A MASS SPECTROMETRIC INVESTIGATION OF MOLYBDENUM, TUNGSTEN, VANADIUM AND CHROMIUM ADDITIVES IN ALKALI-SEEDED H_2-O_2 FLAMES

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A MASS SPECTROMETRIC INVESTIGATION OF ADDITIVES IN ALKALI SEEDED H_2/O_2 FLAMES

PART I: Reactions Involving Tungsten and Molybdenum with Potassium-Seeded H_2/O_2 Flames

PART II: Reactions Involving Vanadium and Chromium with Potassium-Seeded H_2/O_2 Flames

by

Milton Farber and R. D. Srivastava

ABSTRACT

Studies have been made for the reactions involved with molybdenum, tungsten, vanadium and chromium additives in hydrogen-oxygen flames seeded with potassium. The flame was atmospheric and a molecular beam of the "frozen" species was introduced into the mass spectrometer through a four-stage differential pumping system operating from 1 to 10^{-11} atm.

Part I presents thermodynamic data for molybdenum and tungsten compounds obtained by a study of the reactions

$$K(g) + H_2MoO_4(g) = KHMoO_4(g) + H(g)$$

$$2K(g) + H_2MoO_4(g) = K_2MoO_4(g) + 2H(g)$$

$$K(g) + H_2WO_4(g) + KHWO_4(g) + H(g)$$

and

$$2K(g) + H_2WO_4(g) = K_2WO_4(g) + 2H(g)$$

Heats of formation, ΔH_{f298K}, obtained for the species $KHMoO_4(g)$, $K_2MoO_4(g)$, $KHWO_4(g)$ and $K_2WO_4(g)$ were -243.0 ± 5, -272.5 ± 5, -257.4 ± 4 and -278.2 ± 5 kcal/mole, respectively.

Part II presents results obtained by a study of the reactions

$$K(g) + H_2VO_3(g) + KHVO_3(g) + H(g)$$

$$2K(g) + H_2VO_3(g) = K_2VO_3(g) + 2H(g)$$

$$K(g) + H_2CrO_4(g) = KHCrO_4(g) + H(g)$$

and

$$2K(g) + H_2CrO_4(g) = K_2CrO_4(g) + 2H(g).$$

Heats of formation, ΔH_{f298K}, obtained for the K substituted compounds were -173.2 ± 5, -203.8 ± 5, -216.9 ± 5 and -249.0 ± 5 kcal/mole for $KHVO_3(g)$, $K_2VO_3(g)$ $KHCrO_4(g)$, and $K_2CrO_4(g)$, respectively.

PART I

REACTIONS INVOLVING TUNGSTEN AND MOLYBDENUM WITH POTASSIUM-SEEDED H_2/O_2 FLAMES

INTRODUCTION

High temperature flames have been employed successfully to establish chemical reaction mechanisms and to obtain equilibrium data.[1-5] Previous work[4,5] on the effects of molybdenum and tungsten compounds in $H_2/O_2/N_2$ flames containing alkali metals resulted in thermochemical data for the negative ions WO_3^-, HWO_4^-, MoO_3^- and the compounds $KHWO_4$, and $KHMoO_4$. In these experiments concentrations of free potassium atoms were measured spectroscopically by absorption; free electron concentrations were measured by the microwave cavity resonance method; positive ion concentrations were determined with an electrostatic probe; and negative ions were identified with the mass spectrometer. No thermochemical data concerning gaseous K_2WO_4 and K_2MoO_4 has been publsihed.

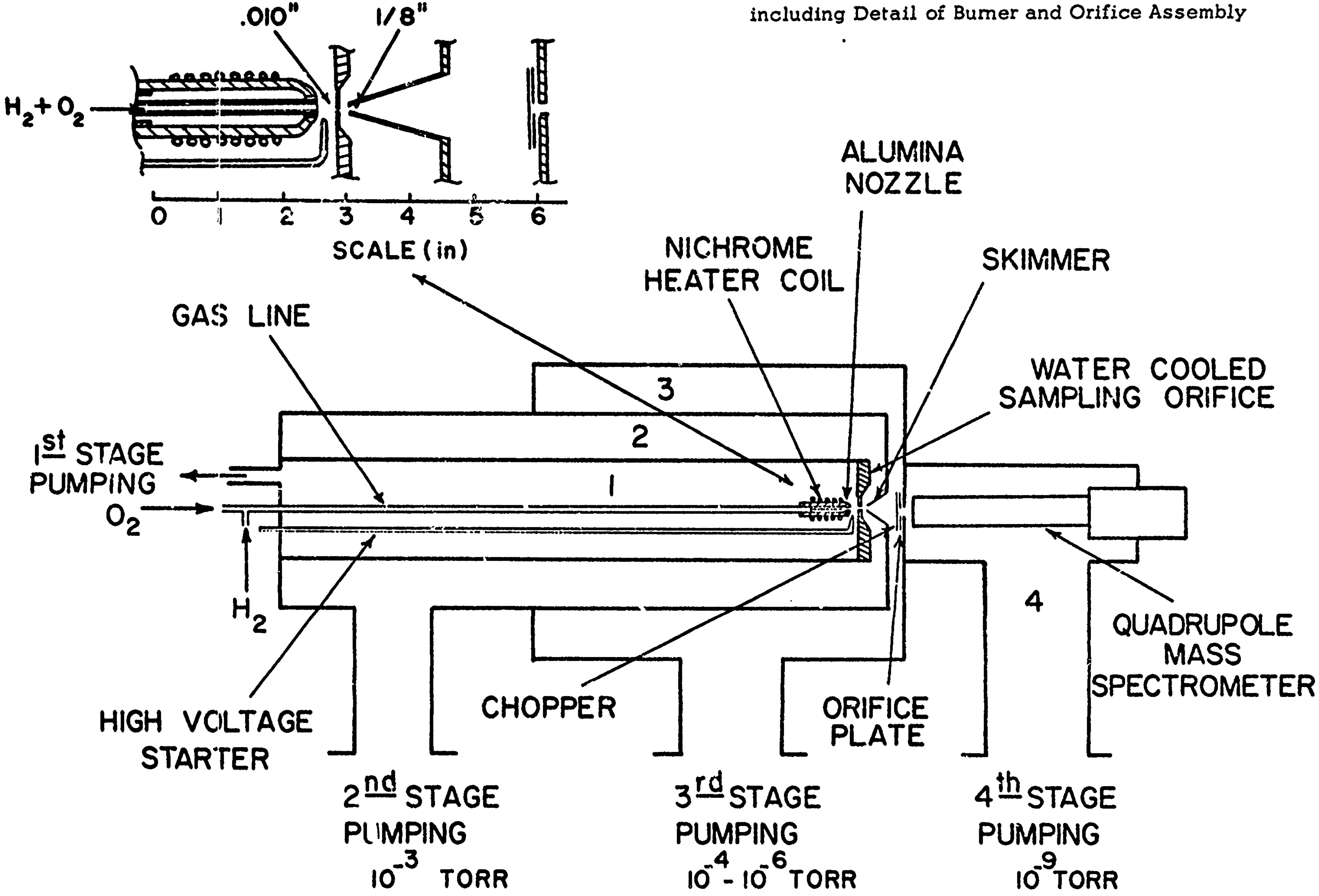
Results of a mass spectrometric study of the formation of stable compounds by addition of tungsten or molybdenum to H_2/O_2 flames containing potassium are reported here.

EXPERIMENTAL APPARATUS AND PROCEDURES

To accomplish the operation of a flame at a pressure of one atmosphere and at the same time obtain the mass spectra of the combustion "frozen" species produced in the atmospheric flame required the construction and assembly of a four-stage differentially pumped vacuum system. This system provided a pressure variation from one atmosphere in the flame to 10^{-11} atmospheres at the mass spectrometer. The four-stage differential vacuum system is shown schematically in Fig. 1. A brief technical description of the apparatus is presented below.

