that further work is needed.

Lascelles, Shelton, and Schäfer[104] have carried out high-temperature measurements on the $CrCl_2$–$AlCl_3$ system. We are unable to use either their reported K values or their equation for $K(T)$, which is inconsistent with the reported K values, for calculation of thermodynamic properties to list in Table I for the postulated $CrCl_2 \cdot 2AlCl_3(g)$.

Vasil'kova et al.[105] have reported results of their calorimetric measurements on various "chlorochromates (III)" and summarized results of some related earlier work. Although it is possible to calculate values of ΔH_f° (from the elements) for various $M_3CrCl_6(c)$ and $M_3Cr_2Cl_9(c)$ compounds (M = alkali metal) from their results, it may be more useful to have available the enthalpies of formation from the constituent halides as in Table II. We also call attention to related high-temperature vaporization measurements by Galitskii et al.,[106] whose results do not permit us to calculate any thermodynamic properties for our tables. It should also be noted that Cook[107] has concluded from phase equilibrium data that $Na_3Cr_2Cl_9(c)$ is apparently nonexistent.

Now we turn to consideration of the thermodynamic properties of aqueous chromic [Cr(III)] and chromous [Cr(II)] ions, beginning with the latter and then continuing with a large number of Cr(III) species.

Gregory and Burton[96] have measured the enthalpy of solution of $CrCl_2(c)$ in 1.0 M $Cl^-(aq)$, with a result in fair agreement with an earlier[45] enthalpy of solution. Combination of these experimental results with our estimated enthalpies of dilution and the ΔH_f° of $CrCl_2(c)$ is consistent with $\Delta H_f^\circ = -34._3$ kcal mol^{-1} for $Cr^{2+}(aq)$ as listed in NBS 270-4. We estimate $S^\circ = (-24)$ cal K^{-1} mol^{-1} and combine with the ΔH_f° to obtain $\Delta G_f^\circ = -35$ kcal mol^{-1} for $Cr^{2+}(aq)$. This ΔG_f° leads to the potential

$$Cr^{2+}(aq) + 2e^- = Cr(c) \qquad E^\circ = -0.76 \text{ V}$$

Jenkins, Mamantov, and Manning[108] have reported E° for the Cr(II)|Cr(c) couple in molten fluoride medium.

The NBS 270-4 lists $\Delta H_f^\circ = -477.8$ kcal mol^{-1} for $Cr(H_2O)_6{}^{3+}(aq)$, which corresponds to $\Delta H_f^\circ = -477.8 - 6(-68.315) = -67.9$ kcal mol^{-1} for $Cr^{3+}(aq)$ in which we do not explicitly include any water. Our assessment of various experimental results leads us to a considerably less negative ΔH_f° as described below.

The calorimetrically determined[109] enthalpy of reduction of Cr(VI) in acidic solution to Cr(III) in combination with our tabulated properties of $Cr_2O_7{}^{2-}(aq)$ and $HCrO_4{}^-(aq)$ leads to $\Delta H_f^\circ = -58$ kcal mol^{-1} for $Cr^{3+}(aq)$.

We have other calorimetric results (cited below) that we can use for evaluation of ΔH_f° of $Cr^{3+}(aq)$. For this purpose we must make use of ΔH° values for dissociation of $CrCl^{2+}(aq)$ and $CrCl_2{}^+(aq)$ as discussed later in this section.

Neuman, Kroger, and Kunz (cited by Bichowsky and Rossini[45]) have determined the enthalpy of solution of Cr(c) in HCl(aq). Assuming that $CrCl_2{}^+(aq)$ was the principal Cr(III) species in their solutions, we obtain $\Delta H_f^\circ = -61$ kcal mol^{-1} for $Cr^{3+}(aq)$. Assuming that $CrCl^{2+}(aq)$ was the principal species leads to $\Delta H_f^\circ = -56$ kcal mol^{-1} for $Cr^{3+}(aq)$.

Gregory and Burton[96] have measured the enthalpy of solution of $CrCl_3(c)$ in 1.0 M $Cl^-(aq)$. Assuming that $CrCl_2{}^+(aq)$ was the principal species in solution, we calculate $\Delta H_f^\circ = -56$ kcal mol^{-1} for $Cr^{3+}(aq)$, while the choice of $CrCl^{2+}(aq)$ as principal species in solution leads to $\Delta H_f^\circ = -51$ kcal mol^{-1} for $Cr^{3+}(aq)$.

TABLE II. Enthalpies of Reaction[105]

$$nMCl(c) + mCrCl_3(c) = M_nCr_mCl_{3m+n}(c)$$

$M_nCr_mCl_{3m+n}$	ΔH°/kcal mol^{-1}	$M_nCr_mCl_{3m+n}$	ΔH°/kcal mol^{-1}
Na_3CrCl_6	0.7	$NaRb_2CrCl_6$	−14.9
K_3CrCl_6	−11.0	$NaCs_2CrCl_6$	−20.6
Rb_3CrCl_6	−16.0	$K_3Cr_2Cl_9$	−12.7
Cs_3CrCl_6	−18.4	$Rb_3Cr_2Cl_9$	−25.8
NaK_2CrCl_6	−8.0	$Cs_3Cr_2Cl_9$	−34.7

Shchukarev et al.[95] have also measured the enthalpy of solution of $CrCl_3(c)$, using 0.12 M $Cl^-(aq)$ as solvent. Assuming that $CrCl^{2+}(aq)$ was the principal species in solution leads to $\Delta H_f^\circ = -57$ kcal mol^{-1} for $Cr^{3+}(aq)$, while choice of $CrCl_2{}^+(aq)$ as principal solute species leads to $\Delta H_f^\circ = -62$ kcal mol^{-1} for $Cr^{3+}(aq)$.

On the basis of all of the results above [$\Delta H_f^\circ = -58$, -61, -56, -56, -51, -57, and -62 kcal mol^{-1} for $Cr^{3+}(aq)$], we choose $\Delta H_f^\circ \simeq -57$ kcal mol^{-1} for $Cr^{3+}(aq)$, which corresponds to $\Delta H_f^\circ \simeq -467$ kcal mol^{-1} for $Cr(H_2O)_6{}^{3+}(aq)$. These values are 11 kcal mol^{-1} less negative than corresponding values from NBS 270-4. Further measurements are required to establish satisfactorily the thermodynamic properties of this important ion.

We note that Gross, Wilson, and Gutteridge[110] have measured the enthalpy of solution of Cr(c) in aqueous HCl–$FeCl_3$ at 110 °C with results that are roughly consistent with our choice above.

Now we have two unsatisfactory routes to the ΔG_f° and S° of $Cr^{3+}(aq)$. Grube and Schlecht[111] have measured potentials for Cr(III)|Cr(II) couples in several solutions, using several different "inert" electrodes. We select $E^\circ \simeq -0.4_3$ V (uncertainty $\pm 0.1_3$ V?) for the $Cr^{3+}(aq)|Cr^{2+}(aq)$ couple and combine with the ΔG_f° of $Cr^{2+}(aq)$ cited above to obtain $\Delta G_f^\circ \simeq -45$ kcal mol^{-1} for $Cr^{3+}(aq)$. Combination of this ΔG_f° with our selected $\Delta H_f^\circ = -57$ kcal mol^{-1} for $Cr^{3+}(aq)$ leads to $S^\circ \simeq -81$ cal K^{-1} mol^{-1} for this ion. Because this entropy seems to be too negative in comparison with entropies of some other 3+ aqueous ions, we also consider an alternative approach that begins with an estimated (more reasonable?) $S^\circ \simeq (-72)$ cal K^{-1} mol^{-1} for $Cr^{3+}(aq)$. Now combination of this entropy with our selected ΔH_f° leads to $\Delta G_f^\circ \simeq -48$ kcal mol^{-1} for $Cr^{3+}(aq)$ and thence to a calculated $E^\circ \simeq -0.5_6$ V for the $Cr^{3+}(aq)|Cr^{2+}(aq)$ couple. Because of substantial uncertainties throughout the calculations summarized here, we arbitrarily select mean values as follows: $\Delta G_f^\circ \simeq -46._5$ kcal mol^{-1} and $S^\circ \simeq -76$ cal K^{-1} mol^{-1} for $Cr^{3+}(aq)$. These values correspond to $\Delta G_f^\circ \simeq -386._6$ kcal mol^{-1} and $S^\circ \simeq 24$ cal K^{-1} mol^{-1} for $Cr(H_2O)_6{}^{3+}(aq)$ in which specifically indicated waters of solvation are included in the thermodynamic properties. Our selected ΔG_f° values correspond to the following potentials:

$$Cr^{3+}(aq) + e^- = Cr^{2+}(aq) \qquad E^\circ = -0.5_0 \text{ V}$$

$$Cr^{3+}(aq) + 3e^- = Cr(c) \qquad E^\circ = -0.67 \text{ V}$$

$$Cr_2O_7{}^{2-}(aq) + 14H^+(aq) + 6e^- = 2Cr^{3+}(aq) + 7H_2O(liq)$$

$$E^\circ = 1.29 \text{ V}$$

$$HCrO_4{}^-(aq) + 7H^+(aq) + 3e^- = Cr^{3+}(aq) + 4H_2O(liq)$$

$$E^\circ = 1.31 \text{ V}$$

Jenkins, Mamantov, and Manning[108] have measured the Cr(III)/Cr(II) potential in molten fluoride medium.

In the early years of this century N. Bjerrum found it necessary to interpret his emf determinations of H^+(aq) in Cr(III) solutions in terms of hydrolytic dimers and polymers as well as such monomeric species as $Cr(OH)^{2+}$(aq). Since that time a number of investigators have confirmed the importance of species containing more than one Cr(III), and by taking advantage of kinetic inertness have isolated a few such species. Results[75,112,113] are summarized briefly as follows. Solutions containing appreciable concentrations of dimers and larger species can be obtained by refluxing chromium(III) perchlorate solutions, by making the pH of many solutions containing Cr(III) greater than about 3, and by oxidation of Cr(II) or reduction of Cr(VI) solutions. Dimeric and trimeric species bearing charges of +4 and +5 have been identified and equilibrium quotients for their formation have been reported. Dimers and larger species must certainly be considered in connection with many solutions in equilibrium with precipitated chromic hydroxide.

We begin our consideration of hydrolytic species of Cr(III) with the first hydroxy complex, which can be represented by $Cr(H_2O)_5(OH)^{2+}$(aq) or by $Cr(OH)^{2+}$(aq, inner sphere). Meyenburg, Siroky, and Schwarzenbach[114] have recently investigated the equilibrium that we represent by

$$Cr(H_2O)_6{}^{3+}(aq) = Cr(H_2O)_5(OH)^{2+}(aq) + H^+(aq) \qquad (4)$$

at 5 and 20 °C in 0.1 M solution. Swaddle and Kong[115] have investigated the same reaction at 25° and other temperatures in 0.5 M solution. Earlier investigations have been cited by Sillén.[75] On the basis of all these results, we choose K ($\mu = 0$, 298 K) $= 1.6 \times 10^{-4}$ for the equilibrium represented by (4). We use this value with our $\Delta G_f°$ of $Cr(H_2O)_6{}^{3+}$(aq) to calculate $\Delta G_f° = -381._4$ kcal mol^{-1} for $Cr(H_2O)_5(OH)^{2+}$(aq). We also obtain $\Delta G_f° = -98._0$ kcal mol^{-1} for the equivalent $Cr(OH)^{2+}$(aq, inner sphere).

The NBS 270-4 $\Delta H_f°$ values correspond to $\Delta H° = 14.2$ kcal mol^{-1} for (4), while values tabulated in the older NBS Circular 500[73] lead to $\Delta H° = 14.3$ kcal mol^{-1} for this reaction. Results in the papers cited there[73] *suggest* to us that a smaller $\Delta H°$ might be better for this reaction. Three more recent investigations[114–116] of equilibrium constants at different temperatures are all consistent with $\Delta H° = 10$ kcal mol^{-1} for the reaction represented by (4), which is the value we adopt and use in calculating $\Delta H_f° = -457$ kcal mol^{-1} for $Cr(H_2O)_5(OH)^{2+}$(aq). Combination of $\Delta H_f°$ and $\Delta G_f°$ values leads to $S° = 42$ cal K^{-1} mol^{-1} for $Cr(H_2O)_5(OH)^{2+}$(aq). We also obtain $\Delta H_f° = -115$ kcal mol^{-1} and $S° = -42$ cal K^{-1} mol^{-1} for the equivalent $Cr(OH)^{2+}$(aq, inner sphere). This latter entropy is more negative than is usual for 2+ ions, which suggests that there may be an error in the results for reaction 4 or that there is an error in the entropy adopted for Cr^{3+}(aq).

It is important to emphasize here that the $\Delta H_f°$, $\Delta G_f°$, and $S°$ values in the paragraph above are based on our choices for $Cr(H_2O)_6{}^{3+}$(aq) and Cr^{3+}(aq), with our $\Delta H_f°$ values for these ions 11 kcal mol^{-1} less negative than previously selected in NBS 270-4. Further, our $\Delta H_f°$ values for $Cr(H_2O)_5(OH)^{2+}$(aq) and $Cr(OH)^{2+}$(aq, inner sphere) are different from those in NBS 270-4 because we have selected a different $\Delta H°$ for reaction 4 than was selected by the authors of NBS 270-4.

For the second hydrolysis of Cr^{3+}(aq) that can be represented by

$$Cr(H_2O)_5(OH)^{2+}(aq) = Cr(H_2O)_4(OH)_2{}^+(aq) + H^+(aq)$$

we choose $K = 10^{-7}$ from the results of several investigations.[75,114] The $\Delta H_f°$ values listed in NBS 270-4 correspond to $\Delta H° = 7.8$ kcal mol^{-1} for this reaction, in agreement with results of Bjerrum cited previously[73,75] and with the more recent results of Meyenburg, Siroky, and Schwarzenbach.[114] All of these results, in combination with our tabulated properties of $Cr(H_2O)_5(OH)^{2+}$(aq), lead to $\Delta G_f° = -372$ kcal mol^{-1}, $\Delta H_f° = -449$ kcal mol^{-1}, and $S° \simeq 35$ cal K^{-1} mol^{-1} for $Cr(H_2O)_4(OH)_2{}^+$(aq). We also obtain $\Delta G_f° = -145$ kcal mol^{-1}, $\Delta H_f° = -176$ kcal mol^{-1}, and $S° \simeq -32$ cal K^{-1} mol^{-1} for the equivalent $Cr(OH)_2{}^+$(aq, inner sphere). We note that this latter entropy is considerably more negative than is usual for 1+ ions.

On the basis of old[75] and recent[114] investigations, we choose the following solubility product for precipitated chromic hydroxide:

$$Cr(OH)_3(ppt) = Cr^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = 10^{-30}$$

Combination of this K_{sp} with our $\Delta G_f°$ for Cr^{3+}(aq) leads to $\Delta G_f° = -200._2$ kcal mol^{-1} for $Cr(OH)_3$(ppt). The $\Delta H°$ of the reaction above that is derived from the NBS 270-4 $\Delta H_f°$ values in combination with our other thermodynamic properties leads to a negative $S°$ for $Cr(OH)_3$(ppt), which is clearly unacceptable. We may also obtain an approximate $\Delta H°$ for this reaction from the work of Meyenburg, Siroky, and Schwarzenbach,[114] which leads to $S° \simeq 8$ cal K^{-1} mol^{-1} for $Cr(OH)_3$(ppt). This $S°$ is only about one-third of a "reasonable" estimate for this quantity. In view of these calculations, we omit $\Delta H_f°$ and $S°$ values for $Cr(OH)_3$(ppt) from our Table I.

It is well established that $Cr(OH)_3$(ppt) and various other Cr(III) compounds dissolve in excess OH^-(aq) to yield anions containing Cr(III). The work of Schug and King[117] has shown that these "chromite" solutions cannot be realistically described in any simple way. Nevertheless, we use results summarized by Sillén[75] to calculate an approximate $\Delta G_f° \simeq -236$ kcal mol^{-1} for "chromite" ion that we represent in over-simplified fashion by $Cr(OH)_4{}^-$(aq). This $\Delta G_f°$ is consistent with the following:

$$Cr(OH)_3(ppt) + OH^-(aq) = Cr(OH)_4{}^-(aq) \qquad K \simeq 10^{-1}$$

$$CrO_4{}^{2-}(aq) + 4H_2O(liq) + 3e^- = Cr(OH)_4{}^-(aq) + 4OH^-(aq)$$

$$E° \simeq -0.2_1 \text{ V}$$

We also use calorimetric results from Schug and King[117] to obtain $\Delta H_f° = -298$ kcal mol^{-1} and $S° \simeq -26$ cal K^{-1} mol^{-1} for $Cr(OH)_4{}^-$(aq). In connection with these thermodynamic properties it must be emphasized that Schug and King[117] have stated clearly that "chromite" solutions do *not* have the properties that might be expected for solutions of "$Cr(OH)_4{}^-$(aq)."

The stability of CrF^{2+}(aq) has been investigated by Swaddle and King,[118] who have also cited earlier work. The CrF^{2+}(aq) ion is less stable with respect to dissociation than the corresponding ions of iron, scandium, and aluminum, but is more stable than similar ions of indium, yttrium, and lanthanum.

Results of several investigators[119–123] are in reasonable agreement with $K = 0.2$ for the reaction

$$Cr(H_2O)_6{}^{3+}(aq) + Cl^-(aq) = Cr(H_2O)_5Cl^{2+}(aq) + H_2O(liq)$$

This K value leads to $\Delta G_f° = -360.3$ kcal mol^{-1} for $Cr(H_2O)_5Cl^{2+}$(aq) and also to $\Delta G_f° = -76.9$ kcal mol^{-1} for the equivalent $CrCl^{2+}$(aq, inner sphere). Results of some of these investigations[120–122] are also consistent with $\Delta H° = 5$ kcal mol^{-1} for this reaction. We calculate $\Delta H_f° = -434$ kcal mol^{-1} and $S° = 35$ cal K^{-1} mol^{-1} for $Cr(H_2O)_5Cl^{2+}$(aq), and also obtain $\Delta H_f° = -92$ kcal mol^{-1} and $S° = -49$ cal K^{-1} mol^{-1} for the equivalent $CrCl^{2+}$(aq, inner sphere).

The work of Morris and Hammond[123] leads to K ($\mu = 1.0$ M) $= 0.9$ for formation of the outer-sphere complex represented by

$$Cr(H_2O)_6{}^{3+}(aq) + Cl^-(aq) = Cr(H_2O)_6Cl^{2+}(aq)$$

A somewhat smaller equilibrium quotient was found by Gates and King[122] for solutions having higher ionic strength. We use the former result[123] to obtain $\Delta G_f^\circ = -417._9$ kcal mol^{-1} for $Cr(H_2O)_6Cl^{2+}(aq)$ and also $\Delta G_f^\circ = -77._8$ kcal mol^{-1} for the equivalent $CrCl^{2+}$(aq, outer sphere).

From investigations cited by Sillén[75,112] we adopt $K = 0.1$ for

$$Cr(H_2O)_5Cl^{2+}(aq) + Cl^-(aq) = Cr(H_2O)_4Cl_2^{+}(aq) + H_2O(liq) \quad (5)$$

This K leads to $\Delta G_f^\circ \simeq -336._3$ kcal mol^{-1} for $Cr(H_2O)_4Cl_2^{+}(aq)$ and also to $\Delta G_f^\circ \simeq -109._6$ kcal mol^{-1} for the equivalent $CrCl_2^{+}$(aq, inner sphere). Measurements by King et al.[117,122] lead to $\Delta H^\circ = 5$ kcal mol^{-1} for this reaction and thence to $\Delta H_f^\circ \simeq -401$ kcal mol^{-1} for $Cr(H_2O)_4Cl_2^{+}(aq)$ and to $\Delta H_f^\circ \simeq -127$ kcal mol^{-1} for the equivalent $CrCl_2^{+}$(aq, inner sphere). Combination of enthalpies and free energies leads to $S^\circ \simeq 52$ cal K^{-1} mol^{-1} for $Cr(H_2O)_4Cl_2^{+}(aq)$ and to $S^\circ \simeq -15$ cal K^{-1} mol^{-1} for $CrCl_2^{+}$(aq, inner sphere).

Results of several investigators[124] are in agreement with $K = 2 \times 10^{-6}$ for

$$Cr(H_2O)_4Cl_2^{+}(aq) = Cr(H_2O)_3(OH)Cl_2(aq) + H^+(aq)$$

We calculate $\Delta G_f^\circ \simeq -328._5$ kcal mol^{-1} for $Cr(H_2O)_3(OH)Cl_2(aq)$ and $\Delta G_f^\circ \simeq -158._4$ kcal mol^{-1} for the equivalent $Cr(OH)Cl_2$(aq, inner sphere).

