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MASS SPECTROMETRIC INVESTIGATION OF THE
VAPORIZATION OF SODIUM AND POTASSIUM
CHROMATES: PRELIMINARY RESULTS

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MASS SPECTROMETRIC INVESTIGATION OF THE VAPORIZATION OF

SODIUM AND POTASSIUM CHROMATES: PRELIMINARY RESULTS

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SUMMARY

Knudsen cell mass spectrometry has been used to study the vaporization of sodium and potassium chromates. For both salts the vaporization proceeds predominately by the reactions $M_2CrO_4(c) = 2M(g) + 5/4 O_2(g) + 1/2 Cr_2O_3(s)$ and $M_2CrO_4(c) = M_2CrO_4(g)$ where $M \equiv Na$ or K . The distribution of the ions M^+ , O_2^+ and $M_2CrO_4^+$ in the measured mass spectrum has been found to depend on the material used for the Knudsen cell, even for materials such as platinum and gold. In the case of sodium chromate the decomposition reaction appears to be less important than the molecular vaporization reaction. A preliminary value of 72 kcal/mole at 1141 K has been measured for the heat of the molecular vaporization reaction for sodium chromate. In the case of potassium chromate it has not been possible to conclude which mode of vaporization dominates. For potassium chromate a value of 101 kcal/mole at 1173 K was obtained for the heat of the molecular vaporization reaction.

INTRODUCTION

Knowledge of the vaporization thermodynamics of sodium chromate is considered to be an important aspect for a complete understanding of the hot corrosion process responsible for the degradation of gas turbine engine hot-gas-path components. The vaporization of sodium chromate is not well characterized and although the gaseous molecule $Na_2CrO_4(g)$ has been identified (refs. 1 and 2), there is a paucity of data for this species. Afonskii (ref. 3) measured the "vapor pressure" of sodium chromate but reported a suspiciously low value for the heat of vaporization, $\Delta H_{1014K, vap} = 23.2$ kcal/mole. Furthermore, the weight loss method he used did not yield any information on the mode of vaporization or on the composition of the vapor phase. This lack of reliable data for the sodium chromate system has impeded understanding the chemistry of interaction and mechanisms involved when the chromia constituent of the protective oxide scale (which form at high temperatures on nickel and cobalt based superalloys used in gas turbine engines) is exposed at high temperatures under oxidizing conditions to such salts as sodium sulfate or sodium chloride. For such conditions the $Na_2CrO_4(g)$ molecule has been postulated as the species responsible for the undesirable vapor phase transport of chromium away from the superalloy materials (refs. 4 to 6). However, no direct

evidence exists to establish this mechanism and the postulate probably is derived from the fact that "yellow chromate deposits" are often observed to condense in cooler regions of certain experimental arrangements (refs. 7 and 8).

The work reported herein was undertaken to provide data for the vaporization of sodium chromate. Difficulties encountered in the sodium chromate measurements prompted an expansion of the study to include potassium chromate. The rationale here was that experience gained with the more tractable potassium chromate might provide insights and contribute to the understanding of the results observed for sodium chromate. In addition, there is a keen interest in potassium chromate because of its possible involvement in corrosion problems expected to be encountered in high temperature systems using coal-derived combustion products and in MHD systems. The $K_2CrO_4(g)$ molecule has been identified as forming in Cr/K-doped H_2/O_2 flames by Farber and Srevastava (ref. 9) who estimated the heat of formation for $K_2CrO_4(g)$ as $\Delta H_{298,f} = -249.0 \pm 5$ kcal/mole.

Results reported herein are considered to be preliminary because measurements are still in progress and further work is needed to characterize completely the vaporization thermodynamics of sodium and potassium chromates.

EXPERIMENTAL

The mass spectrometer apparatus with a high temperature Knudsen cell inlet system has been described previously (ref. 10). Recently this apparatus has been modified by the addition of a beam modulation system whose function is to increase the signal-to-noise ratio and thereby increase mass spectrometer sensitivity. The Knudsen cell inlet system is coupled to a Mattauch-Herzog type double focusing mass spectrometer. The physical arrangement is such that the neutral molecular beam emanating from the Knudsen cell orifice is coaxial with the ion beam produced by electron impact in the ion source. The Knudsen cell, ion source and mass analyzer are each located in separate vacuum chambers that are interconnected but differentially pumped.