Burner and First Stage. A unique feature of the system was the placement of the sampling orifice to the mass spectrometer inlet (within 3"). The burner was designed as an integral part of the system surrounded by two stages of pumping. In order to facilitate dismantling,

Fig. 1. Four-Stage Differentially Pumped Vacuum System including Detail of Burner and Orifice Assembly



modification and realignment of the burner and first two orifices (sampling orifice and molecular beam skimmer) the burner and orifice assembly was constructed as a demountable portable unit to be attached to the high vacuum pumping stages (which are large fixed facilities). The first stage was connected to a low capacity vacuum pump to achieve pressures below atmospheric. The first stage vacuum system was fabricated from 3" glass pipe and was mounted inside a 6" i.d. glass pipe T-section which was connected to the second stage of pumping. The flame was ignited by an electric spark and appropriate electrical leads and connections were provided. The burner was surrounded (except for a sight hole) by a copper tube to prevent localized overheating of the glass pipe by the flame. The 12" vacuum chamber (third stage) had a port through which the flame could be observed.

An H_2/O_2 burner was designed consisting of an outer alumina tube 3/8" o.d. by 1/4" i.d. and an inner stainless steel tube 1/16" i.d. through which H_2 and O_2 were passed. The refractory tube was electrically heated by means of a nichrome heater and acted as a reservoir for the potassium. Potassium vapor was introduced into the flame by vaporizing potassium iodide.

Ceramic orifices, such as alumina, were employed to prevent the plugging of the orifice with the metallic oxides produced in the flame. These orifices were heated directly with the flame to temperatures above the condensation temperature of the oxides, thus allowing the metallic oxides to escape through the orifice in the gaseous phase. The orifice was fitted between two copper plates, and water cooled.

Molybdenum or tungsten was introduced into the atmospheric H_2/O_2 flame in the form of the gaseous fluorides, MoF_6 or WF_6, which were pre-mixed with the O_2.

Second Stage and Molecular Beam Skimmer. The second stage of pumping consisted of a mechanical pump combined with a 6" diffusion pump. The second stage pumping station was connected to the 12" vacuum chamber (third stage) through 6" i.d. glass pipe, which was connected to the 6" T-section mentioned above.

Inside the 12" vacuum chamber the molecular beam skimmer was attached to the cover plate closing the end of the 6" glass pipe. The skimmer was a conical probe located within one mean-free-path of the sampling orifice (mean-free-path of N_2 at 10^{-2} mm is 0.5 cm) for the purpose of conducting a portion of the first expansion jet into a second chamber at a pressure less than 10^{-5} mm. The second orifice was sufficiently large to swallow any shock wave which could otherwise be formed at the cone tip. The skimmer was designed to form a molecular beam representative of the flame gases with a minimum of influence from collisions with surfaces. The skimmer had an exit diameter of 1.0". In addition, the tip of the skimmer cone was made of .001" brass foil presenting a very sharp edge to the supersonic gas flow.

Third Stage. The third stage was a 12" i.d. by 15" long stainless steel vacuum chamber connected to a mechanical pump combined with a 4" diffusion pump. Inside the vacuum chamber were the aperture plate and the mechanical chopper.

Fourth Stage. The fourth stage (also of stainless steel) was attached to the rear of the 12" vacuum chamber and was an integral part of that system. It was evacuated by a mechanical pump and a diffusion pump, nominally of 4" inlet diameter.

The third and fourth stages were interconnected through a 3/8" diameter hole. The mass spectrometer was of the quadrupole type, with its inlet aperture in a line-of-sight position with the other apertures. The mass spectrometer and beam chopper employed for these studies have been described previously.[6]

The ion species were identified by their masses, isotopic distributions and appearance potentials. The ionizing electron energy of 30 eV was used during the equilibrium measurements. The compounds studied were parent ions, and were not formed as a result of fragmentation.

The temperature of the flame was determined from a mass spectrometric analysis of the flame constituents and a calculation of the adiabatic temperature from the equilibrium species. In order to obtain a smoothly operating flame at a temperature high enough to prevent condensation of the metal oxides, an oxygen-rich mixture ratio was employed ($O_2/H_2 \sim 3/2$). This mixture ratio was employed for all experiments. The temperature of the flame was calculated to be 2300 ± 100°K.

RESULTS AND DISCUSSION

Molybdenum Additives in Potassium-Seeded Hydrogen-Oxygen Flames. Employing the procedures discussed previously, molybdenum in the form of the hexafluoride $MoF_6(g)$ was introduced in concentrations of 1 to 2% and mixed with the oxygen. The initial studies involved the reactions of the MoF_6 in the hydrogen-oxygen flame in the absence of the alkali metal.

The formation of HF was stoichiometric, and the concentration of the molybdenum oxides and molybdic acid agreed with the theoretical equilibrium values. The relative abundance of these species present in the hydrogen-oxygen flame at an average temperature of 2300°K can be seen from the mass spectrometer intensities (Fig. 2). The formation of molybdic acid is established from the equilibrium.

$$MoO_3(g) + H_2O(g) = H_2MoO_4(g) \qquad (1)$$

From the relative intensities a value of -3.0 kcal is obtained for the free energy at an average flame temperature of 2300 ± 100°K. Employing this free energy and JANAF thermochemical data[7] a value of -200 ± 5 kcal/mole is obtained for ΔH_{f298K} for $H_2MoO_4(g)$. This is in excellent agreement with the experimental thermodynamic data[8] based on transpiration experiments for $H_2MoO_4(g)$, yielding a value of -202.6 ± 0.3 kcal/mole for ΔH_{f298K}. This excellent agreement between the thermodynamic data obtained from atmospheric flame studies and those obtained from thermochemical experimentation indicates that high temperature flames may be used successfully to establish chemical reaction mechanisms and to obtain equilibrium data.