The $Cr(H_2O)_4Cl_2^{+}(aq)$ species can exist in cis and trans forms. Two investigations[125] are consistent with $K = 0.5$ for cis = trans and the conclusion that the cis form is 0.4 kcal mol^{-1} more stable than the trans form.

Equilibrium investigations by Espenson and King[126] are consistent with $K = 2 \times 10^{-3}$ and $\Delta H^\circ = 5$ kcal mol^{-1} for

$$Cr(H_2O)_6^{3+}(aq) + Br^-(aq) = Cr(H_2O)_5Br^{2+}(aq) + H_2O(liq)$$

We calculate $\Delta G_f^\circ \simeq -351._1$ kcal mol^{-1}, $\Delta H_f^\circ \simeq -422._7$ kcal mol^{-1}, and $S^\circ \simeq 41._5$ cal K^{-1} mol^{-1} for $Cr(H_2O)_5Br^{2+}(aq)$, and also obtain $\Delta G_f^\circ \simeq -67._7$ kcal mol^{-1}, $\Delta H_f^\circ \simeq -81._1$ kcal mol^{-1}, and $S^\circ \simeq -42$ cal K^{-1} mol^{-1} for the equivalent $CrBr^{2+}$(aq, inner sphere). Old calorimetric results from Recoura[45] lead to $\Delta H_f^\circ = -377._1$ kcal mol^{-1} for $Cr(H_2O)_4Br_2^{+}(aq)$ and to $\Delta H_f^\circ \simeq -103._8$ kcal mol^{-1} for the equivalent $CrBr_2^{+}$(aq, inner sphere).

Results of Spreer and King[127] lead to $K(\mu = 4.1) = 0.2$ for

$$Cr(H_2O)_6^{3+}(aq) + Br^-(aq) = Cr(H_2O)_6Br^{2+}(aq)$$

From Swaddle and Guastalla[128] we have equilibrium quotients at several temperatures for replacement of water in $Cr(H_2O)_6^{3+}(aq)$ by iodide ion; at 25 °C they give $K(\mu = 4.2) = 7 \times 10^{-5}$.

Espenson and Binau[129] have reported $K(\mu = 1.0)$ values from 45–65 °C for

$$Cr(H_2O)_6^{3+}(aq) + H_3PO_2(aq) = [Cr(H_2O)_5H_2PO_2]^{2+}(aq) + H^+(aq) + H_2O(liq)$$

We use their derived enthalpy and entropy to calculate $K(\mu = 1.0) = 17$ at 25 °C.

Two investigations[130] have provided enthalpy data for cis-trans transformations for $[CrCl_2(NH_3)_4]Cl{\cdot}H_2O(c)$ and $[CrBr(H_2O)(NH_3)_4]Br_2(c)$.

Jones and Bjerrum[131] have made measurements on concentrated solutions with results that lead to estimates of the stability of the inner-sphere complex $Cr(H_2O)_5ClO_4^{2+}(aq)$.

Results of Mercer and Hormuth[132] lead to $K(\mu = 0.5) = 1.3 \times 10^2$ for

$$Cr^{3+}(aq) + 2IO_3^-(aq) = Cr(IO_3)_2^{+}(aq)$$

Ardon and Sutin[133] have reported $K(\mu = 1.0) = 1 \times 10^{-2}$ for

$$Cr^{3+}(aq) + NO_3^-(aq) = Cr(NO_3)^{2+}(aq)$$

Their K values at several temperatures also lead to enthalpies and entropies.

Results of two investigations[134] of aqueous chromic sulfate complexes are in poor agreement with each other, although it does appear to be well established that there is a kinetically inert inner-sphere complex and a labile outer-sphere complex.

Measurements by Hume and Kolthoff[135] have led to the following:

$$Cr(CN)_6^{3-}(aq) + e^- = Cr(CN)_6^{4-}(aq) \qquad E^\circ = -1.28\ \text{V}$$

Guzzetta and Hadley[136] have reported calorimetric data for formation of $Cr(CN)_6^{4-}(aq)$, but their results do not justify calculation of a ΔH_f° value.

Poulsen, Bjerrum, and Poulsen[137] and Postmus and King[116] have investigated the chromic thiocyanate complex at several temperatures and ionic strengths. From the latter investigation[116] we take the following:

$$Cr(H_2O)_6^{3+}(aq) + SCN^-(aq) = Cr(H_2O)_5SCN^{2+}(aq) + H_2O(liq)$$

$$K = 1.2 \times 10^3 \quad \Delta H^\circ = -2.13\ \text{kcal mol}^{-1}$$
$$\Delta S^\circ = 6.9\ \text{cal K}^{-1}\ \text{mol}^{-1}$$

We use these values in calculating $\Delta G_f^\circ \simeq -312._0$ kcal mol^{-1}, $\Delta H_f^\circ \simeq -382._5$ kcal mol^{-1}, and $S^\circ \simeq 49$ cal K^{-1} mol^{-1} for $Cr(H_2O)_5SCN^{2+}(aq)$, and also $\Delta G_f^\circ \simeq -28._6$ kcal mol^{-1}, $\Delta H_f^\circ \simeq -40._9$ kcal mol^{-1}, and $S^\circ \simeq -35$ cal K^{-1} mol^{-1} for the equivalent $Cr(SCN)^{2+}$(aq, inner sphere).

Templeton and King[138] have investigated the protonation of the chromic azide complex and report the following (30 °C):

$$Cr(N_3)^{2+}(aq) + H^+(aq) = Cr(N_3)H^{3+}(aq) \qquad K = 2.7 \times 10^3$$

Equilibrium[139] and calorimetric[140] measurements have led to the following:

$$Cr(NH_3)_5(H_2O)^{3+}(aq) = Cr(NH_3)_5(OH)^{2+}(aq) + H^+(aq)$$

$$K = 1 \times 10^{-5} \quad \Delta H^\circ = 8.3\ \text{kcal mol}^{-1}$$
$$\Delta S^\circ = 5._5\ \text{cal K}^{-1}\ \text{mol}^{-1}$$

Duffy and Earley[141] have made extensive measurements on the replacement of H_2O by thiocyanate and chloride in $Cr(NH_3)_5(H_2O)^{3+}(aq)$ and have also investigated outer-sphere complex or ion-pair species involving this cation with thiocyanate and chloride. They have reported several K, ΔH°, and ΔS° values for these reactions. Guastalla and Swaddle[142] have carried out both equilibrium and rate measurements on the aquation of chromic ammine halides and have obtained ΔV° and $\Delta V^{\ddagger}$ values for these reactions.

Equilibrium constants for formation of such species as $Cr(NCS)Hg^{4+}(aq)$, $Cr(NC)Hg^{4+}(aq)$, and $\{[Cr(NH_3)_5(NCS)]Ag\}^{3+}(aq)$ have been reported.[143]

DTA measurements leading[144] to ΔH values for deaquation of such compounds as $[Cr(NH_3)_5(H_2O)]X_3(c)$ and $K_3[Cr(C_2O_4)_3]{\cdot}3H_2O(c)$ are generally in poor agreement with other measurements on the same compounds. Some reported ΔH values for reactions where the products are H_2O(liq) and H_2O(g), respectively, are inconsistent with the well-known enthalpy of vaporization of water.

For the spinel $FeCr_2O_4(c)$ the NBS 270-4 lists $S^\circ = 34.9$ cal K^{-1} mol^{-1}, which is the same as the value derived from results previously cited by Kelley and King.[22] The $\Delta H_f^\circ = -345.3$ kcal mol^{-1} and $\Delta G_f^\circ = -321.2$ kcal mol^{-1} given in NBS 270-4 for this compound are consistent with the high-temperature emf and equilibrium results obtained by Tretjakow and Schmalzried,[39] Boericke and Bangert,[145] Chen and Chipman,[146] and Katsura and Muan.[147] We therefore adopt the $\Delta H_f°$ and $\Delta G_f°$ values listed in NBS 270-4, rather than the properties derived from the high-temperature results of Novokhatskii and Lenev.[36]

The NBS 270-6 lists $S° = 25.34$ cal K^{-1} mol^{-1} for the spinel $MgCr_2O_4$(c), in agreement with the value derived from results cited by Kelley and King.[22] The $\Delta H_f° = -426.3$ kcal mol^{-1} that is listed in NBS 270-6 for this compound is in good agreement with the value we calculate from the high-temperature emf results of Tretjakow and Schmalzried[39] [with $(H_T - H_{298})$ values from Kelley[37]]. A slightly different and probably better $\Delta H_f° = -426.9$ kcal mol^{-1} can be similarly calculated from the recent high-temperature (900 °C) calorimetric results of Müller and Kleppa.[148] We combine this latter $\Delta H_f°$ with the $S°$ above to obtain $\Delta G_f° = -399.5$ kcal mol^{-1} for $MgCr_2O_4$(c).

Calorimetric measurements by Müller and Kleppa[148] lead to $\Delta H°$ of formation of $NiCr_2O_4$(c) from the constituent oxides at 900 °C. Combination of this value with our estimated $(H_T - H_{298})$ leads to $\Delta H_f° = -330.6$ kcal mol^{-1} for $NiCr_2O_4$(c) at 298 K. This value appears to be preferable to that derived from the temperature derivative of the emf results of Tretjakow and Schmalzried.[39] Although the $\Delta H°$ based on these latter[39] results appears to have a large uncertainty, the uncertainty associated with $\Delta G°$ at any temperature is less large and can be used with estimated $(H_T - H_{298})$ and $(S_T - S_{298})$ values and the calorimetric $\Delta H°$ cited above to obtain $\Delta G_f°$ and $S°$ at 298 K. Or we can directly estimate $S°$ at 298 K and combine with the above $\Delta H_f°$ to obtain $\Delta G_f°$ at 298 K. On the basis of these two approaches, we adopt $S° = (31._5)$ cal K^{-1} mol^{-1} and $\Delta G_f° = -305.3$ kcal mol^{-1} for $NiCr_2O_4$(c).

Calorimetric measurements by Müller and Kleppa[148] have led to $\Delta H°$ values for formation of $ZnCr_2O_4$(c) and $CdCr_2O_4$(c) from their constituent oxides at 900 °C. Combination of these values with estimated $(H_T - H_{298})$ values leads to $\Delta H_f° = -370.9$ kcal mol^{-1} for $ZnCr_2O_4$(c) and $\Delta H_f° = -344.3$ kcal mol^{-1} for $CdCr_2O_4$(c), both at 298 K. We estimate $S° = (30._5)$ cal K^{-1} mol^{-1} for $ZnCr_2O_4$(c) and calculate its $\Delta G_f° = -344.4$ kcal mol^{-1}. We also estimate $S° = (34)$ cal K^{-1} mol^{-1} for $CdCr_2O_4$(c) and calculate its $\Delta G_f° = -318.1$ kcal mol^{-1}.

Calorimetric results from Müller and Kleppa[148] lead to $\Delta H°$ for formation of $CuCr_2O_4$(c) from the oxides at 900 °C. We combine this result with our estimated $(H_T - H_{298})$ to obtain $\Delta H_f° = -307.3$ kcal mol^{-1} at 298 K. We adopt this value rather than that derived from the temperature derivative of the high-temperature results of Schmahl and Minzl.[149] We proceed as described above for $NiCr_2O_4$(c) to obtain $S° = (33)$ cal K^{-1} mol^{-1} and $\Delta G_f° = -282.2$ kcal mol^{-1} for $CuCr_2O_4$(c).

Tretjakow and Schmalzried[39] and also Aukrust and Muan[150] have made measurements leading to apparently reliable $\Delta G°$ values (in satisfactory agreement with each other) for formation of $CoCr_2O_4$(c) at high temperatures. Because there are substantial uncertainties in the derived $\Delta H°$ values and our calculation of thermodynamic properties at 298 K also requires estimated C_p or related properties, we omit this compound from our Table I.

Gross, Wilson, and Gutteridge[110] have made calorimetric measurements leading to $\Delta H°$ of formation of $NaCrO_2$(c) from Na_2O(c) and Cr_2O_3(c) by way of somewhat uncertain reactions. We use their $\Delta H°$ value for this reaction with $\Delta H_f° = -99.9$ kcal mol^{-1} for Na_2O(c) from the JANAF tables[151] with $\Delta H_f°$ for Cr_2O_3(c) from Table I to obtain $\Delta H_f° = -210$ kcal mol^{-1} for $NaCrO_2$(c).

Zalazinskii et al.[152] have carried out high-temperature equilibrium measurements on the reduction of "cuprous chromite" of formula $CuCrO_2$(c). Our calculations with their results lead to $S° \simeq 6$ cal K^{-1} mol^{-1} for this compound. Because this unreasonably small entropy value indicates either error or very large uncertainty, we do not list $CuCrO_2$(c) in our Table I.

E. Cr(IV) and Cr(V): Compounds and Aqueous Ions

The NBS 270-4 lists $\Delta H_f° = -298$ kcal mol^{-1} for CrF_4(c), which is in agreement with the results of Wartenberg.[153] We estimate $S° = (33)$ cal K^{-1} mol^{-1} and calculate $\Delta G_f° = -277$ kcal mol^{-1} for CrF_4(c).

The results of several investigators[91,154,155] are in reasonable agreement with the NBS 270-4 $\Delta H_f° = -102$ kcal mol^{-1} (maybe a slightly more negative value would be better) for $CrCl_4$(g). We combine this $\Delta H_f°$ with $S° = 87._5$ cal K^{-1} mol^{-1} from Maier[91] to obtain $\Delta G_f° = -97._5$ kcal mol^{-1} for $CrCl_4$(g).

We can use the somewhat uncertain results of Sime and Gregory[156] for reaction of $CrBr_3$(c) with Br_2(g) with the more uncertain $\Delta H_f°$ of $CrBr_3$(c) discussed in the preceding section to obtain a $\Delta H_f°$ value for $CrBr_4$(g) that seems far too negative in comparison to $\Delta H_f°$ values for $CrCl_4$(g) and CrI_4(g). Shieh and Gregory[102] have estimated $\Delta H_f° = (-42.6)$ kcal mol^{-1} for $CrBr_4$(g), a value which seems more reasonable to us than the value we have calculated as described above. The $S°$ has been estimated as (100.1) and (106.9) cal K^{-1} mol^{-1}. Because of all the uncertainties, we omit $CrBr_4$(g) from our Table I.

The results of Shieh and Gregory[102] in combination with our $\Delta H_f°$ for CrI_3(c) leads to $\Delta H_f° = 3$ kcal mol^{-1} for CrI_4(g). Combination of this $\Delta H_f°$ with $S° = 112$ cal K^{-1} mol^{-1} from Shieh and Gregory[102] gives $\Delta G_f° = -12$ kcal mol^{-1} for CrI_4(g).

We now consider approximate potentials for various couples involving aqueous Cr(IV) and Cr(V), beginning with alkaline solutions. Bailey and Symons[18] have deduced an approximate $\Delta G_f°$ for the Cr(V) species they represent by CrO_4^{3-}(aq). Revision of their value to make it consistent with our $\Delta G_f°$ for CrO_4^{2-}(aq) leads to $\Delta G_f° = -176._3$ kcal mol^{-1} for CrO_4^{3-}(aq) and thence the following potentials:

$$CrO_4^{2-}(aq) + e^- = CrO_4^{3-}(aq) \qquad E° = 0.1\ V$$

$$CrO_4^{3-}(aq) + 4H_2O(liq) + 2e^- = Cr(OH)_3(ppt) + 5OH^-(aq)$$
$$E° = -0.6\ V$$

$$CrO_4^{3-}(aq) + 4H_2O(liq) + 2e^- = Cr(OH)_4^-(aq) + 4OH^-(aq)$$
$$E° = -0.7\ V$$

Kinetic evidence[157] leads to generally consistent (approximate) potentials for various half reactions involving Cr(IV) and Cr(V) in acidic solutions. Another approach is to assume that the Cr(V) species in acidic solution is H_3CrO_4(aq) and then calculate its free energy from the $\Delta G_f°$ above for CrO_4^{3-}(aq) and a $\Delta G°$ of protonation estimated by way of the known $\Delta G°$ of protonation of PO_4^{3-}(aq). The following potentials (for acidic solutions) are consistent with all of this.

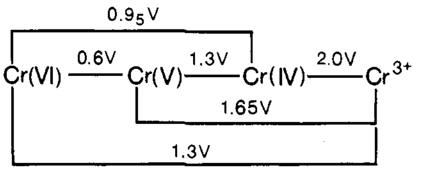
$$Cr(VI) + e^- = Cr(V) \qquad E° = 0.6\ V$$
$$Cr(VI) + 2e^- = Cr(IV) \qquad E° = 0.9_5\ V$$
$$Cr(V) + e^- = Cr(IV) \qquad E° = 1.3\ V$$
$$Cr(V) + 2e^- = Cr^{3+}(aq) \qquad E° = 1.6_5\ V$$
$$Cr(IV) + e^- = Cr^{3+}(aq) \qquad E° = 2.0\ V$$

These potentials (acidic solution) are conveniently summarized in the following potential diagram.

TABLE III. $\Delta H_f°$(298 K) Values for Chromium Carbides

	$\Delta H_f°$/kcal mol^{-1}							
Carbide	NBS 270-4	Mah[a]	Mah[b]	Kulkarni[c]	Kulkarni[d]	Mabuchi[e]	Kleykamp[f]	Storms[g]
Cr_3C_2(c)	*−19.3*	−22.5	−22.2			−16.75	−13.5	−13.6 to −29.4
Cr_7C_3(c)	*−38.7*	−43.3	−42.6	−36.7	−34.3		−26.8	
$Cr_{23}C_6$(c)	*−87.2*	−94.7	−92.4	−81.9	−77.1			−69, −81.9

[a] Reference 35 (combustion calorimetry). Published values quoted here are based on $\Delta H_f°$ = −272.6 kcal mol^{-1} for Cr_2O_3(c). [b] Results of ref 35 recalculated on the basis of our adopted $\Delta H_f°$ = −272.4 kcal mol^{-1} for Cr_2O_3(c). Similar recalculation on the basis of $\Delta H_f°$ = −270.0 kcal mol^{-1} for Cr_2O_3(c) as suggested by Kulkarni and Worrell[42] leads to $\Delta H_f°$ values that are 1.2 kcal mol^{-1} of Cr less negative than values given here. [c] Reference 42 (high-temperature equilibrium). Published values quoted here are based on their selected $\Delta H_f°$ = −270.0 kcal mol^{-1} for Cr_2O_3(c). [d] Results of ref 42 recalculated to conform with our tabulated $\Delta H_f°$ = −272.4 kcal mol^{-1} for Cr_2O_3(c). [e] Reference 161 (high-temperature emf). This value does not depend on $\Delta H_f°$ of Cr_2O_3(c). [f] Reference 162 (high-temperature emf). These values do not depend on $\Delta H_f°$ of Cr_2O_3(c). [g] Reference 27 (review of earlier works from 1926 to 1965). Some of these values are independent of properties assigned to Cr_2O_3(c).



F. Other Inorganic Compounds of Chromium

Wolf[158] has measured heat capacities of CrH_x(c) (x = 0.84, 0.91, and 0.94) and has evaluated entropies at 298 K as listed in Table I. For the compound or mixture of phases with composition described by Cr_7H_2(c) we adopt $\Delta H_f°$ = −3.8 kcal mol^{-1} as listed in NBS 270-4 and as consistent with the published results of Sieverts and Gotta.[159] We also note that Stock and Hardcastle[160] have carried out phase and composition analysis of the chromium hydride system.