In the beam modulation system, the neutral beam is periodically interrupted by a motor driven segmented disc. This beam chopping is performed as close as possible to the source of the gas beam (i.e., the Knudsen cell) as shown schematically in figure 1. The beam chopping disc also generates a reference electrical signal at the chopping frequency by interrupting a light beam directed onto a photodiode detector. The reference signal is used to drive the reference channel of a frequency tracking lock-in amplifier.

Ion intensities are measured with a seventeen stage Allen-type copper/beryllium electron multiplier. The electrical output of the multiplier is routed to the signal channel of the lock-in amplifier that produces an output signal proportional to the in-phase component of the modulated beam signal.

Individual Knudsen cells were fabricated from pure gold and from a platinum -10% rhodium alloy. Effusion orifices ranged in diameter from 0.046 to 0.056 cm. In various experiments the Knudsen cell was fitted

with a ceramic liner to contain the sample material. Cell liners were made of alumina or zirconia and the hole in the liner was used to define the effusion orifice.

The sodium and potassium chromates used as sample material were commercially available certified grade chemicals.

The ion source was operated with an electron current of 150 microamperes of 30 electron-volt electrons. Vapor species were identified by mass-to-charge ratio and isotopic abundance. Measured ion currents were converted to corresponding species partial pressures, P_i , through the relationship:

$$P_i = \frac{k I_i T}{\sigma_i \gamma_i n_i} \quad (1)$$

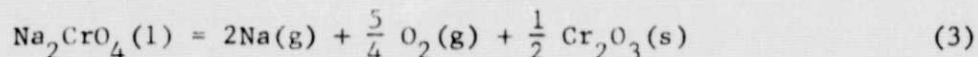
where, for species i , I_i is the ion current, σ_i is the relative ionization cross section, γ_i is the relative multiplier gain, n_i is the fractional isotopic abundance, T is the temperature and k is the apparatus sensitivity constant. A gold calibration technique was used to determine k . The gold ion current was measured at a known temperature and related to the pressure through equation (1) and the well-established vapor pressure of the high purity gold at the respective temperature (ref. 11).

RESULTS AND DISCUSSION

Sodium Chromate

Experiments were initially performed with the sodium chromate sample contained in a Pt-10Rh Knudsen cell without a liner. The mass spectrum shown in figure 2 was obtained at a temperature of 1224 K. The $\text{Na}_2\text{CrO}_4^+$ ion was readily detected and its appearance potential was measured as 8.0 ± 0.5 eV. This value of the appearance potential is taken to indicate that this ion is a parent species of the $\text{Na}_2\text{CrO}_4(\text{g})$ molecule. The ions Na^+ and O_2^+ are also considered to be parents although some fragmentation may have contributed to their measured ion intensities. The other species, i.e. Na_2O^+ , NaCrO_2^+ , NaCrO_3^+ and $\text{Na}_2\text{CrO}_3^+$, are thought to be fragments. Because their intensities were so low, it was not possible to make reliable appearance potential measurements on these species to confirm our fragmentation conjecture.

From the initial experiments and the results shown in figure 2, we surmise that the vaporization of sodium chromate in a vacuum proceeds almost exclusively by the reactions:



These initial experimental results seemed to establish the mode of vaporization of sodium chromate. However, as we proceeded to measure ion inten-

sities as a function of temperature we observed that $\text{Na}_2\text{CrO}_4^+$ and Na^+ intensities were decreasing with time at temperature. The experiment was therefore terminated.

Visual inspection of the Knudsen cell revealed that liquid sodium chromate had apparently crept out of the cell through the orifice. The exterior of the cell was covered with the green dissociation product $\text{Cr}_2\text{O}_3(\text{s})$ and the interior of the cell appeared to only contain a residue of $\text{Cr}_2\text{O}_3(\text{s})$. These observations would seem to indicate that the decreasing ion intensities were the result of depletion of the sodium chromate sample.

The creeping of liquid sample out of the Knudsen cell through the orifice is undesirable. Besides contributing to rapid sample depletion and a nonequilibrium situation, liquid sample on the cell exterior near the orifice could produce enhanced ion intensities.