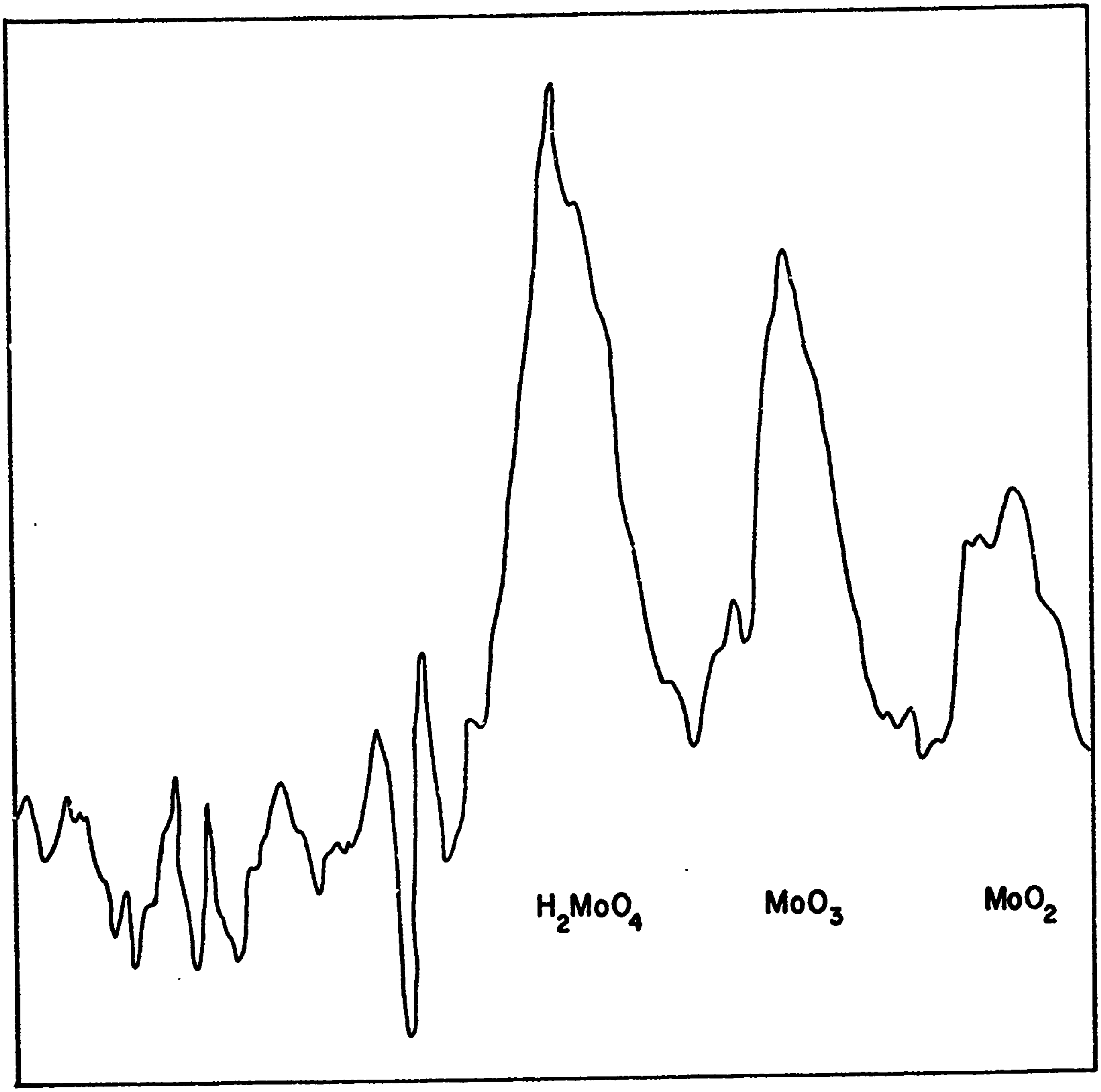


Fig. 2. Mass Spectrometer Intensities of the Principal Molybdenum Species Present in an Atmospheric H_2/O_2 Flame at an Average Temperature of 2300°K (molybdenum introduced as $MoF_6(g)$)

Upon completion of the studies involving the distribution of the molybdenum in the hydrogen-oxygen flame, experiments were performed to study the reactions occurring in the flame containing potassium. Potassium of concentrations between 0.1 to 0.5% was introduced into the hydrogen-oxygen flame through the vaporization of KI. The mass spectrometric studies showed two new compounds, $KHMoO_4$ and K_2MoO_4, in addition to the molybdenum compounds previously observed. The relative concentrations of these new species are shown in Fig. 3. From this figure it can be seen that the intensity of $KHMoO_4$ is nearly five times greater than that of H_2MoO_4, and that the intensity of K_2MoO_4 is nearly equal to that of H_2MoO_4.

The reactions involved included

$$K(g) + H_2MoO_4(g) = KHMoO_4(g) + H(g) \qquad (2)$$

$$2K(g) + H_2MoO_4(g) = K_2MoO_4(g) + 2H(g). \qquad (3)$$

Equilibrium intensities at an average flame temperature of 2300°K yielded a ΔG of -7.2 kcal/mole for reaction (2), and a ΔG of 1.5 kcal/mole for reaction (3). Since thermal data are not available for the species $KHMoO_4(g)$ and $K_2MoO_4(g)$, free energy functions for these two compounds were calculated by statistical mechanical methods. Estimated frequencies, bond angles, bond distances and quantum weights are presented in Tables I and II. The values thus obtained at 2300°K for the free energy functions for $KHMoO_4(g)$ and $K_2MoO_4(g)$ are 126.4 and 135.3 cal/deg/mole, respectively.

The third law heat of reaction was calculated to be $\Delta H_{r298K} =$ -8.7 ± 5.0 kcal for reaction (2), in good agreement with the value of -11 ± 10 kcal reported by Jensen and Miller.[5] A ΔH_{r298K} value of -7.5 ± 5.0 kcal was obtained for reaction (3). The stated uncertainties include errors involved in estimating the free energy functions.

Employing the calculated enthalpy functions, together with the experimental heats of reaction, values of -243.0 ± 5 and -272.5 ± 5

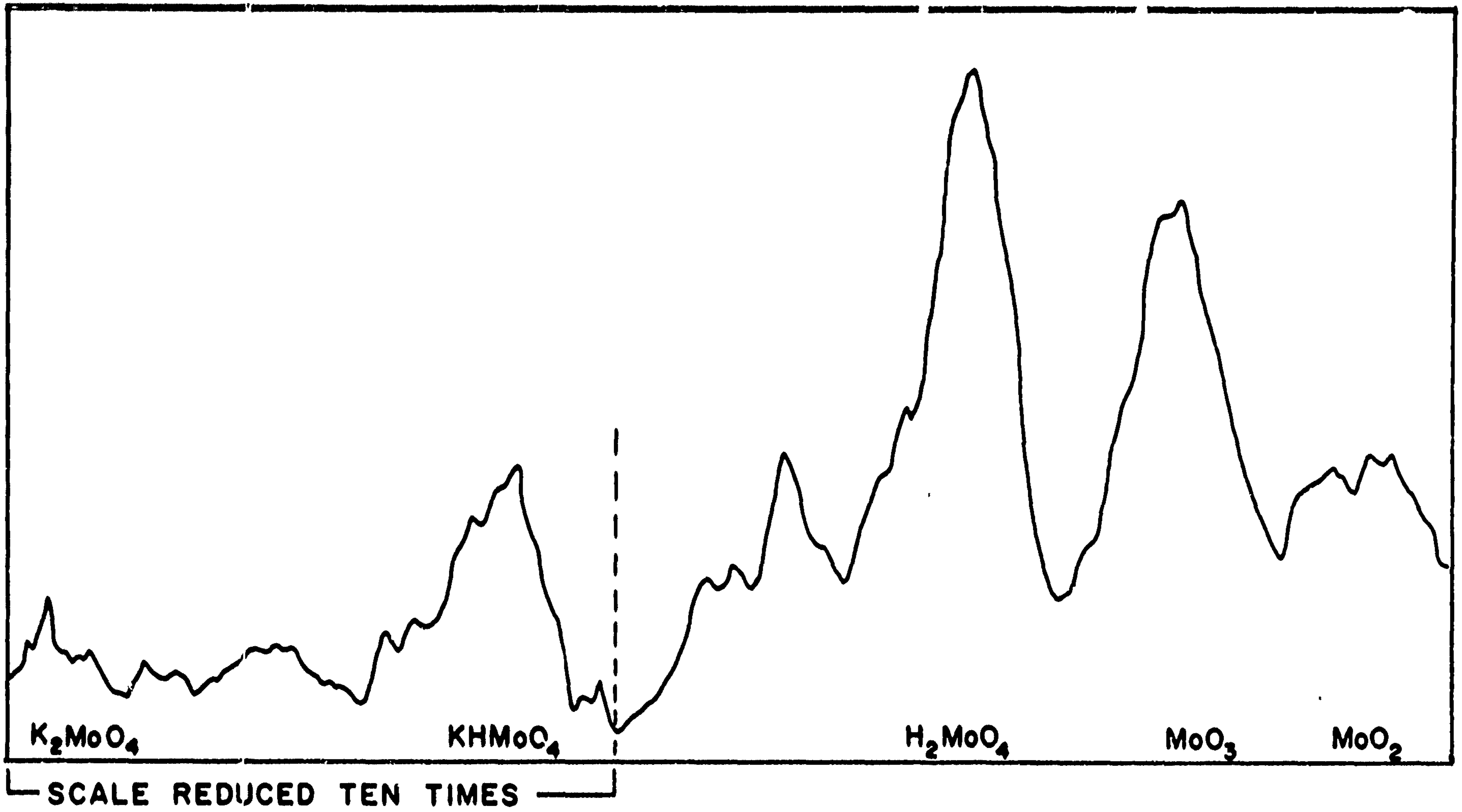


Fig. 3. Mass Spectrometer Intensities of Molybdenum Species Present in a Potassium-Seeded Atmospheric H_2/O_2 Flame at an Average Temperature of 2300°K (molybdenum introduced as $MoF_6(g)$ and potassium introduced as $KI(g)$.)