The chromium carbides are of considerable importance in metallurgy and have been investigated several times[27,35,42,161,162] by calorimetric, emf, and equilibrium methods. Results in the form of $\Delta H_f°$ values at 298 K are summarized in Table III. The wide range in reported $\Delta H_f°$ values cannot be resolved by our data analysis; still more measurements are required. The $\Delta H_f°$ values listed in the NBS 270-4 appear to be reasonable choices and are adopted for our Table I. Entropies listed in NBS 270-4 are all consistent with results summarized by Kelley and King.[22] We also have $\Delta H_f° \simeq$ 184 kcal mol^{-1} for CrC_2(g) from the work of Kohl and Stearns.[163]

The NBS 270-4 lists $\Delta H_f°$ = −30.5 kcal mol^{-1} for Cr_2N(c) and $\Delta H_f°$ = −29.8 kcal mol^{-1} for CrN(c). This value for CrN(c) is consistent with results cited previously by Bichowsky and Rossini[45] and in NBS Circular 500.[73] The value above for Cr_2N(c) is identical with the value derived from Mah's[164] combustion calorimetry and the $\Delta H_f°$ = −270.4 kcal mol^{-1} for Cr_2O_3(c) that has been adopted here and in NBS 270-4. Had we adopted $\Delta H_f°$ = −270.0 kcal mol^{-1} for Cr_2O_3(c) as suggested by other considerations,[42] we would obtain $\Delta H_f°$ = −28.1 kcal mol^{-1} for Cr_2N(c) from the combustion results. Results of various other calorimetric and high-temperature equilibrium studies[45,73,165] lead to $\Delta H_f°$ values for CrN(c) and Cr_2N(c) that are equal to or less negative than the values listed in NBS 270-4. On the basis of all of these results, we select $\Delta H_f°$ = −29 kcal mol^{-1} for CrN(c) and $\Delta H_f°$ = −30 kcal mol^{-1} for Cr_2N(c). Combination of these values with $S°$ = (6) cal K^{-1} mol^{-1} for CrN(c) and $S°$ = (12) cal K^{-1} mol^{-1} for Cr_2N(c) leads to the tabulated $\Delta G_f°$ values. Although several investigations[165] have shown that the nitrides are nitrogen deficient with stoichiometries (under particular conditions) that lead to formulas such as $Cr_2N_{0.977}$(c) and $CrN_{0.982}$(c), we have followed earlier practice in using the simple formulas Cr_2N(c) and CrN(c).

Chart[166] has recently carried out a thorough review of the thermodynamic properties of silicides of chromium (and other elements) and has selected "best" values for these properties. Our analysis of recent results[24,167] cited by Chart[166] and earlier results cited in these recent papers leads to our selected (in Table I) $\Delta H_f°$ values that are identical with those selected by Chart[166] for all of the chromium silicides. All of these $\Delta H_f°$ values are less negative than values listed for the same compounds in NBS 270-4. Our selection of entropies is identical with that of Chart[166] except for a small difference for $CrSi_2$(c). Free energies (Table I) are consistent with the tabulated $\Delta H_f°$ and $S°$ values.

Low-temperature C_p measurements by Kalishevich et al.[168] lead to the entropies listed in Table I for CrGe(c), Cr_5Ge_3(c), and $Cr_{11}Ge_{19}$(c).

The high-temperature equilibrium results of Hager and Elliott[169] lead to $\Delta H_f°$ = −32 kcal mol^{-1}, $\Delta G_f°$ = −33 kcal mol^{-1}, and $S°$ = 17 cal K^{-1} mol^{-1} for CrS(c). For CrS(g) we have $\Delta H_f° \simeq$ 83 kcal mol^{-1} from Drowart et al.[170] We estimate $S°$ = (60) cal K^{-1} mol^{-1} and then obtain $\Delta G_f° \simeq$ 69 kcal for CrS(g).

The entropies listed in NBS 270-4 and in our Table I for Cr_2Te_3(c), Cr_3Te_4(c), and Cr_5Te_6(c) are consistent with the C_p results of Grønwold and Westrum.[171] We also note that Grønwold[172] has reported high-temperature C_p and related properties for Cr_3Te_4(c).

The NBS 270-4 has listed $\Delta H_f°$ = −257.4 kcal mol^{-1} for $Cr(CO)_6$(c), which is exactly the same as the value we calculate from the combustion results of Cotton, Fischer, and Wilkinson[173] and $\Delta H_f°$ = −272.4 kcal mol^{-1} for Cr_2O_3(c) from NBS 270-4 and our Table I. More recently, Skinner and Virmani[174] have made calorimetric measurements on decomposition of $Cr(CO)_6$(c) to Cr(c) and CO(g) and have obtained $\Delta H_f°$ = −223.5 kcal mol^{-1} for $Cr(CO)_6$(c). Similar measurements by Connor, Skinner, and Virmani[175] have led to $\Delta H_f°$ = −222.9 kcal mol^{-1} for $Cr(CO)_6$(c). These latter workers have also made calorimetric measurements on the iodination of $Cr(CO)_6$(c). Combination of their results with $\Delta H_f°$ values already adopted here for CrI_2(c) and CrI_3(c) leads to $\Delta H_f°$ = −234.3 kcal mol^{-1} for $Cr(CO)_6$(c). In the absence of any clear indication as to which of the results cited here is best, we hesitantly adopt $\Delta H_f°$ = −234 kcal mol^{-1} (based on iodination measurements[175]) for $Cr(CO)_6$(c).

The $\Delta H_f°$ values listed in NBS 270-4 correspond to $\Delta H°$ = 17.0 kcal mol^{-1} for sublimation of $Cr(CO)_6$(c). This value is consistent with vapor pressure results cited by Cotton et al.[173] and also with more recent results.[176] We use this value with the $\Delta H_f°$ above for $Cr(CO)_6$(c) to obtain $\Delta H_f°$ = −217 kcal mol^{-1} for $Cr(CO)_6$(g). Statistical calculations have led to $S°$ = 116.5 cal K^{-1} mol^{-1} (ref 177) and to an apparently better $S°$ = 111.6 cal K^{-1} mol^{-1} (ref 178) for $Cr(CO)_6$(g). We adopt the latter value and combine with the $\Delta H_f°$ of $Cr(CO)_6$(g) to obtain its $\Delta G_f°$ = −202 kcal mol^{-1}.

The vapor pressure results cited above are also consistent with $\Delta S° = 40$ cal K^{-1} mol^{-1} for sublimation of $Cr(CO)_6(c)$ at 298 K. Combination of this $\Delta S°$ with our adopted $S°$ for $Cr(CO)_6(g)$ leads to $S° = 72$ cal K^{-1} mol^{-1} for $Cr(CO)_6(c)$, for which a value based on C_p measurements would be useful. Combination of this value with the $\Delta H_f°$ adopted above leads to $\Delta G_f° = -207$ kcal mol^{-1} for $Cr(CO)_6(c)$.

Calorimetric measurements by Brown, Connor, and Skinner[179] lead to $\Delta H_f° = -1446.4$ kcal mol^{-1} for $Cr(PF_3)_6(c)$, based on $\Delta H_f° = -228.89$ kcal mol^{-1} for $PF_3(g)$.

G. Organic Compounds and Complexes

Thermochemical properties of a few organochromium compounds have been reviewed by Cox and Pilcher[180] and also by Ashcroft and Mortimer.[181] These latter authors[181] and also Martell[75,112] have reviewed stabilities and other thermodynamic properties of organic complexes of Cr(III) in aqueous solution. In our present review we limit discussion of organic compounds of chromium to brief mention of some recent investigations that have not been cited in these earlier reviews.[75,112,180,181]

Before citing particular investigations, it is important to emphasize that comparisons of quantities reported in original papers or quantities listed in various reviews must be based on the same auxiliary data in order to be useful. For example, enthalpies of formation of organochromium compounds derived from combustion measurements must be based on the same $\Delta H_f°$ of formation of $Cr_2O_3(c)$.

Connor, Skinner, and Virmani[182] have made calorimetric measurements leading to $\Delta H_f°$ values for $Cr(C_6H_6)_2$, $Cr(C_6H_6)(CO)_3$, $Cr[C_6(CH_3)_6](CO)_3$, $Cr(C_6H_6)_2I$, $Cr(c\text{-}C_7H_8)(CO)_3$, and $Cr(C_6H_5CH_3)(CO)_3$.

Calorimetric measurements by Bradley and Hillyer[183] lead to $\Delta H_f°$ of $Cr(OC_4H_9)_4$.

Tel'noi et al.[184] have determined heats of combustion of $Cr(C_6H_6)_2$, $Cr(C_6H_6)_2Cl$, $Cr(C_6H_6)_2Br$, $Cr(C_6H_5CH_3)_2I$, $Cr[C_6H_4(CH_3)_2]_2I$, and $Cr(C_6H_5C_6H_5)_2I$.

Sorai, Tachiki, Suga, and Seki[185] have made C_p measurements on $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl{\cdot}6H_2O(c)$ from 1.5 to 280 K. Sorai and Seki[186] have made C_p measurements from 1.4 to 200 K on $[Cr_4(OH)_6(en)_6](SO_4)_3{\cdot}10H_2O(c)$.

Andrews, Westrum, and Bjerrum[187] have determined C_p from 5 to 350 K and vapor pressures over a range of temperature for $Cr(C_6H_6)_2$. They have calculated $S°$ values and the thermodynamics of vaporization.

Hill and Irving[188] have made solution calorimetric measurements leading to $\Delta H_f°$ of tris(acetylacetonato)chromium(III). Melia and Merrifield[189] have made C_p measurements on this compound from 80 to 300 K and also evaluated the enthalpy of vaporization. Fontaine, Pommier, and Guiochon[190] have reported enthalpies of vaporization of this compound and some derivative compounds.

III. Molybdenum and Tungsten

A. Descriptive Chemistry

Compounds and ions containing molybdenum or tungsten in oxidation states ranging from −2 to +6 are known. In general, compounds and ions containing Mo(VI) or W(VI) are more stable (weaker oxidizing agents) than corresponding Cr(VI) species. There is a much greater tendency for Mo(VI) and W(VI) toward formation of polynuclear species than there is for Cr(VI) for which such reactions ordinarily stop at dichromate. Similarly, the important species of lower oxidation states of molybdenum and tungsten are often more complex than those of chromium in the same oxidation state. In contrast to Cr(III), there are relatively few stable complexes of Mo(III) and W(III).

Cotton and Wilkinson[20] have recently summarized several aspects of the chemistry of molybdenum and tungsten, with particular emphasis on structures of various compounds and ions. Here we will focus on identification of aqueous species and qualitative statements about stabilities that will furnish background appropriate to further discussion of thermodynamic and electrochemical equilibria involving aqueous solutions.

Most molybdenum is obtained from molybdenite, MoS_2, although some is obtained from various molybdates. Tungsten is found in nature chiefly as tungstates of iron, calcium, and a few other metals.

The oxides MoO_3 and WO_3 react at high temperatures with various metal oxides to form corresponding molybdates and tungstates. Both oxides dissolve (WO_3 only slowly at room temperature) in aqueous alkali to yield aqueous molybdate and tungstate ions represented by $MoO_4^{2-}(aq)$ and $WO_4^{2-}(aq)$. These ions have been shown to be tetrahedral (slightly distorted in some compounds) in the solid state[20] and also in aqueous solution.[191] Normal solid molybdates and tungstates can be crystallized from neutral or alkaline solutions. Molybdates and tungstates of the alkali metals and ammonium ion are quite soluble in water, while those of most other metals are only slightly soluble.

The solid isopoly compounds that may be obtained from acidified solutions of molybdates and tungstates are varied and complicated. Structures of several have been determined.[20] Examples of isopoly ions that are well characterized in the solid state are the "paramolybdate" $Mo_7O_{24}^{6-}$ and the "octamolybdate" $Mo_8O_{26}^{4-}$.

When alkaline solutions containing $MoO_4^{2-}(aq)$ or $WO_4^{2-}(aq)$ are acidified under such conditions that no precipitate forms, various condensation reactions take place to yield species that are still inadequately characterized after a large number of investigations employing a variety of experimental methods. Among the aqueous isopoly species that have been postulated are $Mo_3O_{11}^{4-}$, $HMo_3O_{11}^{3-}$, $Mo_4O_{13}^{2-}$, $H_nMo_6O_{20}^{-4+n}$, $H_nMo_6O_{21}^{-6+n}$, various ions related to paramolybdate and octamolybdate above, and still larger ions involving 12 and 24 Mo with various numbers of hydrogen and oxygen atoms per ion. Because of uncertain identifications of the various aqueous species and the absence of activity coefficients for these highly charged ions, all numerical values of equilibrium "constants" or "quotients" involving isopoly species are open to question.

Acidification of molybdate or tungstate solutions can also lead to precipitation of $MO_3{\cdot}nH_2O$ compounds that are commonly called molybdic acid and tungstic acid.

Heteropoly ions and solids are obtained when molybdate and tungstate solutions that also contain other oxo ions (such as PO_4^{3-}) or certain metal ions are acidified. The acids and most salts of heteropoly anions are quite soluble in water and also in many polar organic solvents. Structures and formulas of a number of heteropoly anions have been reviewed by Cotton and Wilkinson.[20] Results of some structural studies have proven useful in connection with studies of aqueous solutions cited later.

Connor and Ebsworth[19] have reviewed the chemistry of peroxy compounds of molybdenum and tungsten, all apparently derived from the +6 oxidation state. Salts prepared by action of excess H_2O_2 on normal molybdates appear to contain four peroxy groups per atom of molybdenum. It seems likely that the $Mo(O_2)_4^{2-}$ ion exists in the solid state and that either this ion or its hydrolysis products exist in aqueous solutions. Many compounds containing fewer than four peroxy groups per Mo (or W) have been reported.

The sulfides MoS_3 and WS_3, various thiomolybdates, and thiotungstates can be precipitated from aqueous solutions. Although these compounds are important in analytical chemistry, solid state science, and heterogeneous catalysis, we have few quantitative data to cite later in this review.

There are several hexahalides and oxyhalides of formulas MX_6, MOX_4, and MO_2X_2. There is also the volatile compound that has been described as $MoO_3{\cdot}2HCl$ or $MoO_2Cl_2{\cdot}H_2O$ or (probably most realistically) $MoO(OH)_2Cl_2$.

Reduction of Mo(VI) and W(VI) compounds or aqueous ions can lead to a large number of compounds or aqueous species, many of which have been described by Cotton and Wilkinson.[20] We shall later cite thermodynamic data for some of these compounds (especially binary compounds with oxygen, sulfur, and halogens) and also potentials that relate various aqueous species.

High-temperature reduction of alkali metal tungstates with hydrogen or reaction of alkali metals with WO_3 leads to "tungsten bronzes" that have semimetallic properties. These substances are mostly unreactive toward water and aqueous solutions, but some are readily oxidized by Ag^+(aq) and other oxidizing agents in acidic solution and by O_2 in alkaline solution. Similar "bronzes" of molybdenum and other metals are less well known, but do exist.

The interest in complexes formed between Mo(VI) [also W(VI)] and organic ligands is partly due to the fact that molybdenum is an essential element in various biological systems. Of particular interest is the role of molybdenum in the fixation of nitrogen by some bacteria commonly associated with legumes. Cotton and Wilkinson[20] have provided a useful introduction with leading references to this important subject.

B. Molybdenum, Molybdenum Oxides, and Molybdic Acid

As for chromium, the best general source of thermodynamic data for molybdenum and its compounds and ions is NBS 270-4. From this source we have $\Delta H_f° = 0$, $\Delta G_f° = 0$, and $S° = 6.85$ cal K^{-1} mol^{-1} for Mo(c) as listed in our Table IV. This entropy is in good agreement with the value derived by Kelley and King[22] from C_p data and is in still better agreement with the value in the JANAF tables[151] calculated from the same experimental results.

For Mo(g) we have $S° = 43.461$ cal K^{-1} mol^{-1} in NBS 270-4, a value in good agreement with earlier statistical calculations.[22,151] The $\Delta H_f° = 157.3$ kcal mol^{-1} in NBS 270-4 for Mo(g) is the same as the value in the JANAF tables,[151] based on high temperature vapor pressure data. This value, which we adopt for our Table IV, is also in satisfactory agreement with the more recent results of Koch and Anable.[192] Combination of $\Delta H_f°$ and $S°$ leads to the tabulated $\Delta G_f° = 146.4$ kcal mol^{-1} for Mo(g).

Earlier investigations of the high-temperature thermodynamic properties of Mo(c) and Mo(liq) have been reviewed in the JANAF tables.[151] Here we call attention to four recent investigations[193] of C_p, $(H°_T - H°_{298})$, and related thermodynamic properties up to nearly 3000 K.

Now we consider the oxides of molybdenum, progressing from MoO to MoO_3.

The NBS 270-4 lists $\Delta H_f° = 101$ kcal mol^{-1} for MoO(g). Our calculations with the results of DeMaria et al.[194] are in agreement with those summarized in the JANAF tables,[151] leading to our adopted $\Delta H_f° \simeq 93$ kcal mol^{-1} as listed in Table IV. The uncertainty in this value is large enough to overlap the value listed in NBS 270-4. We take $S° = (57)$ cal K^{-1} mol^{-1} from the JANAF tables[151] and calculate $\Delta G_f° \simeq 85$ kcal mol^{-1} for MoO(g).

Combustion calorimetry measurements by Staskiewicz, Tucker, and Snyder[195] and also by Mah[196] have led to $\Delta H_f° = -140.86$ and -140.64 kcal mol^{-1} for MoO_2(c). We adopt a mean value, $\Delta H_f° = -140.76$ kcal mol^{-1}, which is also the value listed in NBS 270-4. The JANAF tables[151] list $\Delta H_f° = -140.5$ kcal mol^{-1}, based on these results[195,196] and others that we consider to have sufficiently large uncertainties that it is now better to adopt $\Delta H_f° = -140.76$ kcal mol^{-1} as given above. We also note that some recent high-temperature emf results[197] lead to a calculated $\Delta H_f° = -139.6$ kcal mol^{-1} for this compound.

We adopt $S° = 11.06$ cal K^{-1} mol^{-1} for MoO_2(c) as listed in NBS 270-4 and also by Kelley and King,[22] based on C_p values down to 50 K and an extrapolation to absolute zero. It has been pointed out[151] that there is a possibility of "extra" entropy that might justify a higher value of $S° = 11.95$ cal K^{-1} mol^{-1} for MoO_2(c). In the absence of needed C_p measurements at $T < 50$ K, we continue to use the first $S°$ cited above.

The NBS 270-4 lists $\Delta H_f° = 3$ kcal mol^{-1} for MoO_2(g), which is consistent with the results of two investigations.[194,198] We also adopt $S° = (66)$ cal K^{-1} mol^{-1} from the JANAF tables[151] and calculate $\Delta G_f° \simeq 0$ kcal mol^{-1} for MoO_2(g).

Syntheses, heat capacities, and emf results have been reported[199] for solids with compositions MoO_n $(2 < n < 3)$.

Combustion calorimetry measurements by Staskiewicz, Tucker, and Snyder[195] and by Mah[196] have led to $\Delta H_f° = -178.01$ and -178.16 kcal mol^{-1} for MoO_3(c). We adopt the mean value, $\Delta H_f° = -178.08$ kcal mol^{-1}, which has also been adopted in NBS 270-4. Heat capacity measurements cited by Kelley and King[22] lead to $S° = 18.58$ cal K^{-1} mol^{-1} and thence by combination with the $\Delta H_f°$ to $\Delta G_f° = -159.66$ kcal mol^{-1} as also listed in NBS 270-4. Some high-temperature properties of MoO_3(c) and MoO_3(liq) have been reported.[199,200]

We note that Kirshenbaum and Beardell[201] have made DTA measurements leading to ΔH values for various reactions involving MoO_2, MoO_3, and Mo with other metals and their oxides. These reported ΔH values are in generally poor agreement with values calculated from $\Delta H_f°$ values. The calculated quantities appear to be preferable.

Several investigators[194,198,202-204] have made high-temperature measurements leading to data for $(MoO_3)_n$(g) species. On the basis of their results, we adopt the uncertain thermodynamic properties listed in Table IV.

The NBS 270-4 has listed $\Delta H_f° = -250.0$ kcal mol^{-1} for H_2MoO_4(c), which is sometimes called "molybdic acid" and has also been represented as $MoO_3{\cdot}H_2O$(c). This value, which we adopt, is exactly consistent with the calorimetric results of Graham and Hepler.[205] We estimate $S° = (29)$ cal K^{-1} mol^{-1} and combine with the $\Delta H_f°$ to obtain $\Delta G_f° = -218.1$ kcal mol^{-1} for H_2MoO_4(c). This free energy is consistent with the experience that H_2MoO_4(c) is stable with respect to MoO_3(c) and H_2O(liq) near 298 K. We also use the $\Delta G_f°$ to calculate that the equilibrium vapor pressure of H_2O(g) over H_2MoO_4(c) and MoO_3(c) is ~1 mmHg. In the absence[205] of reliable vapor pressure data, all we can say is that this calculated value seems "reasonable".

As previously discussed,[205] the results of Pechard and of Hüttig and Kurre, who may have worked with "$MoO_3{\cdot}2H_2O$" or "$H_2MoO_4{\cdot}H_2O$", are not sufficiently reliable to justify tabulating properties for this substance.

The NBS 270-4 lists $\Delta H_f° = -212$ kcal mol^{-1} for H_2MoO_4(g), while the JANAF tables[151] list $\Delta H_f° = -203.4$ kcal mol^{-1}. Our assessment of the experimental results (cited in the JANAF tables[151]) leads us to adopt $\Delta H_f° = -203$ kcal mol^{-1} and combine with an estimated[151] $S° = (85)$ cal K^{-1} mol^{-1} to obtain $\Delta G_f° = -188$ kcal mol^{-1} for H_2MoO_4(g).