Because the mass spectrometric sensitivity was not high enough to detect the $\text{Na}_2\text{CrO}_4^+$ species below the sodium chromate melting point of about 1070 K (ref. 12), it appeared essential to be able to contain a liquid phase sample. Experiments were performed with $\text{Na}_2\text{CrO}_4(\text{l})$ contained in alumina or zirconia liners in the Pt-10Rh Knudsen cell. These experiments yielded essentially the same mass spectrum as that obtained previously for the Pt-10Rh cell without a liner before intensities decreased with time.

Ion currents for $\text{Na}_2\text{CrO}_4^+$ were measured as a function of temperature over the range from 1096 to 1188 K. For these results, shown in figure 3, the sodium chromate was contained in a zirconia liner in the Pt-10Rh Knudsen cell. During the course of the experiment where the ten data points shown were measured, no decrease of intensity was observed with time. However after these data were obtained, the $\text{Na}_2\text{CrO}_4^+$ ion intensity began to fall with time and the experiment was terminated.

Visual inspection of the Knudsen cell again indicated that even with the zirconia liner some sample crept out of the cell as evidenced by a slight $\text{Cr}_2\text{O}_3(\text{s})$ residue on the cell exterior near the orifice. The inside of the cell contained $\text{Na}_2\text{CrO}_4(\text{s})$ covered by a layer of $\text{Cr}_2\text{O}_3(\text{s})$. This covering of the sample by $\text{Cr}_2\text{O}_3(\text{s})$ is considered to be a serious limiting problem. If the vaporization is proceeding in any significant way by the decomposition reaction, eventually the $\text{Cr}_2\text{O}_3(\text{s})$ product remaining in the Knudsen cell could interfere with the vaporization by covering over the sodium chromate. This interference would probably be most important in the case where the $\text{Cr}_2\text{O}_3(\text{s})$ would float on the surface of a liquid sample.

Pressures were not calculated for the data shown in figure 3 because it was felt that the intensities might be high in absolute value due to the fact that liquid sample was apparently on the cell exterior near the orifice. However, the relative values of the intensities measured at various temperatures are considered to be valid. A least-squares treatment of the measured data points yielded the line drawn in figure 3 through the data points. From these results a second-law heat of vaporization of 72 kcal/mole, at a mean temperature of 1141 K, was calculated for the molecular vaporization reaction (2).

To preclude the creeping of liquid sodium chromate from the Knudsen cell, it was decided to seek a cell material or liner material that would not be wetted by the liquid sodium chromate. A Knudsen cell was machined from a gold ingot that had been cast in an alumina crucible in our laboratory. The starting material for the ingot was 99.95% pure gold.

Initially with the gold cell an ion intensity ratio, $\text{Na}^+/\text{Na}_2\text{CrO}_4^+$, of about 2 was measured at 1193 K. This ratio increased rapidly with time at temperature as the $\text{Na}_2\text{CrO}_4^+$ peak decreased in intensity to the point when it was no longer detectable. This experiment was concluded and visual inspection of the cell revealed no creeping of the sample. From the appearance of the sodium chromate sample remaining inside the cell, it was concluded that $\text{Na}_2\text{CrO}_4(l)$ does not wet gold. The inspection did not reveal anything that could be construed to account for the rapid increase with time of the ion intensity ratio.

To obtain a larger ion current signal, the gold cell orifice was increased in diameter from the previous original 0.046 to 0.053 cm. Further experiments were initiated with a new $\text{Na}_2\text{CrO}_4(c)$ sample. At 1193 K the ion ratio $\text{Na}^+/\text{Na}_2\text{CrO}_4^+$ was found to be about 40. This indicates that the $\text{Na}_2\text{CrO}_4(g)$ species was here only a minor constituent in the sodium chromate vaporization. This is in direct contradiction to our previous findings, as shown in figure 2, where the ratio was about one and $\text{Na}_2\text{CrO}_4(g)$ was a very significant species in the vaporization. At the present time we cannot explain the contradictory results and obviously further work is required to completely characterize the mode of vaporization of sodium chromate.