TABLE I

ESTIMATED VIBRATIONAL FREQUENCIES FOR POTASSIUM-MOLYBDENUM AND POTASSIUM-TUNGSTEN COMPOUNDS (cm^{-1})

$KMoO_4(g)$ and $KWO_4(g)$	$K_2MoO_4(g)$ and $K_2WO_4(g)$
218, 218	218, 218
360, 360, 360	360, 360, 360
896, 896, 896	896, 896, 896
944	944
250	150
400	150
100	75
1000	250
100	50
150	100

Note 1: The first g frequencies for each molecule were assumed to be identical to the MoO_4^-, or WO_4^- ion.(10)

Note 2: It was assumed that these molecules have the K or H atoms bound with two of the four terminal oxygen atoms, which are arranged tetrahedrally around the Mo or W atom, as in the crystalline Li_2WO_4.(11)

TABLE II

ESTIMATED BOND DISTANCES, ANGLES AND QUANTUM WEIGHTS FOR MOLYBDENUM SPECIES

r (Mo-O) = 1.80 Å

r (O-H) = 0.97 Å

r (O-K) = 2.50 Å

∠OMoO = 109.5°

∠OMoH and OMoK = 105.0°

Ground state quantum weight = 1

TABLE III

ESTIMATED BOND DISTANCES, ANGLES AND QUANTUM WEIGHTS FOR TUNGSTEN SPECIES

r (W-O) = 1.81 Å

r (O-H) = 0.97 Å

r (O-K) = 2.50 Å

∠OWO = 109.5°

∠OWH and OWK = 105.0°

Ground state quantum weight = 1

kcal/mole were obtained for ΔH_{f298K} of $KHMoO_4(g)$ and $K_2MoO_4(g)$, respectively.

Tungsten Additives in Potassium-Seeded Hydrogen-Oxygen Flames. The experimental procedure involving tungsten additives was similar to that employed for the molybdenum studies. Tungsten in the form of $WF_6(g)$ was initially introduced into a hydrogen-oxygen flame in the absence of the alkali metal. The relative intensities of tungsten oxides and tungstic acid are shown in Fig. 4. As in the case of molybdenum, the formation of HF was stoichiometric. The heat of formation of tungstic acid was obtained from a study of the reaction

$$WO_3(g) + H_2O(g) = H_2WO_4(g). \qquad (4)$$

Equilibrium intensity data for reaction (4) at the average flame temperature of 2300°K yielded a ΔG value of -31.0 kcal. Employing JANAF enthalpy functions, together with the experimental free energy, a value of -215 ± 5.0 kcal/mole was obtained for ΔH_{f298K} for $H_2WO_4(g)$. This may be compared to the experimental thermodynamic data[9] based on transpiration experiments, yielding a value of -216.5 kcal/mole for ΔH_{f298K}, $H_2WO_4(g)$.

As in the case of molybdenum, the reactions involving tungsten with hydrogen-oxygen flames containing potassium (concentrations of 0.1 to 0.5%) included the formation of potassium-tungsten compounds, $KHWO_4$ and K_2WO_4. The mass spectrometer intensities for these compounds are shown in Fig. 5. As can be seen, the $KHWO_4$ concentration is approximately 2 1/2 times that of the concentration of H_2WO_4, and approximately ten times greater than K_2WO_4.

The reactions involved included

$$K(g) + H_2WO_4(g) = KHWO_4(g) + H(g) \qquad (5)$$

$$2K(g) + H_2WO_4(g) = K_2WO_4(g) + 2H(g). \qquad (6)$$

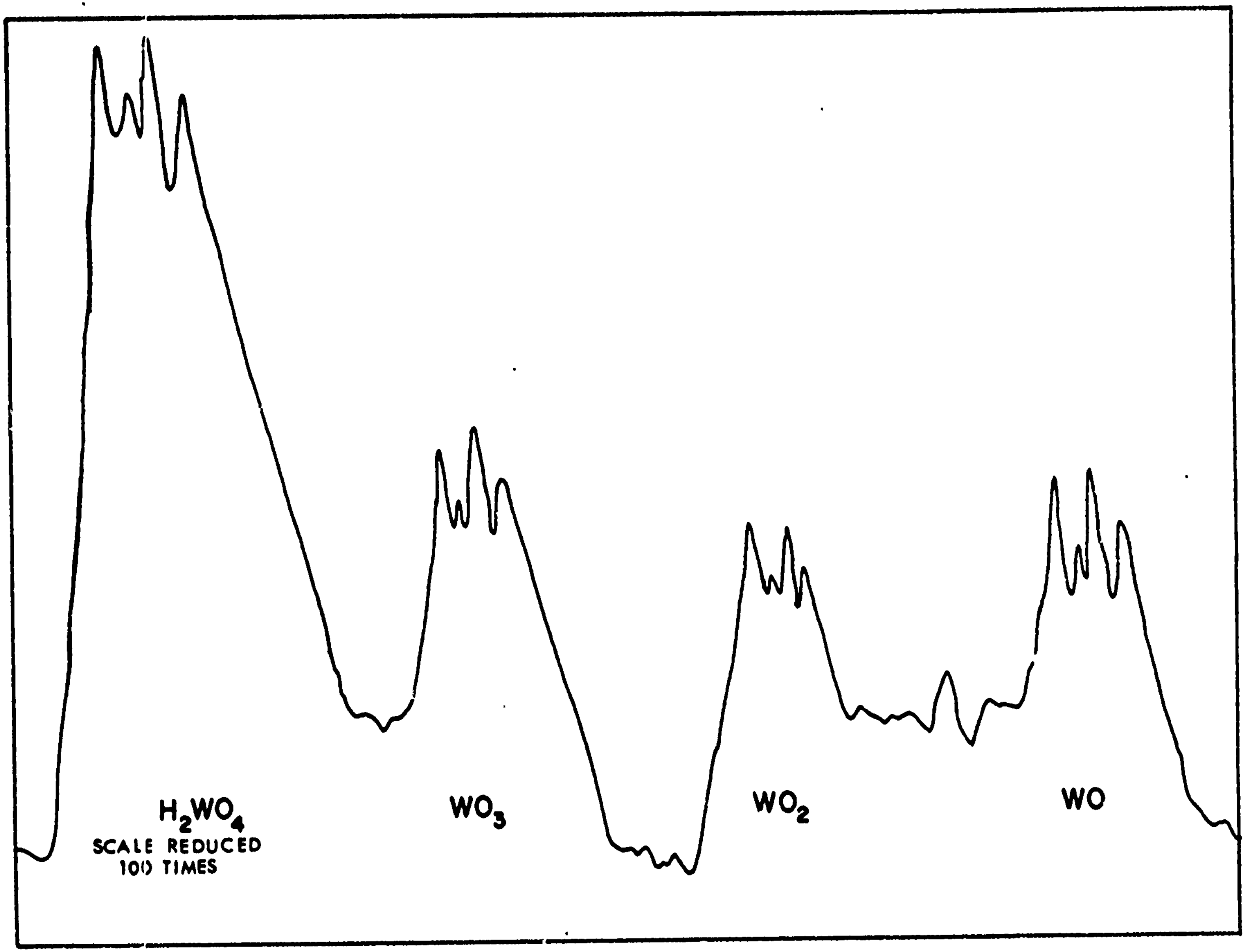


Fig. 4. Mass Spectrometer Intensities of the Principal Tungsten Species Present in an Atmospheric H_2/O_2 Flame at an Average Temperature of 2300°K (tungsten introduced as $WF_6(g)$)