C. MoO_4^{2-}(aq) and Molybdates

Calorimetric measurements of the enthalpy of reaction of

TABLE IV.[a] **Thermodynamic Properties of Molybdenum Compounds at 298 K**

Compound	$\Delta H_f°$ kcal mol^{-1}	$\Delta G_f°$ kcal mol^{-1}	$S°$ cal K^{-1} mol^{-1}
Mo(c)	$\mathit{0}$	$\mathit{0}$	$\mathit{6.85}^{22,151}$
Mo(g)	$\mathit{157.3}^{151,192}$	$\mathit{146.4}$	$\mathit{43.461}^{22,151}$
Mo^{+}(g)	$\mathit{322.5}$		
Mo^{2+}(g)	$\mathit{696.5}$		
Mo^{3+}(g)	$\mathit{1323.8}$		
Mo^{4+}(g)	$\mathit{2395.2}$		
Mo^{5+}(g)	$\mathit{3807.2}$		
Mo^{6+}(g)	$\mathit{5378}$		
Mo^{7+}(g)	$\mathit{8298}$		
Mo^{8+}(g)	$\mathit{11\,830}$		
MoO(g)	$\sim 93^{151,194}$	~ 85	$(57)^{151}$
MoO_2(c)	$-\mathit{140.76}^{195,196}$	$-\mathit{127.40}$	$\mathit{11.06}^{22}$
MoO_2(g)	$\sim \mathit{3}^{194,198}$	~ 0	$(66)^{151}$
MoO_3(c)	$-\mathit{178.08}^{195,196}$	$-\mathit{159.66}$	$\mathit{18.58}^{22}$
MoO_3(g)	$\sim -85^{194,198,202}$	~ -81	$(67)^{151}$
$(MoO_3)_2$(g)	$\sim -281^{198,203,204}$		
$(MoO_3)_3$(g)	$\sim -460^{198,203,204}$		
$(MoO_3)_4$(g)	$\sim -626^{203,204}$		
$(MoO_3)_5$(g)	$\sim -791^{203,204}$		
H_2MoO_4(c)	$-\mathit{250.0}^{205}$	$-218._{1}$	(29)
H_2MoO_4(g)	-203^{151}	-188	$(85)^{151}$
MoO_4^{2-}(aq)	$-238.3^{205,206}$	-200.4	9
Li_2MoO_4(c)	-363.3^{209}	-337.1^{209}	$(31)^{209}$
Li_2MoO_4(g)	$\sim -244^{217}$		
Na_2MoO_4(c)	$-350.8^{205,215}$	-323.6	38.1^{210}
$Na_2MoO_4 \cdot 2H_2O$(c)		-437.3^{216}	
$Na_2Mo_2O_7$(c)	-536.6^{215}	-492.0	59.9^{218a}
K_2MoO_4(c)	-358.0^{219}	-331.0	$(45)^{209}$
K_2MoO_4(g)	-272^{220}		
$KHMoO_4$(g)	-242^{220}		
Rb_2MoO_4(c)	-357.0^{206}	-331.5	$(56)^{206}$
Cs_2MoO_4(c)	-362.0^{207}	-336.3	59.35^{221}
Cs_2MoO_4(g)	-293^{209}		
$BeMoO_4$(c)	$\sim -330^{73}$		
$MgMoO_4$(c)	-334.8_{2}^{211}	-309.7_{0}	$\mathit{28.4}^{210}$
$MgMoO_4$(g)	$\sim -\mathit{224}^{222}$		
$CaMoO_4$(c)	-369.5^{211}	-344.0	$\mathit{29.3}^{210}$
$CaMoO_4$(ppt)	-367.3^{212}	-341.8	(29.3)
$CaMoO_4$(g)	-225^{222}		
$SrMoO_4$(c)	-369	$-343._{1}^{209}$	(32)
$SrMoO_4$(g)	$\sim -249^{222}$		
$BaMoO_4$(c,ppt)	-369.4^{213}	-344.0	$34._{5}^{213}$
$BaMoO_4$(g)	$\sim -242^{223}$		
Ag_2MoO_4(c)	-200.6^{224}	$-179.4^{209,224}$	$54._{2}$
Tl_2MoO_4(c)		-226.8^{79}	
$MnMoO_4$(c)	-284.7_{6}^{225}		
$FeMoO_4$(c)	$-\mathit{257}$	$-\mathit{233}$	$\mathit{30.9}^{227}$
$PbMoO_4$(c)			$\mathit{39.7}^{228}$
$Mo_7O_{24}^{6-}$(aq)	-1451^{233}	-1255^{233}	72^{233}
MoF_5(c)	$-331._{5}^{244}$		
MoF_5(g)			78.3^{245}
MoF_6(liq)	$-378.92^{237,240,241}$	-352.05	$\mathit{62.06}^{237,240}$
MoF_6(g)	$-\mathit{372.29}^{241}$	$-\mathit{351.88}$	$\mathit{83.75}^{237,238}$
$MoOF_4$(c)	$-329._{8}^{244}$		
MoO_2F_2(g)	-268^{248}		
$MoCl_2$(c)	-68^{249}	-59	$(30)^{249}$
$MoCl_3$(c)	$-96._{7}^{249,251}$	-83	$(41)^{249}$
$MoCl_4$(c)	-114^{249}	-96	$(53)^{151}$
$MoCl_4$(g)	$-92^{249,250}$	-85	$(89)^{151}$
$MoCl_5$(c)	$-\mathit{126}^{249}$	-101	$(57)^{151}$
$MoCl_5$(g)	$-107^{151,249}$	-94	$(95)^{151}$
$MoOCl_2$(c)	$-126._{2}^{250}$	-110	$(31)^{250}$
$MoOCl_3$(c)	$-150._{7}^{251}$	-130	$(42)^{251}$
$MoOCl_3$(g)	$-123._{1}^{251}$	-116	$(88)^{251}$
$MoOCl_4$(c)	$-157._{6}^{249,251}$	-133	$(55)^{251}$
$MoOCl_4$(g)	$-140._{3}^{251}$	-126	$(91)^{251}$
MoO_2Cl_2(c)	$-170._{5}^{252}$	-148	(33)
MoO_2Cl_2(g)	$-150._{4}^{254,255}$	-142	$(82)^{151,254}$
$MoO_2Cl_2 \cdot H_2O$(c)	-245.9^{252}	-210	(43)
$MoBr_2$(c)	$-51._{0}^{257,258}$	-48	$(33)^{258}$
$MoBr_2$(g)	$-20._{8}^{258}$	-24	$(53)^{258}$
$MoBr_3$(c)	$-62._{7}^{257,258}$	-60	$(52)^{258}$
$MoBr_4$(c)	$-70._{4}^{259}$	-68	(70)
$MoBr_4$(g)	$-36._{7}^{258}$	-46	$(110)^{258}$
$MoOBr_3$(c)	$-111._{2}^{261}$	-99	$(45)^{261}$
$MoOBr_3$(g)	$-75._{2}^{261}$	-80	$(101)^{261}$
MoO_2Br_2(c)	$-152._{3}^{254,260}$	-135	$(34)^{254}$
MoO_2Br_2(g)	$-126._{4}^{254}$	-125	$(86)^{254}$
MoI_2(c)	$(-25._{5})^{262,263}$		
MoI_2(g)	$\mathit{32}^{264}$		
MoI_3(c)	$-27._{0}^{262,263}$		
MoO_2I_2(g)	$\sim -100^{265}$	~ -101	$(86)^{265}$
$CaMoO_3$(c)	$-296^{266a,b}$		
$SrMoO_3$(c)	$-\mathit{306}^{267}$		
$SrMoO_3$(g)	$\sim -141^{222}$		
$BaMoO_3$(c)	$-\mathit{295}^{213}$		
$BaMoO_3$(g)	$\sim -156^{223}$		
MoS_2(c)	-65.8^{270}	-63.7	$\mathit{14.96}^{268}$
Mo_2S_3(c)	$\sim -97^{270}$		
Mo_2N(c)	$-\mathit{19.5}^{164}$		
MoC(c)	$-\mathit{2.4}\ (?)^{273}$		
Mo_2C(c)	$-\mathit{10.9}^{273}$	-11.1	15.74^{274}
$MoSi_2$(c)	$-31._{5}^{166}$	$-31._{7}$	16.2^{166}
Mo_3Si(c)	$-27._{8}^{166}$	$-27._{7}$	$\mathit{25.4}^{166}$
Mo_5Si_3(c)	$-74._{1}^{166}$	$-74._{7}$	49.6^{166}
Mo_3Ge(c)	$-\mathit{5}^{276}$		
$KMoF_6$(c)	-496^{282}		
$RbMoF_6$(c)	-498^{282}		
$CsMoF_6$(c)	-500^{282}		
Na_2MoCl_6(c)	-328^{284}		
K_2MoCl_6(c)	-350^{284}		
$Mo(CO)_6$(c)	-236.5^{262}	-211.5	$78.0^{22,291}$
$Mo(CO)_6$(g)	$-219.7^{173,290}$	-206.5	117.8^{290}

[a] Italicized values agree with values in NBS 270-4 or NBS 270-6. Values in parentheses are estimates.

MoO_3(c) with excess OH^-(aq) by Graham and Hepler[205] and by O'Hare and Hoekstra[206] both lead to $\Delta H_f° = -238.3$ kcal mol^{-1} for MoO_4^{2-}(aq). This value, which we adopt for our Table IV, is in good agreement with earlier results of O'Hare and Hoekstra[207] and is 0.2 kcal mol^{-1} less negative than the value listed in NBS 270-4.

The NBS 270-4 lists $\Delta G_f° = -199.0$ kcal mol^{-1} and $S° = 6.5$ cal K^{-1} mol^{-1} for MoO_4^{2-}(aq). Hepler[208] has calculated $\Delta G_f° = -200.9$ kcal mol^{-1} and $S° = 11 \pm 2$ cal K^{-1} mol^{-1} for this ion. Most recently, O'Hare, Jensen, and Hoekstra[209] have selected $\Delta G_f° = -200.0 \pm 0.3$ kcal mol^{-1} for MoO_4^{2-}(aq), which corresponds to $S° = 7.6$ cal K^{-1} mol^{-1}. We adopt $\Delta G_f° = -200.4$ kcal mol^{-1} and $S° = 9$ cal K^{-1} mol^{-1} for MoO_4^{2-}(aq) on the basis of our new calculations that are described below in connection with various molybdates. This adopted $\Delta G_f°$ corresponds to the following potential:

$$MoO_4^{2-}(aq) + 4H_2O(liq) + 6e^- = Mo(c) + 8OH^-(aq)$$

$$E° = -0.913 \text{ V}$$

The NBS 270-6 lists $S° = 29.3$ cal K^{-1} mol^{-1} for $CaMoO_4$(c), as calculated by Weller and King[210] from results of their C_p measurements. Calorimetric measurements by Barany[211] have provided a $\Delta H°$ of reaction that leads to $\Delta H_f° = -369.5$ kcal mol^{-1} for $CaMoO_4$(c). We emphasize that their "$CaMoO_4$(c)" was well-defined crystalline material. Muldrow and Hepler[212] have made calorimetric measurements leading to the enthalpy of precipitation and thence to $\Delta H_f° = -367.3$ kcal mol^{-1} for material we designate $CaMoO_4$(ppt). The NBS

270-6 has listed the mean value $\Delta H_f° = -368.4$ kcal mol^{-1} for $CaMoO_4$(c), but we believe it is better to regard the crystalline material denoted by (c) and the precipitated material denoted by (ppt) as different substances and therefore list both experimental $\Delta H_f°$ values[211,212] cited above in our Table IV.

Combination of the $S°$ from Weller and King[210] with the $\Delta H_f°$ from Barany[211] leads to $\Delta G_f° = -344.0$ kcal mol^{-1} for $CaMoO_4$(c), which is the value we adopt for crystalline calcium molybdate. We have no third law entropy for precipitated calcium molybdate, but estimate that is is the same as for $CaMoO_4$(c) and combine this value with the $\Delta H_f°$ from the enthalpy of precipitation[212] to obtain $\Delta G_f° = -341.8$ kcal mol^{-1} for $CaMoO_4$(ppt).

Graham and Hepler[205] have calculated $K_{sp} \simeq 1 \times 10^{-8}$ from older solubility data for calcium molybdate, while O'Hare, Jensen, and Hoekstra[209] have cited $K_{sp} = 3.16 \times 10^{-9}$ from more recent work. These K_{sp} values correspond to $\Delta G° = 10.9$ and 11.6 kcal mol^{-1} for the reaction represented by

$$CaMoO_4(\text{solid}) = Ca^{2+}(aq) + MoO_4^{2-}(aq)$$

in which $CaMoO_4$(solid) might refer to either $CaMoO_4$(c) or $CaMoO_4$(ppt). We now describe two extreme calculations. Using the larger K_{sp} and the $\Delta G_f°$ for $CaMoO_4$(c), we obtain $\Delta G_f° = -200.8$ kcal mol^{-1} for MoO_4^{2-}(aq) and thence $S° = 10.3$ cal K^{-1} mol^{-1} for this ion. Using the smaller K_{sp} and the $\Delta G_f°$ for $CaMoO_4$(ppt) leads to $\Delta G_f° = -197.9$ kcal mol^{-1} and $S° = 0.5$ cal K^{-1} mol^{-1} for MoO_4^{2-}(aq). Other combinations lead to $\Delta G_f°$ and $S°$ values intermediate between the values just quoted here.

The more negative $\Delta G_f°$ and more positive $S°$ values above are most nearly consistent with other values we report below.

O'Hare[213] has made calorimetric measurements leading to the enthalpy of precipitation of barium molybdate, with considerable attention paid to experimental conditions in an effort to make the resulting $\Delta H_f° = -369.4$ kcal mol^{-1} apply to $BaMoO_4$(c). O'Hare[213] has cited $S° = 34.5 \pm 1.5$ cal K^{-1} mol^{-1} for this substance and we calculate its $\Delta G_f° = -344.0$ kcal mol^{-1}. O'Hare[213] has also cited two older (1891 and 1953) investigations that are in good agreement with $K_{sp} = 3.6 \times 10^{-8}$ for barium molybdate. More recent measurements by Jost[214] lead to $K_{sp} = 3.16 \times 10^{-9}$. These K_{sp} values correspond to $\Delta G° = 10.1_5$ and 11.5_9 kcal mol^{-1} for the solution reaction. The larger K_{sp} in combination with the $\Delta G_f°$ of $BaMoO_4$(c) above leads to $\Delta G_f° = -199.8$ kcal mol^{-1} and $S° = 7.0$ cal K^{-1} mol^{-1} for MoO_4^{2-}(aq), while the smaller K_{sp} leads to $\Delta G_f° = -198.4$ kcal mol^{-1} and $S° = 2.3$ cal K^{-1} mol^{-1} for this ion. If, by analogy with calcium molybdate, we assume that the $\Delta H_f°$ and $\Delta G_f°$ values for "truly crystalline" barium molybdate are more negative than the corresponding values for the precipitated substance, then we obtain a more negative $\Delta G_f°$ and a more postive $S°$ for MoO_4^{2-}(aq).

Graham and Hepler[205] and Koehler, Pankratz, and Barany[215] have made calorimetric measurements that have led to reported values for $\Delta H_f°$ of Na_2MoO_4(c) in good agreement with each other. Recalculation of their[205,215] results in terms of the NBS 270-3 auxiliary data and properties already cited in this review leads us now to $\Delta H_f° = -350.8$ kcal mol^{-1} for Na_2MoO_4(c). We combine this value with $S° = 38.1$ cal K^{-1} mol^{-1} for Na_2MoO_4(c) from Weller and King[210] to obtain $\Delta G_f° = -323.6$ kcal mol^{-1} for this compound. Zhidikova et al.[216] have determined the activity of sodium molybdate and water in saturated solution in equilibrium with $Na_2MoO_4 \cdot 2H_2O$(c), and also the vapor pressure of H_2O(g) in equilibrium with Na_2MoO_4(c) and $Na_2MoO_4 \cdot 2H_2O$(c). Combination of all these results with the $\Delta G_f°$ above for Na_2MoO_4(c) leads to $\Delta G_f° = -437.3$ kcal mol^{-1} for $Na_2MoO_4 \cdot 2H_2O$(c), to $\Delta G_f° = -200.0$ kcal mol^{-1} for MoO_4^{2-}(aq), and to $S° = 7.8$ cal K^{-1} mol^{-1} for this ion.

Consideration of uncertainties associated with the various $\Delta G_f°$ and $S°$ values for MoO_4^{2-}(aq) has led us to the "best" values cited earlier in this section and listed in our Table IV. Our $\Delta G_f°$ value is slightly more negative than the values listed in NBS 270-4 and calculated by O'Hare, Jensen, and Hoekstra.[209] Our $S°$ is correspondingly larger than their values. We note that the second path cited by O'Hare, Jensen, and Hoekstra[209] (their Table 5) is partly based on an estimated entropy, that their fourth path involving Ag_2MoO_4(c) is itself based on a prior selection of $\Delta G_f°$ of MoO_4^{2-}(aq), and that the uncertainty in their fifth path is sufficient to make it agree with all the values that have been cited.

For Li_2MoO_4(c) we adopt $\Delta H_f° = -363.3$ kcal mol^{-1} from the calorimetric results of O'Hare, Jensen, and Hoekstra[209] and the properties of LiOH(aq) cited by O'Hare et al.[209] We agree with their[209] conclusion that the results of an earlier investigation are erroneous. Combination of an estimated[209] $S° = (31)$ cal K^{-1} mol^{-1} with this $\Delta H_f°$ leads to $\Delta G_f° = -337.1$ kcal mol^{-1} for Li_2MoO_4(c).

Yamdagni, Pupp, and Porter[217] have made high-temperature mass spectral investigations of the dissociation of Li_2MoO_4(g) and have calculated its $\Delta H_f° \simeq -244$ kcal mol^{-1}. They have also determined the $\Delta H°$ of vaporization of Li_2MoO_4(liq), but absence of $(H_T - H_{298})$ data for the Li_2MoO_4(c and liq) prevents us from using this result with the above $\Delta H_f°$ of Li_2MoO_4(c) to obtain another value of $\Delta H_f°$ for Li_2MoO_4(g).

We have already cited data for Na_2MoO_4(c) and $Na_2MoO_4 \cdot 2H_2O$(c) in connection with the properties of MoO_4^{2-}(aq). Here we note that there have also been high-temperature investigations[218] of Na_2MoO_4–MoO_3 mixtures.

Recalculation (using the most recent auxiliary data) of the calorimetric results of Koehler, Pankratz, and Barany[215] leads to $\Delta H_f° = -536.6$ kcal mol^{-1} for $Na_2Mo_2O_7$(c). We take $S° = 59.9$ cal K^{-1} mol^{-1} from Weller and Kelley[218a] and calculate $\Delta G_f° = -492.0$ kcal mol^{-1} for $Na_2Mo_2O_7$(c).

The calorimetric results of Nelson, Moss, and Hepler[219] lead to $\Delta H_f° = -358.0$ kcal mol^{-1} for K_2MoO_4(c). O'Hare et al.[209] have estimated $S° = (45)$ cal K^{-1} mol^{-1}, which leads to $\Delta G_f° = -331.0$ kcal mol^{-1} for K_2MoO_4(c). High-temperature measurements by Farber and Srivastava[220] have provided $\Delta H°$ values that lead us to $\Delta H_f° = -272$ kcal mol^{-1} for K_2MoO_4(g) and $\Delta H_f° = -242$ kcal mol^{-1} for $KHMoO_4$(g).

Recent calorimetric measurements by O'Hare and Hoekstra[206] in combination with properties of RbOH(aq) cited by these authors lead to $\Delta H_f° = -357.0$ kcal mol^{-1} for Rb_2MoO_4(c). Combination of the estimated[206] $S° = (56)$ cal K^{-1} mol^{-1} with this $\Delta H_f°$ leads to $\Delta G_f° = -331.5$ kcal mol^{-1} for Rb_2MoO_4(c).

Calorimetric measurements by O'Hare and Hoekstra[207] in combination with properties of CsOH(aq) cited by them lead to $\Delta H_f° = -362.0$ kcal mol^{-1} for Cs_2MoO_4(c). We also have $S° = 59.35$ cal K^{-1} mol^{-1} for Cs_2MoO_4(c) from the heat capacity measurements of Osborne, Flotow, and Hoekstra.[221] The $\Delta H_f°$ and $S°$ above lead to $\Delta G_f° = -336.3$ kcal mol^{-1} for this compound.

The enthalpy of sublimation of Cs_2MoO_4(c) cited by O'Hare et al.[209] leads to $\Delta H_f° = -293$ kcal mol^{-1} for Cs_2MoO_4(g).