Hirayama and Lin (ref. 13) have reported results for some Knudsen cell mass spectrometric experiments with sodium chromate. Their samples were fused in alumina crucibles in air prior to the mass spectrometric measurements. Using fused silica, tungsten- and sapphire-lined tungsten Knudsen cells, they reported that $\text{Na}_2\text{CrO}_4(c)$ vaporizes by dissociation for temperatures up to 1273 K. Furthermore, they report that the $\text{Na}_2\text{CrO}_4(g)$ molecular species was not observed.

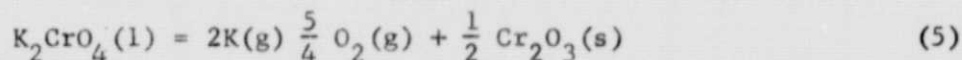
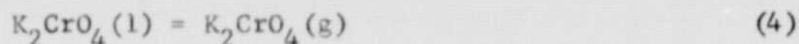
In subsequent experiments, Hirayama (ref. 12) was successful in identifying the $\text{Na}_2\text{CrO}_4(g)$ species vaporizing from sodium chromate contained in a platinum cell or tungsten cells with or without sapphire liners. For the tungsten cell the $\text{Na}^+/\text{Na}_2\text{CrO}_4^+$ ratio was found to be about 100 but with the platinum cell the ratio was about 7.

At the present time it would appear to be premature to draw any conclusions about the mode of vaporization of sodium chromate. Further work is needed to elucidate the apparent dependence on Knudsen cell materials such as gold and Pt-10Rh.

Potassium Chromate

Numerous experiments were performed with $\text{K}_2\text{CrO}_4(s,l)$ contained in a zirconia liner in a Pt-10Rh Knudsen cell. No creeping of liquid sample was observed for this combination with $\text{K}_2\text{CrO}_4(l)$. For some of these experiments a large solid drop of gold (used for calibration purposes) was contained in the cell liner together with the chromate sample. The presence of the gold had no measurable effect on the mass spectra. A typical mass spectrum for the liquid phase sample is shown in figure 4. The species K_2CrO_4^+ is assumed to be entirely a parent and K^+ and O_2^+ are considered to be mainly parents but it is recognized that fragmentation can contribute to their intensity. All other species shown in the mass spectrum are considered to be fragments.

The mass spectrum shown in figure 4 indicates that at 1293 K the $K_2CrO_4(l)$ vaporization proceeds by the reactions



At 1293 K the $K^+/K_2CrO_4^+$ ratio is about one but at a temperature slightly below the melting point of 1208 K, the ratio is 0.7 indicating that at this temperature the molecular vaporization reaction predominates slightly over the dissociation reaction. Thus we see that the mode of vaporization for potassium chromate depends on temperature and/or the physical state of the sample, i.e. solid or liquid phase.

Ion currents for the species $K_2CrO_4^+$ were measured as a function of temperature over the range from about 1100 to 1250 K. The measured ion current-temperature product data is plotted in figure 5. Intensities were converted to partial pressures by a gold calibration sensitivity constant for this cell-liner combination. The line drawn through the measured data points is a least-squares fit of the data and this yields a value of 101 kcal/mole at 1173 K for the heat of reaction for the molecular vaporization reaction (4).

Experimentally derived pressures for $K_2CrO_4(g)$ are compared with $K(g)$ and $O_2(g)$ pressures calculated by using the reported heat of formation value for $K_2CrO_4(c)$ (ref. 15). From table I it is seen that a significant fraction of the potassium is contained in the molecular species $K_2CrO_4(g)$ and this indicates that the molecular vaporization reaction is an important part of the total vaporization process.

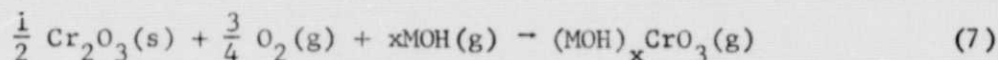
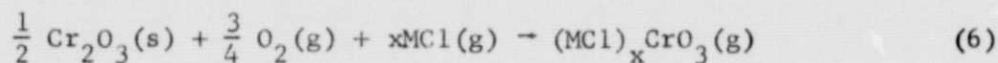
Subsequent to the foregoing experiments $K_2CrO_4(c)$ was vaporized from the gold Knudsen cell used in the sodium chromate work. No liner was used with this cell and again no creeping of the sample was detected. However, in all cases where the gold Knudsen cell was used the dissociation reaction appeared to dominate in the vaporization of potassium chromate. While the measured K^+ ion intensities were about the same as those measured in the previous experiment with the Pt-10Rh cell with the zirconia liner, the $K_2CrO_4^+$ intensity was considerably reduced. With the gold cell and a sample temperature of 1240 K the $K^+/K_2CrO_4^+$ ratio was found to be about 6; at 1224 K it was 25 and at 1211 K it was 5. While it is not possible to assess the significance of the variation of the ratio with temperature, the general results are not in agreement with our previous findings obtained by using the zirconia liner and Pt-10Rh Knudsen cell. The results obtained with the gold cell are especially puzzling when one considers that gold was contained in the zirconia liner with the potassium chromate sample used in the earlier experiments.