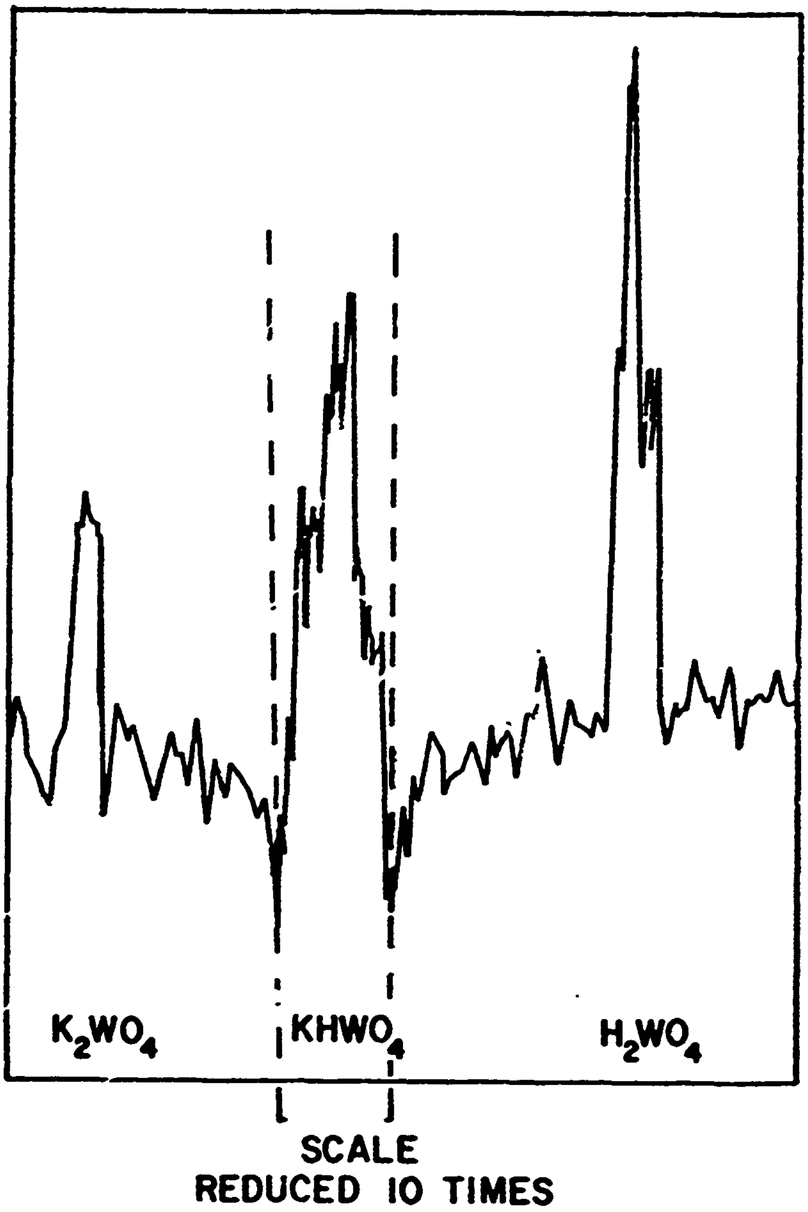


Fig. 5. Relative Mass Spectrometer Intensities of Tungsten Species Present in a Potassium-Seeded Atmospheric H_2/O_2 Flame at an Average Temperature of 2300°K (tungsten introduced as $WF_6(g)$ and potassium introduced as KI(g))

The equilibrium intensities for reaction (5) yielded a ΔG of -4.1 kcal and, for reaction (6), a ΔG of 5.0 kcal at an average temperature of 2300°K. Free energy functions were calculated for the potassium-tungsten compounds employing estimated frequencies, bond distances, angles, and quantum weights and are presented in Tables I and III. The values thus obtained at 2300°K for the free energy functions of $KHWO_4(g)$ and $K_2WO_4(g)$ are 127.5 and 136.2 cal/deg/mole, respectively. Third law heats of reaction yielded values of -10.2 ± 4 and -1.1 ± 5 kcal for ΔH_{r298K} for reaction (5) and reactions (6), respectively. The stated uncertainties include errors involved in estimating the free energy functions. Jensen and Miller[4] obtained a similar value, -10 ± 10 kcal, for reaction (5). Employing the calculated enthalpy functions, together with the experimental heats of reaction, values of -257.4 ± 4 and 278.2 ± 5 kcal/mole were obtained for ΔH_{f298K} of $KHWO_4(g)$ and $K_2WO_4(g)$, respectively.

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PART II

REACTIONS INVOLVING VANADIUM AND CHROMIUM WITH POTASSIUM-SEEDED H_2/O_2 FLAMES

INTRODUCTION

Vanadium and chromium additives have been introduced into H_2-O_2 flames at an average flame temperature of 2250°K and the species formed during the reaction have been studied mass spectrometrically. After the establishment of the chemical reactions involved between the additives and the flame small concentrations of K (1 - 2%) were added and the substitution reactions were investigated.

EXPERIMENTAL APPARATUS AND PROCEDURES

To accomplish the operation of a flame at a pressure of one atmosphere and at the same time obtain the mass spectra of the combustion "frozen" species produced in the atmospheric flame required the construction and assembly of a four-stage differentially pumped vacuum system. This system provided a pressure variation from one atmosphere in the flame to 10^{-11} atmospheres at the mass spectrometer. Details of the apparatus and technical procedures are described in a previous paper.[1]

RESULTS AND DISCUSSION

Vanadium Additives in Potassium-Seeded Hydrogen-Oxygen Flames

Vanadium was introduced into the H_2-O_2 flame in the form of VCl_4(g). A considerable portion of the vanadium was found to form a stable solid oxide, V_2O_3. This was in agreement with the effusion data of Killingbeck,[2] and Frantseva and Semenov,[3] who found an effective vapor pressure of $10^{-1.7}$ and $10^{-1.4}$ atm, respectively, at a temperature of 2250°K.

The vanadium vapor species produced in the flame include V(g), VO(g) and H_2VO_3(g) (see Fig. 1). Equilibrium values at an average temperature of 2250°K for the reaction