Old measurements cited in NBS Circular 500[73] lead to $\Delta H_f° \simeq -330$ kcal mol^{-1} for $BeMoO_4$(c).

Calorimetric results from Barany[211] lead us to $\Delta H_f° = -334.8_2$ kcal mol^{-1} for $MgMoO_4$(c), in agreement with the value in NBS 270-6. The $S° = 28.4$ cal K^{-1} mol^{-1} for this compound that is listed in NBS 270-6 is the same as the value calculated by Weller and King[210] from their C_p results.

The derived $\Delta G_f^\circ = -309.7_0$ kcal mol^{-1} is also consistent with the NBS 270-6.

The NBS 270-6 lists ΔH_f° (at 0 K) = −224 kcal mol^{-1} for $MgMoO_4$(g). This value is within the limits set by investigations of two reactions by Verhaegen et al.[222]

We have already discussed properties of $CaMoO_4$(c) and $CaMoO_4$(ppt) in connection with MoO_4^{2-}(aq). The NBS 270-6 lists ΔH_f° (at 0 K) = −197 kcal mol^{-1} for $CaMoO_4$(g). This value is consistent with the experimental results of Verhaegen et al.[222] and the NBS 270-4 ΔH_f° of MoO_3(g), but use of the ΔH_f° we have adopted for MoO_3(g) leads to our ΔH_f° = −225 kcal mol^{-1} for $CaMoO_4$(g).

O'Hare et al.[209] have quoted $K_{sp} = 2.58 \times 10^{-7}$ for $SrMoO_4$(c). We use this K_{sp} with our ΔG_f° of MoO_4^{2-}(aq) to calculate $\Delta G_f^\circ = -343._1$ kcal mol^{-1} for $SrMoO_4$(c). Combination of this value with S° = (32) cal K^{-1} mol^{-1} leads to ΔH_f° = −369 kcal mol^{-1} for this compound. The NBS 270-6 has listed ΔH_f° = −370 kcal mol^{-1} for $SrMoO_4$(c), taken from a source that is unknown to us.

The NBS 270-6 lists ΔH_f° = −235 kcal mol^{-1} for $SrMoO_4$(g), which is intermediate between values calculated from results of two investigations by Verhaegen et al.[222] in combination with the NBS 270-4 ΔH_f° of MoO_3(g). A similar calculation with our ΔH_f° for MoO_3(g) leads to better agreement between the different reactions and thence to $\Delta H_f^\circ \simeq -249$ kcal mol^{-1} for $SrMoO_4$(g) as listed in our Table IV.

We have already discussed $BaMoO_4$(c) in connection with MoO_4^{2-}(aq). Results of Pupp, Yamdagni, and Porter[223] lead to $\Delta H_f^\circ \simeq -242$ kcal mol^{-1} for $BaMoO_4$(g).

The NBS 270-4 lists ΔH_f° = −225 kcal mol^{-1} for $CuMoO_4$(c), apparently based on results of Tammann and Westerhold previously cited in NBS Circular 500[73] and by Bichowsky and Rossini.[45] Our interpretation of these uncertain results leads to ΔH_f° = −242 kcal mol^{-1}, which is close to the value listed by Bichowsky and Rossini.[45] We omit this uncertain value from our Table IV.

Results[224] of a calorimetric determination of the enthalpy of precipitation and of solubilities at several temperatures are all in accord with ΔH_f° = −200.6 kcal mol^{-1} for Ag_2MoO_4(c). Taking $K_{sp} = 2.2 \times 10^{-12}$ from the investigations cited above[224] and another cited by O'Hare et al.[209] leads to ΔG_f° = −179.4 kcal mol^{-1} for Ag_2MoO_4(c) and thence by combination with the ΔH_f° to $S^\circ = 54._2$ cal K^{-1} mol^{-1} for this compound, whereas S° = 51 cal K^{-1} mol^{-1} is given in NBS 270-4. A third law entropy based on C_p measurements is needed.

We use the ΔG_f° above to calculate the potential:

$$Ag_2MoO_4(c) + 2e^- = 2Ag(c) + MoO_4^{2-}(aq)$$

$$E^\circ = 0.455 \text{ V}$$

Gaultier and Pannetier[79] have made DTA measurements leading to data for phase transitions in Tl_2MoO_4(c) and have also made solubility measurements that lead to $K_{sp} = 1 \times 10^{-8}$ from which we calculate ΔG_f° = −226.8 kcal mol^{-1} for this compound.

We calculate $\Delta H_f^\circ = -284.7_6$ kcal mol^{-1} for $MnMoO_4$(c) from the calorimetric results of Barany.[225] This value, which we adopt, is nearly identical with the value listed in NBS 270-4. The recent results of Ziolkowski and Courtine[226] are in fair agreement with this value.

The NBS 270-4 has listed S° = 30.9 cal K^{-1} mol^{-1} for $FeMoO_4$(c), which is the same as the value reported by Weller[227] on the basis of C_p measurements. The NBS 270-4 has also listed ΔH_f° = −257 kcal mol^{-1} for this compound, apparently based on the results of Tammann and Westerhold cited in NBS Circular 500.[73] Combination of ΔH_f° and S° gives the ΔG_f°. The NBS 270-4 has listed ΔH_f° = −702 kcal mol^{-1} for $Fe_2(MoO_4)_3$(c), also apparently based on the results of Tammann and Westerhold mentioned above. We consider this value to be quite uncertain and do not list it in our Table IV.

For $PbMoO_4$(c) the NBS 270-4 lists S° = 39.7 cal K^{-1} mol^{-1}, which is the same as the third law value found by Weller and Kelley.[228] As pointed out by O'Hare et al.,[209] the ΔG_f° in NBS 270-4 corresponds to a K_{sp} for $PbMoO_4$(c) smaller than any published value they (or we) know of. The $K_{sp} = 3.3 \times 10^{-12}$ cited by O'Hare et al.[209] leads to ΔG_f° = −221.9 kcal mol^{-1} for $PbMoO_4$(c). Combination of this ΔG_f° with the S° leads to ΔH_f° = −246 kcal mol^{-1} for $PbMoO_4$(c). This value differs considerably from ΔH_f° = −251.4 kcal mol^{-1} listed in NBS 270-4 and ΔH_f° = −250.9 kcal mol^{-1} calculated from the calorimetric enthalpy of precipitation reported by Muldrow and Hepler.[212] Because of the uncertainties as to which ΔH_f° and ΔG_f° values are best, we list only the entropy of lead molybdate.

Giauque et al.[229] have investigated magnetic and thermodynamic properties of $Gd_2(MoO_4)_3$(c) at low temperatures.

It has long been known that acidification of solutions containing molybdate ions results in various complicated reactions involving polynuclear species that are commonly called isopolymolybdates. On the basis of many investigations cited by Sillén,[75,112] it now appears certain that the principal species in weakly acidic solutions are heptamolybdates and octamolybdates, whereas in strongly acidic solutions there are depolymerization reactions leading to various cationic species. In addition to the summaries of results tabulated by Sillén,[75,112] we call attention to a review by Souchay[230] and a few recent investigations cited below.

Two recent spectroscopic investigations[231] and one very thorough kinetic investigation[232] are in general agreement with the statement above that the principal isopolymolybdate species in dilute acid are the heptamolybdate and octamolybdate ions that are commonly represented by $Mo_7O_{24}^{6-}$(aq) and $Mo_8O_{26}^{4-}$(aq), and also protonated forms related to these species.

We also have four calorimetric investigations[233] of the formation of isopolymolybdates from molybdate ion or of the formation of molybdate from isopolymolybdates.

It is only for the heptamolybdate ion $Mo_7O_{24}^{6-}$(aq) that equilibrium and calorimetric results of different investigations are in general agreement. We therefore limit our listings in Table IV to this ion.

Further acidification of solutions containing heptamolybdate and octamolybdate ions leads to depolymerization reactions and formation of cationic species. Reactions and equilibrium constants that refer to concentrated solutions have been summarized by Sillén[75,112] and also recently investigated by Krumenacker,[234] whose results are interpreted in terms of equilibrium constants for reactions involving such species as $HMoO_3^+$(aq), $H_2MoO_6^{2+}$(aq), etc.

Many heteropolymolybdates have been investigated and more or less well characterized. Some examples are $H_3CrMo_6O_{21}$, $H_8CeMo_{12}O_{42}$, $H_3PMo_{12}O_{40}$, and various related salts. Sillén[75,112] has cited a number of determinations of solubility products and acid ionization constants for heteropolymolybdates. We call attention to recent polarographic investigations[235] of oxidation-reduction properties and also determinations of acid ionization constants.[236] Jespersen[233] has made calorimetric measurements on $H_3PMo_{12}O_{40}$(aq).

D. Halides and Oxyhalides of Molybdenum

Heat capacity and entropy of vaporization data from Osborne et al.[237] lead to S° = 62.06 cal K^{-1} mol^{-1} for MoF_6(liq) and S° = 83.75 cal K^{-1} mol^{-1} for MoF_6(g), both at 298 K. These are the values listed in NBS 270-4 and adopted for our Table IV. This S° of MoF_6(g) agrees with the results of a statistical thermodynamic calculation by Weinstock and Goodman.[238] We also call attention to two earlier investigations. Brady et al.[239] have made heat capacity measurements leading to a reported $S^\circ = 60.6 \pm 0.7$ cal K^{-1} mol^{-1} for MoF_6(liq), which has been recalculated[237] to be 61.96 cal K^{-1} mol^{-1}. There are also vapor pressure data and derived enthalpy and entropy of vaporization values from Cady and Hargreaves.[240]

We adopt $\Delta H_f^\circ = -372.29$ kcal mol^{-1} for MoF_6(g), based on the fluorine combustion calorimetry of Settle, Feder, and Hubbard.[241] Combination of this value with the enthalpy of vaporization[240] leads to $\Delta H_f^\circ = -378.92$ kcal mol^{-1} for MoF_6(liq). We adopt these ΔH_f° values and combine with the entropies to obtain $\Delta G_f^\circ = -351.88$ kcal mol^{-1} for MoF_6(g) and $\Delta G_f^\circ = -352.05$ kcal mol^{-1} for MoF_6(liq) as listed in Table IV.

We also call attention to some other paths to these enthalpies of formation. Myers and Brady[242] have measured the enthalpy of reaction of MoF_6(liq) with excess OH^-(aq) with results that lead us to $\Delta H_f^\circ = -393.2$ kcal mol^{-1} for MoF_6(liq). More recently, Nuttall, Churney, and Kilday[243] have made similar measurements with results that lead us to $\Delta H_f^\circ = -376.4$ kcal mol^{-1} for MoF_6(liq). Both of these ΔH_f° values are based on the ΔH_f° of F^-(aq) from NBS 270-3. Allowing for six times the uncertainty in ΔH_f° of F^-(aq) (as discussed by Nuttall et al.[243]), we see that this latter ΔH_f° for MoF_6(liq) is in reasonable agreement with the value we have adopted from Settle, Feder, and Hubbard,[241] based on direct combination of the elements. It appears that the work of Myers and Brady[242] contains substantial errors. We calculate $\Delta H_f^\circ = -373.8$ kcal mol^{-1} for MoF_6(g) from the results of Burgess, Haigh, and Peacock[244] on the reaction of MoF_6(g) with excess alkali, which is in fair agreement with our adopted value.

Burgess et al.[244] have made similar experiments with MoF_5(c) and $MoOF_4$(c), leading to our listed ΔH_f° values for these compounds. The entropy of MoF_5(g) has been calculated by statistical thermodynamics.[245]

Paine and McDowell[246] have studied the evaporation of $MoOF_4$(c) at 25 °C with mass spectrometry and have shown that the vapor contains small amounts of oligomeric species, possibly $(MoOF_4)_4$(g). Therefore, we cannot calculate a reliable ΔH_f° of $MoOF_4$(g) from the reported[247] heat of sublimation of $MoOF_4$(c).

Results of Zmbov, Uy, and Margrave[248] lead to $\Delta H_f^\circ = -268$ kcal mol^{-1} for MoO_2F_2(g).

The NBS 270-4 lists thermodynamic properties for $MoCl_2$(c), $MoCl_3$(c), $MoCl_4$(c), $MoCl_4$(g), $MoCl_5$(c), $MoCl_5$(g), MoO_2Cl_2(c), MoO_2Cl_2(g), $MoO_2Cl_2 \cdot H_2O$(c), and $MoOCl_4$(c). In addition to all of these compounds, we also have thermodynamic data for $MoOCl_2$(c), $MoOCl_3$(c), $MoOCl_3$(g), and $MoOCl_4$(g). The thermodynamic properties of these 14 substances are related by way of thermodynamic data for about twice as many reactions. There is no set of thermodynamic properties that is consistent with all of the published results, which shows that at least some of the real uncertainties and errors in thermodynamic data are larger than quoted in the original publications. We have therefore not tried to undertake any purely statistical analysis of the published results in order to obtain a set of thermodynamic properties that leads to a minimum difference between published and calculated reaction thermodynamics. Instead, we have made tentative choices of what appear to be the best experimental results and calculated a few thermodynamic properties that have then been combined in various cycles to obtain still further thermodynamic properties. Recycling and repetition from different starting points have finally led us to the thermodynamic properties that are given in Table IV for the 14 substances listed in the beginning of this paragraph. Rather than describe in detail how we settled on these particular values, we show in following paragraphs how these values are consistent with results of particular measurements, and also how some of them are inconsistent with results of other measurements.

Shchukarev et al.[249] have summarized the results of a large number of previous calorimetric measurements. Some of these results lead to $\Delta H_f^\circ = -114$ kcal mol^{-1} for $MoCl_4$(c) and to $\Delta H_f^\circ = -126$ kcal mol^{-1} for $MoCl_5$(c), as listed for both of these compounds in Table IV. We note that these ΔH_f° values are based on ΔH_f° for MoO_3(c) and do not involve ΔH_f° values for any other molybdenum halides. The JANAF tables[151] cite equilibrium results for the $MoCl_5$(c)–$MoCl_4$(c)–Cl_2(g) system that are in good agreement with the ΔH_f° values given above. The enthalpy of vaporization[151,249] of oCl_5(c) leads to our tabulated ΔH_f° of $MoCl_5$(g).

We obtain $\Delta H_f^\circ = -92$ kcal mol^{-1} for $MoCl_4$(g) from the average of ΔH_f° values from Shchukarev et al.[249] and Oppermann and Stöver[250] for the decomposition of $MoCl_3$(c) to $MoCl_2$(c) and $MoCl_4$(g). For this calculation we have used the ΔH_f° values for $MoCl_2$(c) and $MoCl_3$(c) that are discussed below.

Calorimetric results summarized by Shchukarev et al.[249] lead to $\Delta H_f^\circ = -68$ kcal mol^{-1} for $MoCl_2$(c). This value is dependent on ΔH_f° of MoO_3(c) and also on the ΔH_f° of MoO_2Cl_2(c), which is discussed below.

For $MoCl_3$(c) we have taken $\Delta H_f^\circ = -96._7$ kcal mol^{-1} from the calorimetric results of Shchukarev et al.[249] and the equilibrium results of Oppermann, Stöver, and Kunze.[251] Calculation of ΔH_f° of $MoCl_3$(c) from these equilibrium results[251] is dependent on ΔH_f° values for various other molybdenum halides and oxyhalides.

There have been three independent investigations[252-254] of the enthalpy of reaction of MoO_2Cl_2(c) with excess OH^-(aq). These results lead to $\Delta H_f^\circ = -170._5$, $-173._2$, and $-175._4$ kcal mol^{-1} for MoO_2Cl_2(c). Because of the troublesome reaction of MoO_2Cl_2(c) with atmospheric water, we expect that the most exothermic enthalpy of reaction is best[252] and therefore adopt $\Delta H_f^\circ = -170._5$ kcal mol^{-1} for this compound.

Our tabulated ΔH_f° of MoO_2Cl_2(g) is consistent with the above ΔH_f° for MoO_2Cl_2(c) and the enthalpy of sublimation reported by Oppermann[254] and by Shchukarev et al.[255] The equilibrium data from Shchukarev et al.[255] and from Hultgren and Brewer[256] on the reaction between MoO_3(c) and HCl(g) to form MoO_2Cl_2(g) and H_2O(g) lead to a slightly less negative ΔH_f° for MoO_2Cl_2(g). All of these results support our choice for ΔH_f° of MoO_2Cl_2(c) in the paragraph above.

Our tabulated $\Delta H_f^\circ = -150._7$ kcal mol^{-1} for $MoOCl_3$(c) is consistent with the calorimetric results of Oppermann, Stöver, and Kunze.[251] The $\Delta H_f^\circ = -123._1$ kcal mol^{-1} for $MoOCl_3$(g) is based on the above ΔH_f° for $MoOCl_3$(c) and the enthalpy of sublimation.[251]

For $MoOCl_4$(c) we adopt $\Delta H_f^\circ = -157._6$ kcal mol^{-1} from results of two calorimetric investigations[249,251] that differ from each other by 6 kcal mol^{-1}. The enthalpy of vaporization that leads to $\Delta H_f^\circ = -140._3$ kcal mol^{-1} for $MoOCl_4$(g) is from Oppermann et al.[251]

Our $\Delta H_f^\circ = -126._2$ kcal mol^{-1} for $MoOCl_2$(c) is based on the equilibrium results of Oppermann and Stöver[250] for decomposition of $MoOCl_2$(c) to $MoCl_2$(c) and MoO_2Cl_2(g).

We also list entropies for the molybdenum halides and oxyhalides. These estimated entropies are intended to be consistent with results of various equilibrium investigations referred to above. Entropies based on measured heat capacities and the third law are needed.

We adopt $\Delta H_f^\circ = -245.9$ kcal mol^{-1} for the compound listed in Table IV as $MoO_2Cl_2 \cdot H_2O$(c), based on a calorimetric measurement of the enthalpy of reaction with excess OH^-(aq).[252] This compound, which is commonly prepared by reaction of MoO_3(c) with HCl(g) at about 250 °C, has also been represented as $MoO(OH)_2Cl_2$(c) and $MoO_3 \cdot 2HCl$(c). We estimate that the entropy of this compound is 10 cal K^{-1} mol^{-1} greater than that of MoO_2Cl_2(c) and calculate the ΔG_f°. This ΔG_f° in combination with that of MoO_3(c) leads to a calculated 0.04 atm (at 298 K) for the pressure of HCl(g) in equilibrium with $MoO_3 \cdot 2HCl$(c) and MoO_3(c). A similar calculation with the ΔG_f° of MoO_2Cl_2(c) leads to 2×10^{-5} atm for the pressure of H_2O(g) in equilibrium with $MoO_2Cl_2 \cdot H_2O$(c) and MoO_2Cl_2(c). Both of these calculated equilibrium pressures are in accord with the properties of these compounds.

Our Table IV lists $\Delta H_f^\circ = -51._0$ kcal mol^{-1} for $MoBr_2$(c) and $\Delta H_f^\circ = -62._7$ kcal mol^{-1} for $MoBr_3$(c). A calorimetric determination by Shukurov et al.[257] of the heats of combustion of these compounds leads to $\Delta H_f^\circ = -54 \pm 5$ kcal mol^{-1} for $MoBr_2$(c) and to $\Delta H_f^\circ = -64 \pm 5$ kcal mol^{-1} for $MoBr_3$(c). Equilibrium data from Oppermann[258] lead to $\Delta H^\circ_{\text{reaction}} = 74._8$ kcal for

$$4MoBr_2(c) = 2MoBr_3(c) + Br_2(g) + 2Mo(c)$$

and to $\Delta H^\circ_{\text{reaction}} = 25._5$ kcal for

$$3MoBr_2(c) = Mo(c) + 2MoBr_3(c)$$

Our selected values have been chosen to be reasonably consistent with both the calorimetric and the equilibrium data.

Oppermann[258] has determined the enthalpy of sublimation of $MoBr_2$(c), and we have calculated $\Delta H_f^\circ = -20._8$ kcal mol^{-1} for $MoBr_2$(g) from his data.

The results of two equilibrium studies by Oppermann[258] in combination with our adopted values of ΔH_f° for $MoBr_2$(c) and $MoBr_3$(c) give $\Delta H_f^\circ = -36._7$ kcal mol^{-1} for $MoBr_4$(g). Shchukarev et al.[259] have determined the enthalpies of solution of $MoBr_4$(c) and $MoCl_5$(c), leading to our $\Delta H_f^\circ = -70._4$ kcal mol^{-1} for $MoBr_4$(c). This value depends on our adopted ΔH_f° for $MoCl_5$(c).

Table IV lists $\Delta H_f^\circ = -152._3$ kcal mol^{-1} for MoO_2Br_2(c), which is the average of two calorimetric determinations,[254,260] and also $\Delta H_f^\circ = -126._4$ kcal mol^{-1} for MoO_2Br_2(g) from the heat of sublimation determined by Oppermann.[254] Oppermann et al.[261] have made similar studies on $MoOBr_3$(c) and $MoOBr_3$(g), leading to our $\Delta H_f^\circ = -111._2$ kcal mol^{-1} for $MoOBr_3$(c) and $\Delta H_f^\circ = -75._2$ kcal mol^{-1} for $MoOBr_3$(g).

Our estimated entropies for the molybdenum bromides and oxybromides are consistent with the equilibrium measurements of Oppermann et al.[258,261] The uncertainty in these entropies is considerable (maybe ± 10 cal K^{-1} mol^{-1}), but the internal consistency of the values is (probably) much better.

The $\Delta H_f^\circ = -27._0$ kcal mol^{-1} for MoI_3(c) has been calculated by Skinner et al.[262,263] from the heat of reaction between $Mo(CO)_6$(c) and I_2(g) and the ΔH_f° of $Mo(CO)_6$(c), which we will discuss later. They also estimate ΔH_f° for MoI_2(c) to be 1.5 kcal mol^{-1} less negative than ΔH_f° for MoI_3(c). These estimated and measured values are adopted for Table IV.

NBS 270-4 lists $\Delta H_f^\circ = 32$ kcal mol^{-1} for MoI_2(g), which is consistent with our recalculation of Allen's results[264] for the equilibrium between Mo(c), I(g), and MoI_2(g) at 1200 K.

Oppermann[265] claims to have shown that MoO_2I_2(g) is formed in the reaction between MoO_2(c) and I_2(g) at about 1000 K, and he has derived the uncertain values of ΔH_f° and S° we have included in Table IV for MoO_2I_2(g).

E. Other Molybdenum Compounds

Barancheeva and Zharkova[266] have determined ΔH_f° for calcium molybdite, $CaMoO_3$(c), by combustion calorimetry. We calculate $\Delta H_f^\circ = -280$ kcal mol^{-1} from the published heat of combustion, using our ΔH_f° for $CaMoO_4$(c). Earlier high-temperature equilibrium[266a] and high-temperature emf[266b] investigations lead to $\Delta H_f^\circ = -296$ kcal mol^{-1} for $CaMoO_3$(c), in agreement with the value listed in NBS 270-6. We accept the latter value.

Our $\Delta H_f^\circ = -306$ kcal mol^{-1} for $SrMoO_3$(c) is calculated from combustion calorimetry results from Zharkova and Barancheeva,[267] and is the same as the value listed in NBS 270-6.

NBS 270-6 also lists $\Delta H_f^\circ = -130$ kcal mol^{-1} (at 0 K) for $SrMoO_3$(g), which is the mean of two investigations by Verhaegen et al.,[222] calculated with the NBS 270-4 ΔH_f° for MoO_3(g). With our adopted ΔH_f° for MoO_3(g) we obtain $\Delta H_f^\circ \simeq -141$ kcal mol^{-1} for $SrMoO_3$(g) and a better agreement between the two values of ΔH_f° that can be calculated from Verhaegen's results.

For $BaMoO_3$(c) a calorimetric and a high-temperature equilibrium investigation (discussed by O'Hare[213]) are in good agreement with $\Delta H_f^\circ = -295$ (± 2) kcal mol^{-1}, as adopted in NBS 270-6 and in our Table IV.

Our $\Delta H_f^\circ \simeq -156$ kcal mol^{-1} for $BaMoO_3$(g) is calculated from the high-temperature equilibrium data of Pupp et al.[223] and our adopted ΔH_f° for MoO_2(g).

For MoS_2(c), NBS 270-4 lists $\Delta H_f^\circ = -56.2$ kcal mol^{-1} and $S^\circ = 14.96$ cal K^{-1} mol^{-1}. The entropy is from C_p measurements by Westrum and McBride,[268] while the ΔH_f° value is consistent with the results of two old investigations.[269] O'Hare et al.[270] have made calorimetric measurements that lead to $\Delta H_f^\circ = -65.8$ kcal mol^{-1}. This value, which we adopt, is in reasonable agreement with some high-temperature studies, as discussed by O'Hare et al.[270] We agree with the analysis by O'Hare et al.[270] of high-temperature equilibrium and emf data for Mo_2S_3(c), leading to an approximate $\Delta H_f^\circ \simeq -97$ kcal mol^{-1} for this compound.

Parravano and Malquori[269] have made equilibrium studies on the system MoS_3–MoS_2–S_2, but their conclusion regarding the stability of MoS_3 is at variance with that of another investigation.[271] Therefore, we do not list MoS_3(c) in Table IV.

The enthalpy of decomposition of $(NH_4)_2MoS_4$(c) is known from equilibrium measurements on its thermal decomposition,[272] but the absence of a ΔH_f° value for MoS_3(c) prevents us from calculating a ΔH_f° for $(NH_4)_2MoS_4$(c).

For the nitride, Mo_2N(c), we have $\Delta H_f^\circ = -19.5 \pm 0.3$ kcal mol^{-1} from combustion calorimetry by Mah.[164] This value is listed in NBS 270-4.

Mah[273] has also determined $\Delta H_f^\circ = -2.4$ kcal mol^{-1} for "MoC" and $\Delta H_f^\circ = -10.9$ kcal mol^{-1} for Mo_2C. As it was not known by Mah that the high-carbon carbide is carbon deficient with an actual composition of $MoC_{0.67}$, the heat of formation of "MoC" might be considerably in error.[27] For Mo_2C(c) we have $S^\circ = 15.74$ cal K^{-1} mol^{-1} from C_p measurements.[274] Our ΔG_f° in Table IV is consistent with the S° and ΔH_f° values.

High-temperature heat contents[274] combined with the adopted ΔH_f° and S° lead to a free energy of formation of Mo_2C(c) which at 800 K is about 1.2 kcal mol^{-1} more negative than the value calculated by Solbakken and Emmett[275] from equilibrium measurements on the reaction of Mo(c) and CH_4(g) to form Mo_2C(c) and H_2(g). We have no explanation for this discrepancy.

We adopt enthalpies of formation and entropies for Mo_3Si(c), $MoSi_2$(c), and Mo_5Si_3(c) from Chart's recent review.[166] The slightly less negative ΔH_f° values listed in NBS 270-4 for these compounds are within the uncertainty limits assigned by Chart. The tabulated enthalpies and entropies lead to our free energy values.

NBS 270-4 lists $\Delta H_f^\circ = -5$ kcal mol^{-1} for Mo_3Ge(c), consistent with the results of vapor pressure measurements by Peavler and Searcy.[276]

Potential measurements by El-Shamy and El-Aggan[277] on the Mo(VI)|Mo(V) couple in aqueous HCl lead to $E^\circ = 0.48$ V at 30 °C, but the molybdenum species are ill-defined and we do not try to write a redox equation. Haight[278] has shown that $MoOCl_5^{2-}$ is the most important Mo(V) species in concentrated HCl, and that the dinuclear ion $(MoOCl_4)_2O^{4-}$ is the initial hydrolysis product. Haight[278] has evaluated the equilibrium constants at several temperatures and thence the enthalpy of reaction for this dimerization process. His results are in general agreement with more recent work, in which the formation of dinuclear cationic species in more dilute acid solution has also been demonstrated.[279] Saha et al.[280] have prepared the acids $H_2MoOCl_5{\cdot}2H_2O$ and $HMoCl_4$ in the solid state and have also shown that the corresponding bromides have similar properties. Marov et al.[281] have reported equilibrium constants for the reactions between $MoOX_4^-$ ($X = NCS^-$ or Cl^-) and Br^-, I^-, or H_3PO_4 in strongly acidic solutions.

Solution calorimetry by Burgess et al.[282] has led to the $\Delta H_f°$ values we list in Table IV for $KMoF_6$(c), $RbMoF_6$(c), and $CsMoF_6$(c).

The complex formation between CH_3O^- and Mo(V) in absolute methanol has been investigated by Gut, Schmid, and Serrallach.[283]

Efimov and Belorukova[284] have described the synthesis of Mo(IV) compounds of the type M_2MoCl_6 (M = Na, K, Rb, or Cs) and evaluated $\Delta H_f°$ for the sodium and potassium compounds by solution calorimetry.

The stable complex ion $Mo(CN)_8^{4-}$ forms soluble complexes with tervalent metal ions, and the stability constant of the Fe^{3+} complex has been estimated.[285]

Potentials have been reported[286] for the half-reaction

$$Mo(CN)_8^{3-} + e^- = Mo(CN)_8^{4-} \qquad E° = 0.725\ V$$

but it is necessary to realize that evaluation of activity coefficient and thence of a standard potential is uncertain.

It has been shown that the green solutions of Mo(III) in HCl contain a mixture of Mo(III) species.[287] Recently, the green dinuclear ion $(H_2O)_4Mo(OH)_2Mo(H_2O)_4^{4+}$ and the yellow hexaaquo ion $Mo(H_2O)_6^{3+}$ have been identified.[287,288]

We have no quantitative data on Mo(II) in aqueous solution. The identification of some aqueous Mo(II) species is discussed in recent papers.[289]

NBS 270-4 reports $\Delta H_f° = -234.9$ kcal mol^{-1} for $Mo(CO)_6$(c), in accordance with bomb calorimetric results of Cotton, Fischer, and Wilkinson.[173] More recently, Skinner et al.[262] propose $\Delta H_f° = -236.5$ kcal mol^{-1} as a weighted average of their results for the heat of combustion and heat of decomposition of $Mo(CO)_6$(c). Cotton et al.[173] report $\Delta H°_{vaporization} = 16.3$ kcal mol^{-1}, while Monchamp and Cotton[290] find $\Delta H°_{vaporization} = 17.3$ kcal mol^{-1}. We adopt $\Delta H_f° = -236.5$ kcal mol^{-1} for $Mo(CO)_6$(c) and $\Delta H_f° = -219.7$ kcal mol^{-1} for $Mo(CO)_6$(g), using the average value of the quoted enthalpies of vaporization. From the results of their C_p measurements, Astrov et al.[291] have calculated $S° = 78.17 \pm 0.25$ cal K^{-1} mol^{-1} for $Mo(CO)_6$(c). On the basis of the same data, Kelley and King[22] give $S° = 77.9 \pm 0.8$ cal K^{-1} mol^{-1}. We adopt $S° = 78.0$ cal K^{-1} mol^{-1} in Table IV. Monchamp and Cotton[290] have discussed earlier spectroscopic investigations on $Mo(CO)_6$(g) and have made statistical calculations on the basis of these spectroscopic data, leading to values of $S°$ for $Mo(CO)_6$(g) from 117.6 to 122.6 cal K^{-1} mol^{-1}. From the vapor pressure measurements of Monchamp and Cotton[290] we calculate and adopt $S° = 117.8$ cal K^{-1} mol^{-1} for $Mo(CO)_6$(g).

There are few thermodynamic investigations on organic molybdenum compounds. In addition to data covered by earlier reviews,[180,181] we note that the heats of formation of adducts $MoCl_4{\cdot}2L$ (L = pyridine, tetrahydrofuran, or tetrahydrothiophene) have been determined.[292]

F. Tungsten, Tungsten Oxides, and Tungstic Acid

We take $\Delta H_f° = 0$, $\Delta G_f° = 0$, and $S° = 7.80$ cal K^{-1} mol^{-1} from NBS 270-4 for W(c). The entropy is the same as listed by Kelley and King[22] and in the JANAF tables.[151]

For W(g) we have $S° = 41.549$ cal K^{-1} mol^{-1}, also in agreement with the value given by Kelley and King[22] and in NBS 270-4. On the basis of vapor pressure measurements by Plante and Sessoms[293] and earlier results cited by them, we adopt $\Delta H_f° = 204._5$ kcal mol^{-1} for W(g). Combination of $\Delta H_f°$ and $S°$ leads to $\Delta G_f° = 194._4$ kcal mol^{-1}.

The heat capacity, enthalpy, and related thermodynamic properties of tungsten at high temperatures have been the subject of a recent investigation;[294] earlier results are discussed in the JANAF tables.[151]

For WO(g) we adopt $\Delta H_f° \simeq 102$ kcal mol^{-1} from the work of DeMaria et al.,[194] as also discussed in the JANAF tables.[151] The uncertainty in this value overlaps the NBS 270-4 value of $\Delta H_f° = 108$ kcal mol^{-1}. We use an estimated[151] $S° = (59)$ cal K^{-1} mol^{-1} to calculate $\Delta G_f° \simeq 94$ kcal mol^{-1}.

The $\Delta H_f° = -140.94$ kcal mol^{-1} for WO_2(c) given in NBS 270-4 is based on combustion calorimetry by Mah.[295] Charlu and Kleppa[296] obtained $\Delta H_f° = -140.2 \pm 0.7$ kcal mol^{-1} by this same method. Our recalculations of high-temperature emf results[197,297] lead to $\Delta H_f° = -139.5$ and -140.4 kcal mol^{-1}, respectively. Earlier equilibrium measurements discussed in the JANAF tables[151] lead us to $\Delta H_f° = -140.6 \pm 0.7$ kcal mol^{-1}. We adopt the value from Mah in our Table V, but note that there is some evidence for a slightly less negative value. We adopt $S° = 12.08$ cal K^{-1} mol^{-1} as given by Kelley and King[22] and listed in NBS 270-4, and calculate $\Delta G_f° = -127.6$ kcal mol^{-1} for WO_2(c).

We have $\Delta H_f° \simeq 15$ kcal mol^{-1} for WO_2(g) as a mean value of third law recalculations of the results from DeMaria et al.[194] and Chupka, Berkowitz, and Giese.[298] NBS 270-4 lists $\Delta H_f° = 11$ kcal mol^{-1}. We adopt $S° = (68)$ cal K^{-1} mol^{-1} from the JANAF tables[151] and thence calculate $\Delta G_f° \simeq 12$ kcal mol^{-1} for WO_2(g).

For $WO_{2.72}$(c) (= $\frac{1}{18}W_{18}O_{49}$) we adopt $\Delta H_f° = -186.3$ kcal mol^{-1} from two investigations.[296,297] The analysis of older data in the JANAF tables[151] also supports a more negative value than the $\Delta H_f° = -185$ kcal mol^{-1} listed in NBS 270-4. The $\Delta G_f°$ value in Table V has been calculated from our $\Delta H_f°$ and an estimated[151] $S° = (16.4)$ cal K^{-1} mol^{-1}.

For $WO_{2.90}$(c) (= $\frac{1}{20}W_{20}O_{58}$) we adopt $\Delta H_f° = -196.0$ kcal mol^{-1} as listed in NBS 270-4 and in the JANAF tables.[151] This value is consistent with two investigations.[296,297] Table V gives $\Delta G_f° = -177.7$ kcal mol^{-1}, calculated from our $\Delta H_f°$ and an estimated[151] $S° = (17.5)$ cal K^{-1} mol^{-1}.

Our values for $WO_{2.96}$(c) are the same as listed in the JANAF tables.[151]

For WO_3(c) we adopt $\Delta H_f° = -201.45$ kcal mol^{-1} from NBS 270-4, in agreement with bomb calorimetry results of Mah.[295] This value also agrees well with $\Delta H_f° = -201.84$ kcal mol^{-1} from an earlier investigation.[299] The NBS 270-4 lists $S° = 18.14$ cal K^{-1} mol^{-1}, in good agreement with the value given by Kelley and King,[22] and thence $\Delta G_f° = -182.62$ kcal mol^{-1} for WO_3(c).

A third law analysis of high-temperature data from three investigations[194,298,300] leads to $\Delta H_f° \simeq -70$ kcal mol^{-1} for WO_3(g). Combining this value with an estimated[151] $S° = (68)$ cal K^{-1} mol^{-1} gives $\Delta G_f° \simeq -66$ kcal mol^{-1}.

Our enthalpies of formation for $(WO_3)_n$(g) (n = 2, 3, 4) and for W_3O_8(g) are all based on the high-temperature vapor pressure and mass spectrometric measurements by Ackermann and Rauh.[301] They have been combined with estimated[151] entropies to give $\Delta G_f°$ values. The values listed in NBS 270-4 for $\Delta H_f°$ of $(WO_3)_3$(g) and $(WO_3)_4$(g) are ~20 kcal mol^{-1} less negative than our values and are in better agreement with the results of Norman and Staley,[302] whose results are inconsistent with the free energy functions in the JANAF