$$VO(g) + 2H_2O(g) = H_2VO_3(g) + 2H(g) \qquad (1)$$

yielded a ΔF of 65.0 kcal. The third law heat of reaction was calculated

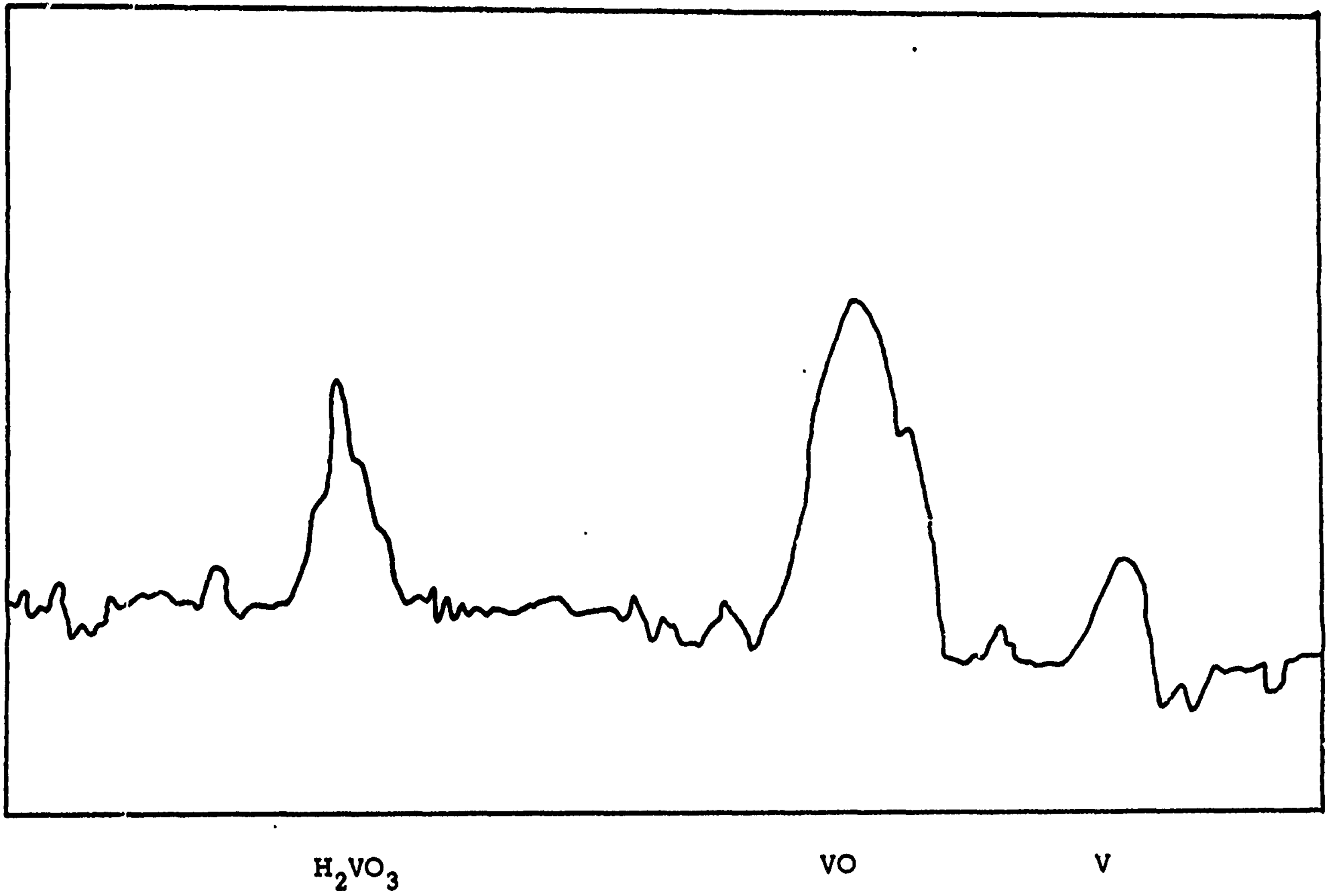

Fig. 1. Equilibrium Concentrations of H_2VO_3 and VO in an H_2/O_2 Flame at an Approximate Temperature of 2250°K

to be $\Delta H_{r298K} = 52.0$ kcal. Employing the calculated fef of 100.3 cal/deg/mole together with the published data,[3,4,5] and the experimental heat of reaction, a value of -132.8 ± 8 kcal/mole was obtained for ΔH_{f298K} of H_2VO_3. The stated uncertainties include errors involved in estimating the free energy functions.

Small amounts of potassium (0.5 to 1%) were introduced into the flame by vaporizing potassium iodide. The major species formed between the K and vanadium compounds was $KHVO_3$.

It has been determined that the major reaction occurring between the VCl_4(g) and the H_2-O_2 flame is the formation of the stable oxide V_2O_3 (c) (M.P. 2243°K),[6] which is in the condensed form at the flame temperature. The vapor species produced in the H_2-O_2 flame include V(g), VO(g) and H_2VO_3(g). Studies were made to measure the equilibria of the potassium atoms and ions in the flame reacting with VCl_4(g) to form the compounds $KHVO_3$ and K_2VO_3.

As can be seen from Fig. 2, the concentration of the vanadium species formed show that $KHVO_3$ is the major species and that the vanadic acid has been depleted considerably. A small amount of K_2VO_3 (approximately 10% of the concentration of $KHVO_3$) is also present, i.e., $KHVO_3 > H_2VO_3 > K_2VO_3$.

The removal of potassium atoms is accounted for by the following reactions:

$$K(g) + H_2VO_3(g) = KHVO_3(g) + H(g) \qquad (2)$$

and

$$2K(g) + H_2VO_3(g) = K_2VO_3(g) + 2H(g) . \qquad (3)$$

The relative ion intensities for the species present in reactions (2) and (3) allow third law calculations for the free energy of reaction and heat of formation of the vanadium species.

Equilibrium values for reaction (2) at an average temperature of 2250°K yielded a ΔF of -3.1 kcal/mole, and, for reaction (3), a ΔF of 3.1 kcal/mole. In order to calculate the heat of formation of $KHVO_3$(g)

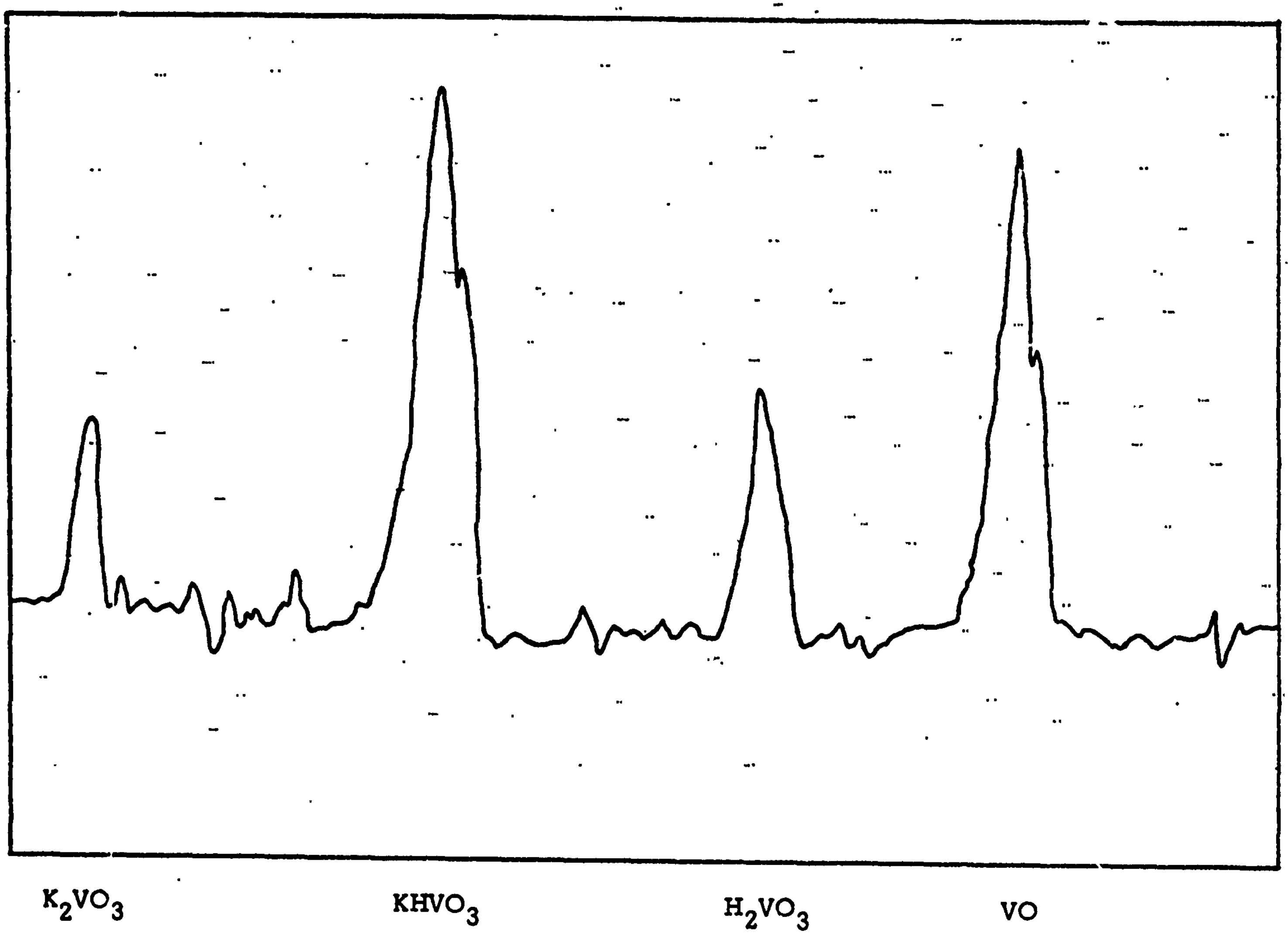

Fig. 2. Equilibrium Concentration of $KHVO_3$, K_2VO_3, H_2VO_3 and VO in an H_2/O_2 Flame at an Approximate Temperature of 2250°K

and K_2VO_3(g) it was necessary to obtain the free energy functions for these two compounds by statistical-mechanical calculations. It was assumed that these molecules have the K or H atoms bound with two of the three terminal oxygen atoms. The values thus obtained at 2250°K for the free energy functions for $KHVO_3$(g) and K_2VO_3(g) are 108.3 and 117.0 cal/deg/mole, respectively.