TABLE V.[a] **Thermodynamic Properties of Tungsten Compounds at 298 K**

Compound	$\Delta H_f°$ kcal mol^{-1}	$\Delta G_f°$ kcal mol^{-1}	$S°$ cal K^{-1} mol^{-1}	Compound	$\Delta H_f°$ kcal mol^{-1}	$\Delta G_f°$ kcal mol^{-1}	$S°$ cal K^{-1} mol^{-1}
W(c)	*0*	*0*	$\mathit{7.80}^{22}$	WO_2F_2(g)	$\sim -215^{248}$		
W(g)	$204._5^{293}$	$194._4$	$\mathit{41.549}^{22}$	WCl_2(c)	$-\mathit{61}^{249}$	−52	$(31)^{151}$
W^+(g)	390.1			WCl_4(c)	$\sim -108^{249}$	∼−88	$(47)^{151}$
WO(g)	$\sim 102^{194}$	∼94	$(59)^{151}$	WCl_4(g)	$\sim -77^{249}$	∼−70	$(91)^{151}$
WO_2(c)	$-\mathit{140.94}^{295}$	*−127.6*	$\mathit{12.08}^{22}$	WCl_5(c)	-122^{249}	−95	$(52)^{151}$
WO_2(g)	$\sim 15^{194,298}$	∼12	$(68)^{151}$	WCl_5(g)	-98^{249}	−85	$(97)^{151}$
$WO_{2.72}$(c)	$-186.3^{296,297}$	−169.0	$(16.4)^{151}$	$(WCl_5)_2$(g)	-206^{249}	−173	$(170)^{151}$
$WO_{2.90}$(c)	$-\mathit{196.0}^{151,296,297}$	−177.7	$(17.5)^{151}$	WCl_6(c,α)	$-141._9^{249}$	−109	$(57)^{151}$
$WO_{2.96}$(c)	-199.6^{151}	−180.9	$(17.9)^{151}$	WCl_6(g)	$-118._0^{151}$	−98	$(100)^{151}$
WO_3(c)	$-\mathit{201.45}^{295}$	*−182.62*	*18.14*	$WOCl_2$(c)	-147^{344}	−131	$(32)^{344}$
WO_3(g)	$\sim -70^{194,298,300}$	∼−66	$(68)^{151}$	$WOCl_3$(c)	-165.9^{344}	−145	$(43)^{344}$
$(WO_3)_2$(g)	$\sim -277^{301}$	∼−258	$(99)^{151}$	$WOCl_4$(c)	$-172._4^{341}$	−143	$(41)^{151}$
$(WO_3)_3$(g)	$\sim -484^{301}$	∼−447	$(121)^{151}$	$WOCl_4$(g)	$-152._4^{151,342}$	−138	92.1^{343}
$(WO_3)_4$(g)	$\sim -671^{301}$	∼−617	$(145)^{151}$	WO_2Cl_2(c)	$-189^{249,341}$	−170	$(48)^{151}$
W_3O_8(g)	$\sim -409^{301}$	∼−379	$(118)^{151}$	WO_2Cl_2(g)	$-162^{151,341}$	−155	$(85)^{151}$
H_2WO_4(c)	-270.0^{305}	−239.0	(33)	WBr_5(c)	-75.4^{345}	−65	$(65)^{151}$
H_2WO_4(g)	$\sim -217^{306}$	∼−201	$(84)^{151}$	WBr_5(g)	-52^{346}	−27	$(110)^{151}$
WO_4^{2-}(aq)	-256.5^{304}	−219	(11)	WBr_6(c)	-83.2^{345}	−71	$(75)^{151}$
$HW_6O_{21}^{5-}$(aq)	-1396.6^{313}	$-1226.8^{311,312}$	86	$WOBr_3$(c)	$-126._0^{351}$	−114	$(46)^{341}$
Li_2WO_4(c)	-383.2^{209}			$WOBr_4$(c)	$-131._8^{347,348}$	−118	$(55)^b$
Li_2WO_4(g)	$\sim -240^{217}$			$WOBr_4$(g)	$-101._8^{348-350}$	−103	$(105)^b$
Na_2WO_4(c)	$-369.6^{215,322}$	−342.2	38.5^{321}	WO_2Br_2(c)	$-170.2^{347,348}$		
$Na_2W_2O_7$(c)	$-573._8^{215}$	$-528._8$	60.8^{218a}	WO_2Br_2(g)	$-133._0^{346-350}$	−131	$(86)^{349}$
$Na_2W_4O_{13}$(c)	$-990._9^{215}$			WI_2(c)	$(-10)^{263}$		
K_2WO_4(c)	-377.9^{209}			WI_3(c)	$\sim -10^{263}$		
K_2WO_4(g)	$\sim -278^{220}$			WO_2I(c)	$\sim -137^{353}$		
$KHWO_4$(g)	$\sim -257^{220}$			WO_2I_2(c)	$-145._4^{353}$		
$MgWO_4$(c)	-362.7^{324}	−336.0	$\mathit{24.18}^{321}$	WO_2I_2(g)	$-102._3^{349,353}$	−104	$(89)^{353}$
$MgWO_4$(g)	$\sim -215^{222}$			WF_5Cl(liq)	-390^{338}		
$CaWO_4$(c)	-392.2^{211}	−366.7	$\mathit{30.21}^{321}$	WF_4Cl_2(liq)	-352^{338}		
$CaWO_4$(g)	$\sim -226^{222}$			$CaWO_3$(g)	$\sim -118^{222}$		
$SrWO_4$(c)	∼−391	$-\mathit{366}^{325}$	*(33)*	KWF_6(c)	-541^{354}		
$SrWO_4$(g)	$\sim -250^{222}$			$KWCl_6$(c)	-238^{355}		
$BaWO_4$(c)	$-\mathit{407}^{45}$			K_2WCl_7(c)	-342^{355}		
$SnWO_4$(g)	$\sim -\mathit{411}^{222}$			$K_3W_2Cl_9$(c)	$\sim -530^{356}$		
Sn_2WO_5(g)	$\sim -\mathit{472}^{222}$			$Rb_3W_2Cl_9$(c)	$\sim -571^{356}$		
$MnWO_4$(c)	$-\mathit{311.9}^{328}$			$Cs_3W_2Cl_9$(c)	$\sim -578^{356}$		
$FeWO_4$(c)	$-\mathit{276}^{45}$	−252	31.61^{330}	$WF_5(CH_3O)$(c)	-417^{338}		
$CoWO_4$(c)	-270.7^{324}			*cis*-$WF_4(CH_3O)_2$(liq)	-404^{338}		
$NiWO_4$(c)	-269.2^{324}			*cis*-$WF_2(CH_3O)_4$(c)	-362^{338}		
$CuWO_4$(c)	-245.5^{324}			WS_2(c)	-54^{357}	−56	29^{357}
$ZnWO_4$(c)	-294.6^{324}	−268.5	28.34^{330}	WC(c)	$-9.6_3^{273,358}$		
$CdWO_4$(c)	-281.8^{324}			W_2C(c)	$-\mathit{6.3}^{273}$		
$PbWO_4$(c)	−271 (?)	−247	$\mathit{40.2}^{228}$	$W(CO)_6$(c)	$-\mathit{227.9}^{173}$		
Ag_2WO_4(c)	-220.7^{322}	$-198._9$	(53)	$W(CO)_6$(g)	-210.2^{173}		
WF(g)	$\sim 86^{340}$			WSi_2(c)	$-\mathit{22}^{166}$	−21	15^{166}
WF_2(g)	$\sim -25^{340}$			W_5Si_3(c)	-32^{166}	−33	55^{166}
WF_3(g)	$\sim -127^{340}$			WTe_2(c)	$-15._3^{361}$	$-12._1$	$20._9^{361}$
WF_4(g)	-246^{340}			$Na_{0.53}WO_3$(c)	-232.5^{364}		
WF_5(c)	-345.9^{336}			$Na_{0.679}WO_3$(c)	-240.9^{364}	−221.0	22.77^{364}
$(WF_5)_4$(g)	-1316^{339}			$Na_{0.77}WO_3$(c)	-245.9^{364}		
WF_6(liq)	$-\mathit{417.7}^{240,337}$	−390.0	$\mathit{60.1}^{240,337}$	$H_{0.18}WO_3$(c)	-202.6^{365}		
WF_6(g)	$-\mathit{411.5}^{335}$	*−390.1*	$\mathit{81.49}^{151}$	$H_{0.35}WO_3$(c)	-203.7^{365}		
WOF_4(c)	-359^{338}	−333	$(42)^{151}$	$(NH_4)_{0.25}WO_3$(c)	-224.4^{365}		
WOF_4(g)	$\sim -316^{246}$	∼−301	$(80.4)^{151}$				

[a] Italicized values agree with values in NBS 270-4 or NBS 270-6. Values in parentheses are estimates. [b] Oppermann and Stöver[348] have estimated $S° = 62 \pm 6$ cal K^{-1} mol^{-1} for $WOBr_4$(c) and $S° = 112 \pm 7$ cal K^{-1} mol^{-1} for $WOBr_4$(g). We have adopted their entropy of sublimation of $WOBr_4$(c), but not their entropy values. These seem to be too high, compared with the estimated entropies of other related compounds.

tables[151] and have not been adopted here.

The existence of W_3O(c) is contested[297,303] and we do not include any data reported[303] for W_3O(c) in our Table V.

For the compound $WO_3{\cdot}H_2O$(c), sometimes written as H_2WO_4(c), the standard enthalpy of solution in aqueous sodium hydroxide has been determined as −13.7 and −13.2 kcal mol^{-1}, respectively.[304,305] We combine the least exothermic heat of solution[305] with our adopted $\Delta H_f°$ for WO_4^{2-}(aq), which we will discuss later, to obtain $\Delta H_f° = -270.0$ kcal mol^{-1} for $WO_3{\cdot}H_2O$(c). We estimate $S° = (33)$ cal K^{-1} mol^{-1}. With these values, a vapor pressure of H_2O(g) over $WO_3{\cdot}H_2O$(c) and WO_3(c) of about 40 mmHg can be calculated. This vapor pressure "should" be of the same order of magnitude as for $MoO_3{\cdot}H_2O$(c), ∼1 mmHg. In the absence of reliable vapor pressure data and third law entropies for $MoO_3{\cdot}H_2O$(c) and $WO_3{\cdot}H_2O$(c), all we can say is that we suspect minor errors in the thermodynamic data for WO_4^{2-}(aq) and $WO_3{\cdot}H_2O$(c). We note that use of the more exothermic enthalpy of solution[304] leads to a still higher calculated vapor pressure.

For $WO_3{\cdot}H_2O$(g) we adopt $\Delta H_f^\circ \simeq -217$ kcal mol^{-1} from equilibrium measurements by Belton and McCarron.[306] This value is in good agreement with the results of Glemser et al.[307] The $\Delta H_f^\circ = -229$ kcal mol^{-1} in NBS 270-4 is consistent with the earlier results of Meyer et al.[308]

G. WO_4^{2-}(aq) and Tungstates

The most direct way to determine ΔH_f° of WO_4^{2-}(aq) is to measure the enthalpy of solution of WO_3(c) in excess base. This is, however, beset with experimental difficulties. Two different investigations of the enthalpy of solution of WO_3(c) in aqueous sodium hydroxide lead to $\Delta H_f^\circ = -257.1$ kcal mol^{-1} (ref 305), as adopted in NBS 270-4, and to $\Delta H_f^\circ = -256.5$ kcal mol^{-1} (ref 304), respectively, for WO_4^{2-}(aq). For reasons discussed in ref 304, we accept this latter value. We also note that Sherfey and Brenner[309] employed electrochemical calorimetry to obtain $\Delta H^\circ = -7.5 \pm 1.5$ kcal for the reaction

$$W(c) + 2OH^-(aq) + 2H_2O(liq) = WO_4^{2-}(aq) + 3H_2(g)$$

and thence $\Delta H_f^\circ \simeq -253._6$ kcal mol^{-1} for WO_4^{2-}(aq).

Whereas several routes were available to calculate thermodynamic properties of MoO_4^{2-}(aq), similar data for tungstates are comparatively scarce, and we are unable to present any reliable experimental values for ΔG_f° or S° for WO_4^{2-}(aq). From $K_{sp} = 1 \times 10^{-8}$ for $CaWO_4$(c)[75] and the ΔG_f° for $CaWO_4$(c) to be discussed later, we calculate $\Delta G_f^\circ = -223.5$ kcal mol^{-1} for WO_4^{2-}(aq) and thence $S^\circ = 26$ cal K^{-1} mol^{-1} for this ion. As this seems to be an unreasonably high entropy value, we prefer to estimate $S^\circ = (11)$ cal K^{-1} mol^{-1} and combine with the above ΔH_f° to find $\Delta G_f^\circ = -219$ kcal mol^{-1} for WO_4^{2-}(aq).

An alkaline tungstate solution contains monomeric WO_4^{2-}(aq), but on acidification complicated polymerization reactions occur. These reactions are not yet well understood. Equilibrium constants for postulated reactions are to be found in Sillén's compilations;[75,112] Kepert[310] has reviewed the literature up to 1961 and some later work has been discussed by Cotton and Wilkinson.[20]

Two recent investigations[311,312] are in general agreement on the equilibrium constant for the formation of the "paratungstate A" ion, $HW_6O_{21}^{5-}$(aq), for which the enthalpy of formation is also known.[313] However, these investigators[311,312] have come to quite different conclusions regarding other thermodynamic and kinetic characteristics of tungstate solutions, clearly showing that our knowledge of the properties of these solutions is far from complete. We therefore limit our listings in Table V to $HW_6O_{21}^{5-}$(aq). Stopped-flow kinetic experiments[314] have shown that $HW_6O_{21}^{5-}$(aq) is formed rapidly (within ~1 s) upon acidification of a tungstate solution and that the intermediate species are not well defined.

Further acidification of solutions containing polytungstate ions leads to depolymerization reactions in which cationic species are formed. Sillén[75,112] quotes some equilibrium constants for such reactions; Nazarenko and Poluektova[315] have investigated the dissociation constant of tungstic acid in solutions of varying ionic strength.

Sillén[75,112] cites an impressive number of determinations of solubility products and ionization constants for various heteropolytungstates. We call attention to recent determinations of reduction potentials,[316] an acid dissociation constant,[317] and heats of solution and neutralization[318,319] for some heteropolytungstates. Weakley[320] has described the preparation of some polytungstate ions containing two heteroatoms and has also measured some redox potentials and stability constants related to such species.

O'Hare et al.[209] cite $\Delta H_f^\circ = -383.2$ kcal mol^{-1} for Li_2WO_4(c), but we cannot assess the reliability of this value.

King and Weller[321] have made C_p measurements on Na_2WO_4(c), leading to $S^\circ = 38.5 \pm 0.5$ cal K^{-1} mol^{-1} as adopted in our Table V. Another extrapolation of the specific heat from 51 to 0 K has led to[151] $S^\circ = 38.32$ cal K^{-1} mol^{-1}. The calorimetric measurements of Koehler et al.[215] [recalculated with our adopted ΔH_f° for H_2WO_4(c)] lead to $\Delta H_f^\circ = -369.5$ kcal mol^{-1} for Na_2WO_4(c), and those of Graham and Hepler[322] give $\Delta H_f^\circ = -369.7$ kcal mol^{-1}. We adopt the mean value, $\Delta H_f^\circ = -369.6$ kcal mol^{-1}, for Na_2WO_4(c).

The ΔH_f° values listed in Table V for $Na_2W_2O_7$(c) and $Na_2W_4O_{13}$(c) are recalculated by us from the work of Koehler et al.[215] Our ΔG_f° for $Na_2W_2O_7$(c) is calculated from the adopted ΔH_f° and the third law entropy,[218a] $S^\circ = 60.8$ cal K^{-1} mol^{-1}.

We cannot account for any experimental values of ΔH_f° for K_2WO_4(c), Rb_2WO_4(c), or Cs_2WO_4(c). O'Hare et al.[209] cite $\Delta H_f^\circ = -377.9$ kcal mol^{-1} for K_2WO_4(c) and have reported estimated ΔH_f° values for Rb_2WO_4(c) and Cs_2WO_4(c).

Yamdagni, Pupp, and Porter[217] have reported the value we list for ΔH_f° (at 0 K) for Li_2WO_4(g), while the values listed for ΔH_f° for K_2WO_4(g) and $KHWO_4$(g) are due to Farber and Srivastava.[220]

The NBS 270-6 gives $\Delta H_f^\circ = -366.3$ kcal mol^{-1} and $S^\circ = 24.18$ cal K^{-1} mol^{-1} for $MgWO_4$(c). The entropy is from C_p measurements by King and Weller.[321] The high-temperature emf data of Rezukhina and Levitskii[323] give $\Delta H_f^\circ = -362.3$ kcal mol^{-1} (third law analysis[151]) or $\Delta H_f^\circ = -372.7$ kcal mol^{-1} (second law analysis[151]). Our recalculation of calorimetric data from Navrotsky and Kleppa[324] leads to $\Delta H_f^\circ = -362.7$ kcal mol^{-1}. We consider this last value to be the best one and adopt it in Table V. Combination of this ΔH_f° with the S° leads to our ΔG_f°.

For $CaWO_4$(c), $S^\circ = 30.21$ cal K^{-1} mol^{-1} is listed in NBS 270-6, in close agreement with the value from King and Weller.[321] Barany's calorimetric data[211] permit us to calculate $\Delta H_f^\circ = -392.2$ kcal mol^{-1} for $CaWO_4$(c). The ΔH_f° value in NBS 270-6 is 1 kcal mol^{-1} more negative, partly due to different choices of ΔH_f° for H_2WO_4(c). From our ΔH_f° value and the S° value we obtain $\Delta G_f^\circ = -366.7$ kcal mol^{-1}. The solubility product for $CaWO_4$(c) is then calculated to be $K_{sp} = 4 \times 10^{-12}$, as compared to an old value,[75] $K_{sp} = 1 \times 10^{-8}$, based on conductance measurements.

NBS 270-6 lists $\Delta H_f^\circ = -391.9$ kcal mol^{-1}, $\Delta G_f^\circ = -366$ kcal mol^{-1}, and $S^\circ = 33$ cal K^{-1} mol^{-1} for $SrWO_4$(c). The ΔG_f° value is the same as reported by Levitskii and Rezukhina[325] from high-temperature emf data, but these latter authors report $\Delta H_f^\circ = -393.5$ kcal mol^{-1} and $S^\circ = 28.3$ cal K^{-1} mol^{-1} for $SrWO_4$(c). This latter entropy seems to be unreasonably small. As the experimental ΔG_f° is more likely to be correct than the derived ΔH_f°, we follow NBS 270-6 and adopt $\Delta G_f^\circ = -366$ kcal mol^{-1}, $S^\circ = (33)$ cal K^{-1} mol^{-1}, and calculate $\Delta H_f^\circ \simeq -391$ kcal mol^{-1}.

For $BaWO_4$(c), NBS 270-6 lists $\Delta H_f^\circ = -407$ kcal mol^{-1}, which is consistent with the results of Tammann and Westerhold, as cited by Bichowsky and Rossini.[45]

The NBS 270-6 lists ΔH_f° (at 0 K) for $MgWO_4$(g), $CaWO_4$(g), and $SrWO_4$(g), while NBS 270-4 lists ΔH_f° (at 0 K) for $SnWO_4$(g) and Sn_2WO_5(g). The values are all consistent with the results of Verhaegen et al.[222] We have recalculated their results, using our properties of WO_2(g) and WO_3(g), and list these recalculated values in Table V. The uncertainty in these ΔH_f° values is about ±10 kcal mol^{-1}.

Our calculations with the high-temperature data of Rezukhina et al.[326,327] lead to $\Delta H_f^\circ \simeq -317$ kcal mol^{-1} for $MnWO_4$(c). Two different calorimetric investigations[328] lead to $\Delta H_f^\circ = -311.9$ kcal mol^{-1} for $MnWO_4$(c), which is the value listed in NBS 270-4 and adopted for our Table V.

The ΔH_f° values listed in NBS 270-4 for $FeWO_4$(c), $FeWO_4{\cdot}$

$3H_2O(c)$, and $Fe_2(WO_4)_3{\cdot}8H_2O(c)$ are apparently derived from old measurements by Tammann and Westerhold, as cited by Bichowsky and Rossini.[45] We adopt $\Delta H_f° = -276$ kcal mol^{-1} for $FeWO_4(c)$ in Table V, but do not include $\Delta H_f°$ values for the other two compounds. The entropy of $FeWO_4(c)$ has recently been determined by Lyon and Westrum.[330] We adopt their $S° = 31.61$ cal K^{-1} mol^{-1}, in good agreement with the value in NBS 270-4, $S° = 31.5$ cal K^{-1} mol^{-1}, which is from Weller.[227]

The enthalpies of formation of $CoWO_4(c)$, $NiWO_4(c)$, $CuWO_4(c)$, $ZnWO_4(c)$, and $CdWO_4(c)$ can all be calculated from the measured heats of reaction of the corresponding oxides with $WO_3(c)$ at 970 K.[324] We have recalculated $\Delta H_f°$ for $CoWO_4(c)$, using C_p data from Yakovleva and Rezukhina,[327] and for the other compounds estimated that the enthalpy of reaction is 0.2 kcal mol^{-1} less negative at 298 K than it is at 970 K to obtain the $\Delta H_f°$ values listed in our Table V. We note that the data from Tammann and Westerhold (as cited by Bichowsky and Rossini[45]) lead to $\Delta H_f° = -251$ kcal mol^{-1} for $CuWO_4(c)$ instead of -245.5 kcal mol^{-1} as chosen by us. NBS 270-4 lists $\Delta H_f° = -264$ kcal mol^{-1} for $CuWO_4(c)$, from a source unknown to us. An older calorimetric[328] $\Delta H_f°$ for $NiWO_4(c)$ is 1.8 kcal mol^{-1} more negative than our adopted value.

The value in Table V for $\Delta H_f°$ of $ZnWO_4(c)$ agrees well with the value deduced from high-temperature equilibrium data, as discussed by Lyon and Westrum.[329] The C_p measurements of Lyon and Westrum[330] on $ZnWO_4(c)$ lead to $S° = 28.34 \pm 0.1$ cal K^{-1} mol^{-1}. From the calculated $\Delta G_f° = -268.5$ kcal mol^{-1}, the solubility product of $ZnWO_4(c)$ is found to be $K_{sp} = 2.5 \times 10^{-11}$. We are not aware of any experimental determination of this quantity.

For $PbWO_4(c)$ the NBS 270-4 lists $S° = 40.2$ cal K^{-1} mol^{-1}, which is the third law value found by Weller and Kelley.[228] The $\Delta H_f° = -277.0$ kcal mol^{-1} for $PbWO_4(c)$ has been reported by Zharkova and Gerasimov[331] on the basis of earlier high-temperature equilibrium results. The solubility product is[332] $K_{sp} = 8.6 \times 10^{-17}$. We cannot assess the reliability of any of these values. They lead to an improbable $S° = 32$ cal K^{-1} mol^{-1} for $WO_4^{2-}(aq)$ [using the quoted $S°$ for $PbWO_4(c)$ and data for $Pb^{2+}(aq)$ from NBS 270-3]. If we take our adopted $S° = (11)$ cal K^{-1} mol^{-1} for $WO_4^{2-}(aq)$ and $\Delta H_f° = -277.0$ kcal mol^{-1} for $PbWO_4(c)$, we calculate $K_{sp} = 2.5 \times 10^{-21}$ and $\Delta H°(ppt) = -20.1$ kcal mol^{-1}. If we instead begin with $K_{sp} = 8.6 \times 10^{-17}$, then $\Delta H_f° = -270.8$ kcal mol^{-1} and $\Delta H°(ppt) = -13.9$ kcal mol^{-1} are calculated. As this last value is closer to the heats of precipitation of $PbMoO_4(c)$, $CdWO_4(c)$, $ZnWO_4(c)$, and $CuWO_4(c)$ than the more exothermic heat of precipitation is, we hesitantly adopt $\Delta H_f° = -271$ kcal mol^{-1} for $PbWO_4(c)$, noting that the discrepancies discussed here make a calorimetric determination of the $\Delta H_f°$ for $PbWO_4(c)$ desirable.

The enthalpy of solution of $Ag_2WO_4(c)$ has been determined as 14.7 kcal mol^{-1} from calorimetric measurements[322] (in which the experimental conditions were chosen to avoid the formation of polytungstates), and as 12.1 kcal mol^{-1} from the temperature variation of the solubility product.[333] We adopt the former heat of solution, and estimate $S° = (53)$ cal K^{-1} mol^{-1}. We can then calculate for $Ag_2WO_4(c)$: $\Delta H_f° = -220.7$ kcal mol^{-1}, $\Delta G_f° = -198._9$ kcal mol^{-1}, $K_{sp} = 4 \times 10^{-13}$, and also

$$Ag_2WO_4(c) + 2e^- = 2Ag(c) + WO_4^{2-}(aq) \qquad E° = 0.434 \text{ V}$$

Pan's[333] electrochemical measurements have led to $K_{sp} = 5 \times 10^{-12}$ and $E° = 0.466$ V. The differences between the values calculated by us and the experimental values exceed the stated uncertainties. A third law entropy for $Ag_2WO_4(c)$ is needed.

The free energies of formation of lanthanum and neodymium tungstates have been investigated by emf methods at high temperatures.[334] We cannot make calculations to relate the published data to our standard state at 298 K.

H. Halides and Oxyhalides of Tungsten

Fluorine combustion calorimetry by O'Hare and Hubbard[335] has led to $\Delta H_f° = -411.5$ kcal mol^{-1} for $WF_6(g)$. This value, which is in excellent agreement with the results of two more recent calorimetric investigations,[336] is adopted in NBS 270-4 and our Table V. We also follow NBS 270-4 in adopting $S° = 81.49$ cal K^{-1} mol^{-1} from statistical calculations cited in the JANAF tables.[151] Our calculated $\Delta G_f° = -390.1$ kcal mol^{-1} is consistent with the listed $\Delta H_f°$ and $S°$ values.

The NBS 270-4 gives $\Delta H_f° = -417.7$ kcal mol^{-1} and $S° = 60.1$ cal K^{-1} mol^{-1} for $WF_6(liq)$, values that are consistent with the above $\Delta H_f°$ for $WF_6(g)$ and vapor pressures from Cady et al.[240,337] We adopt these values, which lead to $\Delta G_f° = -390.0$ kcal mol^{-1} for $WF_6(liq)$.

The mass spectrometric investigation by Zmbov, Uy, and Margrave[248] leads to our adopted $\Delta H_f° \simeq -215$ kcal mol^{-1} for $WO_2F_2(g)$ and $\Delta H_f° \simeq -316$ kcal mol^{-1} for $WOF_4(g)$. Burgess et al.[338] have reported a calorimetric $\Delta H_f° = -359$ kcal mol^{-1} for $WOF_4(c)$. The enthalpy of sublimation of $WOF_4(c)$ reported by Cady and Hargreaves,[247] $\Delta H°(subl) = 17._0$ kcal mol^{-1}, cannot be used to calculate $\Delta H_f°$ for $WOF_4(g)$, as it has been shown[246] that oligomeric species are formed in the gas phase over $WOF_4(c)$. We combine the heats of formation with estimated entropies to calculate the free energies of formation in Table V.

Calorimetric measurements[336] lead to $\Delta H_f° = -345.9$ kcal mol^{-1} for $WF_5(c)$ on the basis of our adopted value of $\Delta H_f°$ for $WF_6(g)$. The enthalpy of sublimation has been determined,[339] leading to our adopted $\Delta H_f° = -1316$ kcal mol^{-1} for $(WF_5)_4(g)$.

Dittmer et al.[340] have made equilibrium experiments at various temperatures leading to $\Delta H_f°$ values for the lower valent gaseous tungsten fluorides. The enthalpy of formation of $WF_4(g)$ is probably determined with good accuracy from these experiments, while the uncertainties in the values we list for $WF(g)$, $WF_2(g)$, and $WF_3(g)$ probably are considerable.

The enthalpies of formation listed in Table V for the tungsten chlorides are mainly derived from measurements by Shchukarev et al.[249] Solution calorimetry leads to $\Delta H_f° = -142._9$ kcal mol^{-1} for $WCl_6(c,\alpha)$, based on our adopted $\Delta H_f°$ for $WO_3{\cdot}H_2O(c)$. Three investigations, cited in the JANAF tables,[151] are in good agreement with the enthalpy of sublimation of $WCl_6(c,\alpha)$ and thence $\Delta H_f° = -118._0$ kcal mol^{-1} for $WCl_6(g)$.

The uncertain $\Delta H_f°$ values listed in Table V for $WCl_5(c)$, $WCl_5(g)$, $(WCl_5)_2(g)$, $WCl_4(c)$, and $WCl_4(g)$ are all derived from the equilibrium measurements by Shchukarev et al.,[249] while $\Delta H_f°$ for $WCl_2(c)$ is from combustion calorimetry.[249]

There are two calorimetric determinations of the enthalpy of reaction of $WO_2Cl_2(c)$ with aqueous hydroxide. We calculate $\Delta H_f° = -187.0$ kcal mol^{-1} from Shchukarev's data[249] and $\Delta H_f° = -190.6$ kcal mol^{-1} from Oppermann's data.[341] We adopt $\Delta H_f° = -189$ kcal mol^{-1} for $WO_2Cl_2(c)$. The enthalpy of sublimation is 26 kcal mol^{-1} (at 298 K) according to a third law recalculation of the data of Shchukarev and Suvorov as cited in the JANAF tables[151] or 28 kcal mol^{-1} according to Oppermann.[341] We adopt the mean value and then obtain $\Delta H_f° = -162$ kcal mol^{-1} for $WO_2Cl_2(g)$.

For $WOCl_4(c)$ the NBS 270-4 lists $\Delta H_f° = -161.7$ kcal mol^{-1}, in good agreement with the results of Shchukarev et al.[249] Oppermann's data[341] lead to $\Delta H_f° = -172.4$ kcal mol^{-1}, which we adopt, as this value seems to be more reasonable in relation to the $\Delta H_f°$ of $MoOCl_4(c)$.

It has been observed that the enthalpy of sublimation of

$WOCl_4$(c) varies considerably with the temperature,[342] which might partly explain the difference between the value we calculate from the data of Enghag and Staffansson[342] [ΔH°(sublimation) = $19._0$ kcal mol^{-1}] and that calculated[151] from the data of Shchukarev and Suvorov [ΔH°(subl) = 23.4 kcal mol^{-1}]. We weight the more recent value more heavily, adopt ΔH°(subl) = $20._0$ kcal mol^{-1}, and calculate ΔH_f° = $-152._4$ kcal mol^{-1} for $WOCl_4$(g).

An apparently reliable S° = 92.1 cal K^{-1} mol^{-1} for $WOCl_4$(g) has been calculated from spectroscopically determined molecular parameters.[343]

Table V lists ΔH_f° = -165.9 kcal mol^{-1} for $WOCl_3$(c) from calorimetric measurements by Oppermann, Stöver, and Kunze[344] on the reaction between $WOCl_3$(c) and hydrogen peroxide in alkaline solution. We have used our adopted ΔH_f° value for Na_2WO_4(c) in this calculation, as well as for the corresponding calculations for WO_2Cl_2(c) and $WOCl_4$(c) described above.

Oppermann et al.[344] also calculate ΔH° = 32.5 kcal mol^{-1} of $WOCl_2$(c) for the reaction between $WOCl_3$(c) and $WOCl_2$(c) to form $WOCl_4$(g), whence ΔH_f° = -147 kcal mol^{-1} for $WOCl_2$(c). This equilibrium study also leads to S° = 110 ± 5 cal K^{-1} mol^{-1} for $WOCl_4$(g), in substantial disagreement with the value listed above, which casts suspicion also on the accuracy of the value quoted for ΔH_f° of $WOCl_2$(c).

Burgess et al.[338] have reported enthalpies of alkaline hydrolysis of WF_5Cl(liq) and WF_4Cl_2(liq), from which we calculate the ΔH_f° values listed in Table V for these compounds.

Shchukarev and Kokovin[345] have made calorimetric measurements on the enthalpy of solution of WBr_6(c) and WBr_5(c), leading to our adopted ΔH_f° values. The values in NBS 270-4 for these compounds are apparently also derived from this source. Shchukarev et al.[346] have studied the sublimation of WBr_5(c). Our interpretation of their results leads to ΔH_f° = -52 kcal mol^{-1} for WBr_5(g). The uncertainty in this value overlaps the value given in NBS 270-4, ΔH_f° = -55.4 kcal mol^{-1}.

Two calorimetric investigations[347,348] are in good agreement with ΔH_f° = -170.2 kcal mol^{-1} for WO_2Br_2(c). The enthalpy of sublimation,[348-350] 36.5 ± 1.0 kcal mol^{-1}, leads to ΔH_f° = -133.7 kcal mol^{-1} for WO_2Br_2(g). Gupta[349] has studied the equilibria

$$WO_2(c) + Br_2(g) = WO_2Br_2(g)$$

and

$$WO_2I_2(g) + Br_2(g) = WO_2Br_2(g) + I_2(g)$$

with results that lead to ΔH_f° = -131 ± 2 kcal mol^{-1} for WO_2Br_2(g). We adopt ΔH_f° = $-133._0$ kcal mol^{-1} for WO_2Br_2(g). The entropy of WO_2Br_2(g) has been calculated by Gupta[349] from estimated molecular parameters.

From the heat of reaction of $WOBr_4$(c) with aqueous hydroxide as reported by Oppermann and Stöver[348] and by Shchukarev et al.,[347] we obtain ΔH_f° = $-131._8$ kcal mol^{-1} for $WOBr_4$(c). The value listed in NBS 270-4 is consistent with the results of the latter investigation.[347] We adopt ΔH°(subl) = 30.0 ± 0.5 kcal mol^{-1} as an average of three investigations[348-350] to obtain ΔH_f° = $-101._8$ kcal mol^{-1} for $WOBr_4$(g).

One calorimetric investigation by Oppermann et al.[351] leads to ΔH_f° = $-126._0$ kcal mol^{-1} for $WOBr_3$(c), as listed in Table V. They[351] have also studied the decomposition of $WOBr_3$(c) and calculated ΔH_f° for $WOBr_2$(c) from their data. As it has been suggested[352] that their measurements refer to nonequilibrium conditions, we have not included thermodynamic properties of $WOBr_2$(c) in Table V.

The reaction between $W(CO)_6$ and I_2 at 530 K has been studied calorimetrically by Virmani, Barnes, and Skinner.[263] The values of ΔH_f° for WI_2(c) and WI_3(c) listed in Table V are derived from their results, using our adopted ΔH_f° for $W(CO)_6$(c), which we discuss later. As the products formed in the calorimetric reaction are not well defined, the uncertainties in the listed ΔH_f° values are fairly large (~3 kcal mol^{-1}).

Gupta[349,353] has investigated the thermal stabilities of tungsten oxyiodides and discussed earlier work. On the basis of his results and earlier data quoted by him, we adopt ΔH_f° = $-145._4$ kcal mol^{-1} for WO_2I_2(c), ΔH_f° = $-102._3$ kcal mol^{-1} for WO_2I_2(g), and S° = (89) cal K^{-1} mol^{-1} for WO_2I_2(g). The entropy is calculated from estimated molecular parameters.[353] The measurements also permit calculation of ΔH_f° = -137 ± 5 kcal mol^{-1} for WO_2I(c).

I. Other Tungsten Compounds

The enthalpies of formation of the gaseous calcium and strontium tungstites can be deduced from the mass spectrometric results of Verhaegen et al.[222] We list ΔH_f° (at 0 K) $\simeq$ -118 kcal mol^{-1} for $CaWO_3$(g), but omit $SrWO_3$(g), as the values for this compound seem to be erroneous.

The enthalpies of formation of KWF_6(c), $KWCl_6$(c), and K_2WCl_7(c), listed in our Table V, have been determined calorimetrically.[354,355] Kudryashova et al.[356] have reported enthalpies of combustion and alkaline oxidative hydrolysis for the compounds $M_3W_2Cl_9$(c), where M = K, Rb, or Cs. We calculate ΔH_f° = -524 kcal mol^{-1} or -536 kcal mol^{-1} for $K_3W_2Cl_9$(c) from the two experiments, using our adopted ΔH_f° values for K_2WO_4(c), WCl_5(c), and WCl_6(c). Our listed ΔH_f° values for the other two compounds are calculated from the results of the hydrolysis experiments. Although it is possible to use the bomb calorimetric results for calculation of ΔH_f° values for Rb_2WO_4(c) and Cs_2WO_4(c), the discordant ΔH_f° values listed above for $K_3W_2Cl_9$(c) indicate that the errors are too great to make such calculated ΔH_f° values useful.

Our Table V also includes ΔH_f° values for $WF_5(OMe)$(c), *cis*-$WF_4(OMe)_2$(liq), and *cis*-$WF_2(OMe)_4$(c), where OMe denotes the methoxide group. These enthalpies have been determined via alkaline hydrolysis.[338]

Emf measurements[357] on the equilibrium

$$WS_2(c) + 2H_2(g) = W(c) + 2H_2S(g)$$

have led to ΔH_f° = -54 kcal mol^{-1} and S° = 29 cal K^{-1} mol^{-1} for WS_2(c).

The enthalpies of formation of the tungsten carbides have been determined by combustion calorimetry. Our adopted ΔH_f° = -6.3 kcal mol^{-1} for W_2C(c) is from Mah,[273] while ΔH_f° = -9.6_3 kcal mol^{-1} for WC(c) is the mean of the values from Mah[273] and from McGraw, Seltz, and Snyder.[358]

For $W(CO)_6$(c) we adopt the same value as listed in NBS 270-4, ΔH_f° = -227.9 kcal mol^{-1}, calculated from the heat of combustion of $W(CO)_6$(c) reported by Cotton, Fischer, and Wilkinson.[173] These authors[173] also quote from earlier measurements the enthalpy of sublimation, 17.7 kcal mol^{-1}. We calculate ΔH_f° = -210.2 kcal mol^{-1} for $W(CO)_6$(g). We are not able to account for the value (-208.3 kcal mol^{-1}) listed in NBS 270-4, which corresponds to 19.6 kcal mol^{-1} for the enthalpy of sublimation.

Virmani, Barnes, and Skinner[263] have recently proposed ΔH_f° = -229.0 ± 0.8 kcal mol^{-1} for $W(CO)_6$(c). This value has not been considered here, as it is based on calorimetric work that (as far as we know) is not yet published.

The most important W(IV) complex is the stable octacyanide, $W(CN)_8{}^{4-}$. Baadsgaard and Treadwell[359] have made measurements leading to

$$W(CN)_8{}^{3-} + e^- = W(CN)_8{}^{4-} \qquad E^\circ = 0.46\ V$$

Activity coefficients of $K_4W(CN)_8$(aq) have been reported.[360]

Chart's recent review[166] of thermodynamic properties of silicides also covers tungsten and we agree with his analysis, leading to our adopted $\Delta H_f°$ and $S°$ values for WSi_2(c) and W_5Si_3(c). The listed free energies are consistent with the tabulated $\Delta H_f°$ and $S°$ values. The only value listed in NBS 270-4 for these compounds is $\Delta H_f° = -22$ kcal mol^{-1} for WSi_2(c), which agrees with our selected value.

High-temperature equilibrium measurements by Opalovskii et al.[361] lead to our listed values of $\Delta H_f°$ and $S°$ for WTe_2(c), from which we calculate $\Delta G_f°$.

The thermal decomposition of some potassium peroxotungstates has been studied, but we are not able to calculate any $\Delta H_f°$ values from the published data.[362]

Morozova and Ovcharova[363] have prepared a series of sodium–tungsten bronzes, Na_xWO_3 with $0.4 < x < 0.8$, and demonstrated that the enthalpy of formation is a linear function of x. Their values are in reasonable agreement with the enthalpies of formation of $Na_{0.53}WO_3$ and $Na_{0.77}WO_3$ reported by Dickens and Neild.[364] The values listed in our Table V for $Na_{0.679}WO_3$(c) are also taken from Dickens and Neild.[364] Dickens et al.[365] have reported the $\Delta H_f°$ values for $H_{0.18}WO_3$(c), $H_{0.35}WO_3$(c), and $(NH_4)_{0.25}WO_3$(c) that we adopt.

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IV. Appendix

In this Appendix we call attention to some results that have become available to us since the main body of this review was completed.

Measurements by Kim and Belton[366] lead to properties of CrO_3(g) that differ from those listed in Table I. They[366] also provide information about CrO_2OH(g). Further measurements and calculations by Sano and Belton[367] complement results already cited for CrO_2Cl_2(g).

Jones et al.[368] have reported solubilities of Ag_2CrO_4(c) from 5 to 80 °C.

O'Hare et al.[369] have made calorimetric measurements leading to $\Delta H_f°$ values for Cs_2CrO_4(c), $Cs_2Cr_2O_7$(c), $Cs_2Mo_2O_7$(c), $MoC_{0.502}$(c), and $MoC_{0.651}$(c).

High-temperature properties of Na_2CrO_4(c and liq) and Na_2WO_4(c and liq) have been reported.[370]

Enthalpies of solution have been reported[371] for $Pr_2(CrO_4)_3\cdot 7H_2O$(c), $Pr_2(CrO_4)_3$(c and amorph), and some related compounds.

New calorimetric measurements leading to $\Delta H_f°$ values for $PbCrO_4$(c), $PbMoO_4$(c), and $PbWO_4$(c) have been made.[372]

High-temperature emf results[373] are in reasonable agreement with our tabulated properties of $CrCl_2$(c) and $CrCl_3$(c).

New results on vaporization of $CrCl_2$(c) have been reported by Ratykovskii et al.,[374] leading to possibly improved properties of $CrCl_2$(g) and to new properties for gaseous dimers and trimers.

Aits and Schäfer[375] have reported high-temperature equilibrium results for formation of $CrAl_2Cl_8$(g).

New calorimetric measurements[376] have led to $\Delta H_f° = -60.0 \pm 1.5$ kcal mol^{-1} for Cr^{3+}(aq), as compared to -67.9 kcal mol^{-1} from NBS 270-4 and -57 kcal mol^{-1} previously adopted here. New $\Delta H_f°$ values are also reported[376] for the inner-sphere complexes CrF^{2+}(aq), $CrCl^{2+}$(aq), $CrBr^{2+}$(aq), and $CrSO_4{}^+$(aq).

Results of equilibrium measurements on chromium hydride have been reported.[377]

Vecher et al.[378] have reported high-temperature emf results for formation of CrSb(c) and $CrSb_2$(c).

Rosén[379] has described new high-temperature emf measurements involving $CuCrO_2$(c), with results that appear superior to those[152] that we rejected earlier.

In an important paper that has significance beyond this particular group of elements, Benz, Elliot, and Chipman[380] have reported results of their measurements on the system Fe–Cr–C.

Pittam et al.[381] have reported new measurements leading to $\Delta H_f°$ for $Cr(CO)_6$(c) in excellent agreement with the value we tentatively adopted earlier. From the same laboratory we also have results[382] of new statistical thermodynamic calculations of properties of $Cr(CO)_6$(g), $Mo(CO)_6$(g), and $W(CO)_6$(g).

In the main body of this review we distinguished between $CaMoO_4$(c) and $CaMoO_4$(ppt). It now appears[383] well established that the substance we represented by $CaMoO_4$(ppt) is actually $CaMoO_4\cdot \frac{1}{2}H_2O$(c), which requires revisions of some of our thermodynamic calculations.

Calorimetric measurements have led[384] to $\Delta H_f°$ for $Cs_2Mo_2O_7$(c) and to[385] high-temperature properties of Cs_2MoO_4(c). We also have new low-temperature heat capacities and derived thermodynamic properties for $FeMoO_4$(c).[386]

Johnson[387] has reported results of his study of vaporization of Cs_2MoO_4(c and liq) and Na_2MoO_4(liq).

Kiwia and Westrum[388] have measured heat capacities and evaluated reliable third law entropies for $MoSe_2$(c), $MoTe_2$(c), and various chlorides and oxychlorides of molybdenum. Use of these entropies with equilibrium results cited earlier will lead to significantly improved thermodynamic properties for several compounds.

DSC measurements by Kigoshi[389] lead to ΔH values for vaporization and decomposition of $NOMoF_4$(c).

McKnight and Haight[390] have extended and improved on earlier work[285] on association of $Mo(CN)_8{}^{4-}$(aq) with H^+(aq) and Fe^{3+}(aq).

Chart[391] has published an account of his experimental investigations and thermodynamic analysis of the Mo–Si system.

High-temperature emf investigations have led to information about thermodynamic properties of tungstates of scandium,[392] manganese,[393] nickel,[393] strontium,[394] and yttrium.[395]

Gusarov et al.[396] have reported results of their mass spectrometric investigation of WF_5, with related thermodynamic calculations.

Statistical calculations[397] have led to $S°_{298} = 73.22$ cal K^{-1} mol^{-1} for WCl_6(g), as compared to $S°_{298} = (100)$[151] that was listed in Table V.

Free energies based on emf measurements[398] and heat capacities based on DTA measurements[399] have been reported for sodium tungsten bronzes, Na_xWO_3.

Results of new calorimetric measurements[400] lead to a $\Delta H_f°$ for $W(CO)_6$(c) that is probably better than our previously selected value.

V. References and Notes

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