The third law heats of reaction were calculated to be $\Delta H_{r298K} = -9.64 \pm 5$ kcal for reaction (2), and $\Delta H_{r298K} = -8.4 \pm 5$ kcal for reaction (3). The stated uncertainties include errors involved in estimating the free energy functions. Employing the calculated enthalpy functions combined with ΔH_{f298K} $H_2VO_3 = -132.8$ kcal/mole, values of -173.2 ± 5 and -203.8 ± 5 kcal/mole were obtained for ΔH_{f298K} of $KHVO_3$(g) and K_2VO_2(g), respectively.

Chromium Additives in Potassium-Seeded Hydrogen-Oxygen Flames

Chromium additives were studied by the introduction of small amounts of chromium dichloride (1 to 2%) into the H_2-O_2 flame. The $CrCl_2$ was vaporized by means of a nichrome wire heater wrapped around an alumina tube in which the $CrCl_2$ vapor was pre-mixed with the O_2 prior to combustion. This resulted in various Cr species, including H_2CrO_4, CrO_3, CrO_2 and CrO. The relative ion intensities are shown in Fig. 3, with values of 8, 1, 13 and 6 for the ionic species H_2CrO_4, CrO_3, CrO_2 and CrO, respectively. The ion intensity measurements allowed calculation of the equilibrium at an average flame temperature of 2250°K for the reaction

$$CrO(g) + 3H_2O(g) = H_2CrO_4(g) + H_2(g) . \qquad (4)$$

The free energy of reaction obtained from these data was 27.3 ± 5 kcal/mole. In order to obtain a heat of reaction it was necessary to employ a value for fef of H_2CrO_4. This thermal function was estimated as 121.0 cal/deg/mole from the analogous acids, H_2MoO_4, H_2WO_4 and H_2VO_3 previously studied.[1] The values for the chromium oxides were obtained from Grimley, et al,[7]

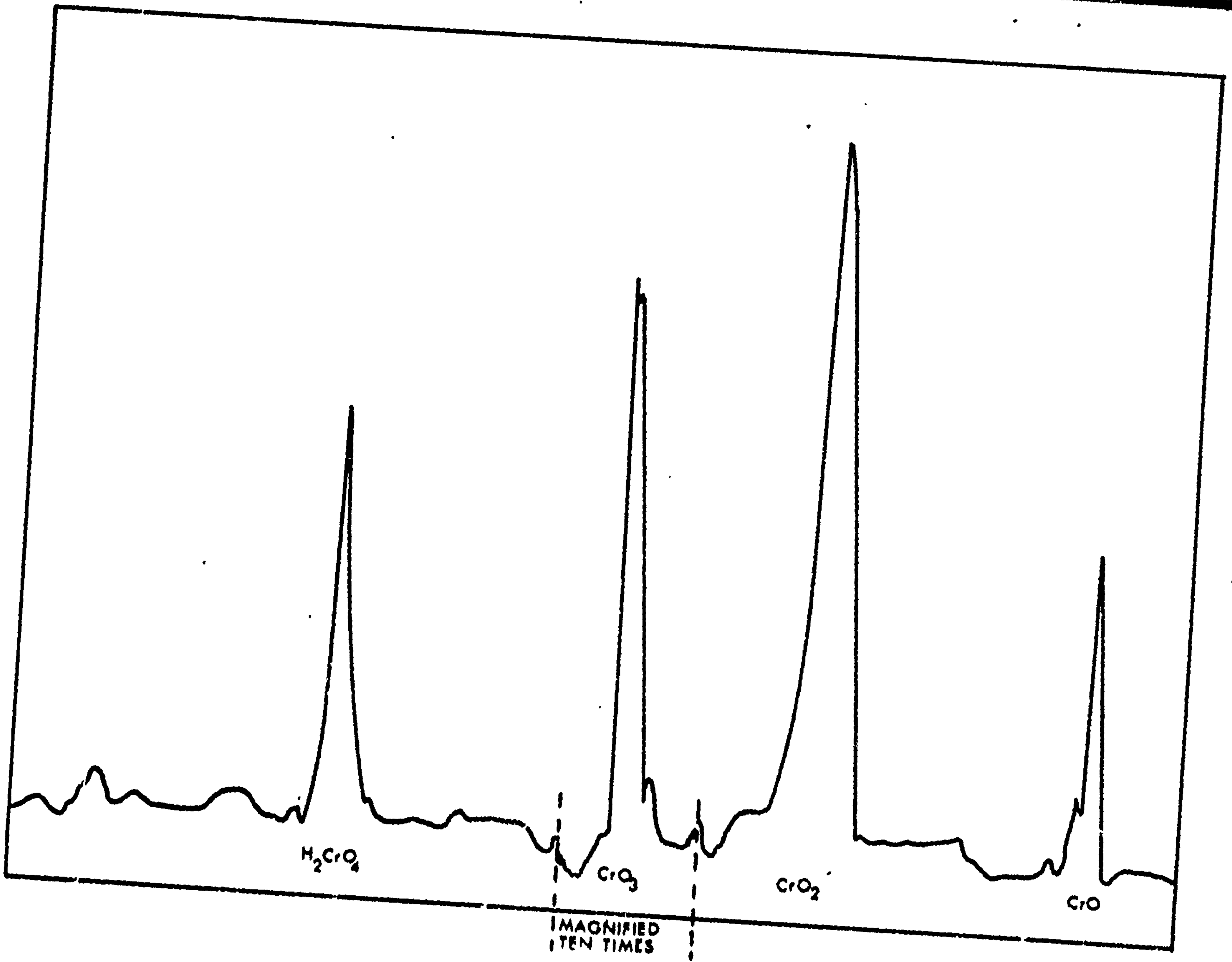

Fig. 3. Relative Mass Spectrometric Ion Intensities for the Major Species of Chromium in an H_2/O_2 Flame

and the remaining values from the JANAF Tables.[5] The third law heat of reaction was calculated to be $\Delta H_{r298K} = -57.0 \pm 5$ kcal. This measured heat of reaction when combined with the heat of formation of gaseous CrO of 53.0 ± 7 kcal/mole[7] leads to the value of ΔH_{f298K} $H_2CrO_4(g) = -176.4 \pm 7$ kcal/mole. The stated uncertainties include errors involved in estimating the free energy functions.

The only other reported study involving the possible formation of $H_2CrO_4(g)$ was that of Glemser and Muller[8] who performed a transpiration study of the reaction

$$CrO_3(c) + H_2O(g) = H_2CrO_4(g). \tag{5}$$

From the weight loss measurements they reported an enthalpy of 23 kcal/mole for reaction (5). Employing a value of ΔH_{f298K} $CrO_3(c) = -138.4$ kcal/mole[9] one obtains a value of ΔH_{f298K} $H_2CrO_4(g) = -174.0$ kcal/mole, which is in good agreement with the value obtained in the present study.

The ion intensity data also allowed the quantitative determination of thermodynamic data for $CrO_2(g)$ and $CrO_3(g)$ species produced in the flame. These species are involved in the equilibrium reactions

$$CrO_2(g) + 2H_2O(g) = H_2CrO_4(g) + 2H(g) \tag{6}$$

and

$$CrO_3(g) + H_2O(g) = H_2CrO_4(g). \tag{7}$$

Equilibrium values at an average flame temperature of 2250°K for reaction (6) yielded a ΔF of 51.5 kcal, and for reaction (7) yielded a ΔF of -10.5 kcal. The third law heat of reaction was calculated to be $\Delta H_{r298K} =$ 45.0 kcal for reaction (6) and -54.2 kcal for reaction (7). Employing a value of ΔH_{f298K} $H_2CrO_4(g) = -176.4 \pm 7$ kcal/mole, the values of -3.0 ± 7 kcal/mole and -64.6 ± 7 kcal/mole were obtained for ΔH_{f298K} of $CrO_2(g)$ and $CrO_3(g)$, respectively. The only previously reported thermodynamic data for $CrO_2(g)$ and $CrO_3(g)$ was the work of Grimley, et al.[7] From mass spectrometric effusion data they reported heats of formation for

$CrO_2(g)$ and $CrO_3(g)$ of -14 ± 15 kcal/mole and -69 ± 20 kcal/mole, respectively. These high uncertainties of 15 to 20 kcal/mole were stated as possibly resulting from reduced activity in the solid phase of Cr_2O_3 or that the solid was non-homogeneous. The new value of -3.0 ± 7 kcal/mole for ΔH_{f298K} $CrO_2(g)$ obtained in the present study indicates that $CrO_2(g)$ is less stable by approximately 10 kcal than would be indicated by Grimley's value.

Small amounts of K (.5 to 1%) were introduced into the hydrogen-oxygen flame through vaporization of KCl. Experimental studies were performed to establish the equilibria of the various compounds formed in the flame. In addition to the Cr compounds, CrO, CrO_2, CrO_3 and H_2CrO_4, the stable potassium compounds, $KHCrO_4$ and K_2CrO_4 were also seen. As can be seen from Fig. 4, the $KHCrO_4$ concentration is approximately half that of H_2CrO_4, and the K_2CrO_4 concentration is an order of magnitude smaller than that of H_2CrO_4.

The reactions involving the formation of these compounds can be written as

$$K(g) + H_2CrO_4(g) = KHCrO_4(g) + H(g) \qquad (8)$$

and

$$2K(g) + H_2CrO_4(g) = K_2CrO_4(g) + 2H(g). \qquad (9)$$

Equilibrium values for reaction (8) at an average temperature of 2250°K yielded a ΔF of 3.1 kcal/mole, and for reaction (9), a ΔF of 11.1 kcal/mole. In order to calculate the heats of formation of $KHCrO_4(g)$ and $K_2CrO_4(g)$ it was necessary to obtain the free energy functions for these compounds. These thermal functions were estimated from the analogous compounds, $KHMoO_4$, $KHWO_4$ and K_2WO_4 previously studied.[1] The values thus obtained at 2250°K for the free energy functions for $KHCrO_4(g)$ and $K_2CrO_4(g)$ are 126.2 and 133.1 cal/deg/mole, respectively.

The third law heats of reaction were calculated to be ΔH_{r298K} = -9.7 ± 5 kcal for reaction (8), and ΔH_{r298K} = -10.7 ± 5 kcal for reaction (9). The stated uncertainties include errors involved in estimating the free energy functions. Employing the calculated enthalpy functions combined with ΔH_{f298K} $H_2CrO_4(g)$ = -176.4 kcal/mole values of

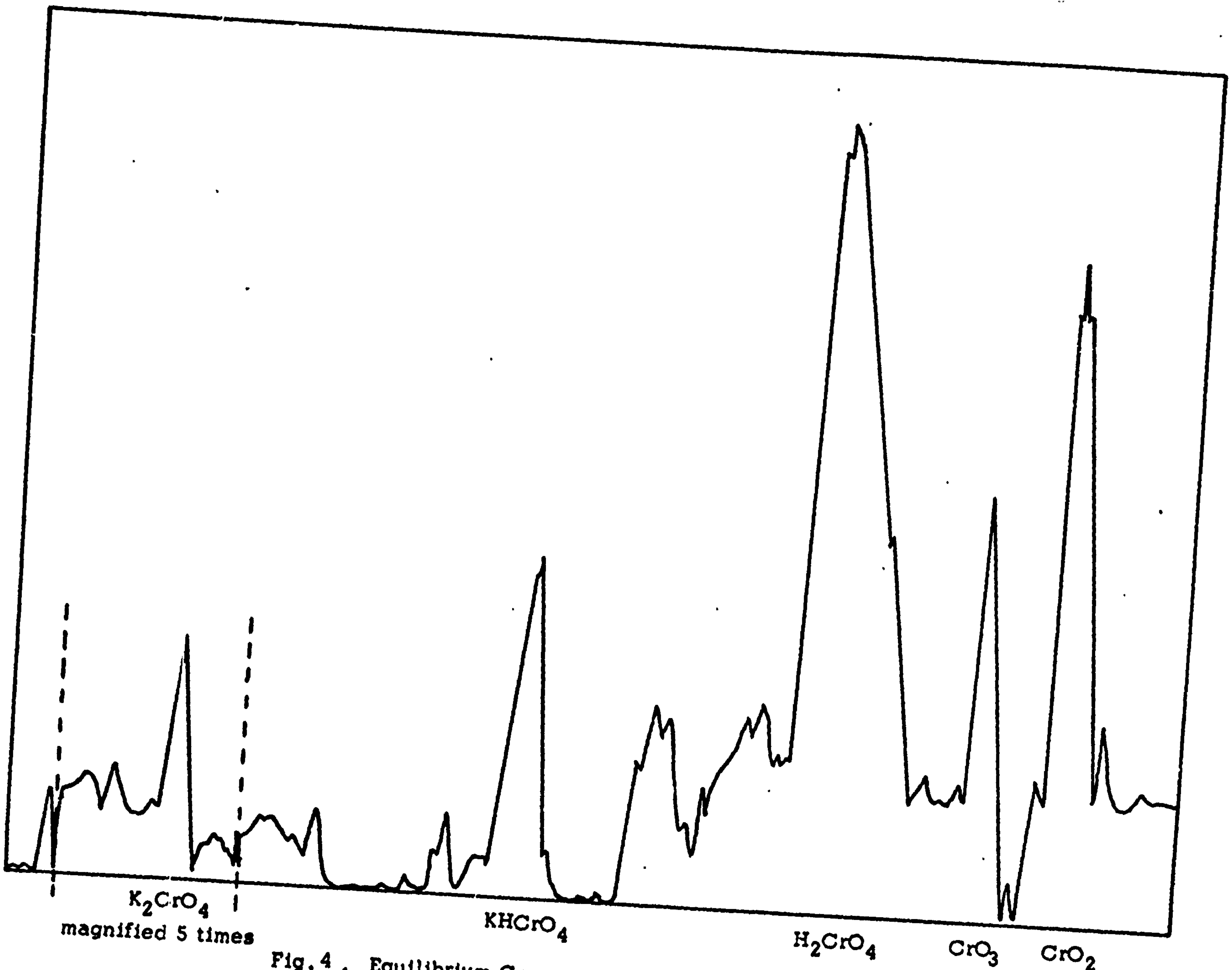

Fig. 4 . Equilibrium Concentrations of the Major Species of Chromium in the Alkali Seeded Atmospheric H_2/O_2 Flame

-216.9 ± 5 and -249.0 ± 5 kcal/mole were obtained for ΔH_{f298K} $KHCrO_4(g)$ and $K_2CrO_4(g)$, respectively.

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