Using a platinum Knudsen cell and a tungsten cell with sapphire liner, Hirayama (ref. 14) measured values of 2.5 and 40 respectively for the $K^+/K_2CrO_4^+$ ratio with the two cell materials and sample temperatures around 1125 K. These results seem to indicate that even though Hirayama had a solid sample in a sapphire lined cell, the more reactive cell material (tungsten) drives the vaporization of potassium chromate toward the dissociation reaction (e.g., by taking up oxygen). Platinum apparently is less reactive with $K_2CrO_4(s)$ and does not interfere with the vaporization.

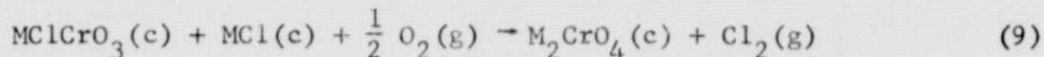
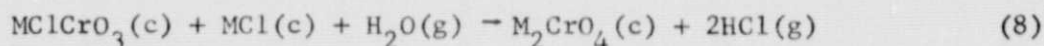
Our results with the Pt-10Rh cell with zirconia liner and gold drop are in general agreement with those of Hirayama. However, the findings with the gold Knudsen cell are completely unexpected and further work is necessary to elucidate the observed behavior.

CONCLUDING REMARKS

The preliminary results reported herein for sodium and potassium chromates allow us to calculate tentative equilibrium vaporization rates for these salts. These calculated rates can be compared with those calculated for other sodium and potassium salts relevant to hot corrosion processes. Table II lists the rates for six salts and the respective vaporization processes for each salt. From this table one sees that the respective chromates are less volatile than the corresponding chlorides and sulfates. Thus for hot corrosion considerations, one would not expect the volatilization of chromates to be a very significant mechanism to account for the depletion of chromium from alloys exposed to high temperature oxidation-sulfidation conditions. Indeed, we have recently shown (refs. 2, 16, and 17) that molecules of the type $(MCl)_xCrO_3$ or $(MOH)_xCrO_3$ are responsible for the transport of chromium in atmospheres containing $O_2(g)$, $H_2O(g)$ and $NaCl(g)$. These molecules are formed by reactions such as:



where $x = 1, 2$ or 3 and $M = Na$ or K . We believe that upon condensation these molecules dissociate to form condensed phase chromates by reactions of the type:



Thus the observation of the vapor phase transport of chromium under hot corrosion conditions can be explained without the involvement of $M_2CrO_4(g)$ molecules.

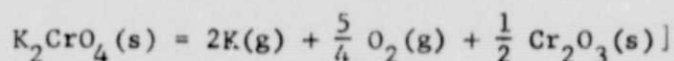
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TABLE I. - VAPORIZATION OF POTASSIUM CHROMATE



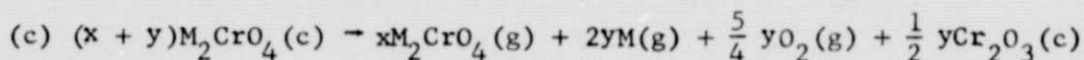
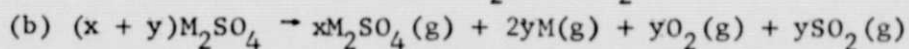
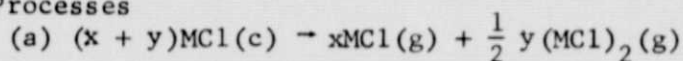
Temp., K	$P_{\text{K}(\text{g})}$, atm	$P_{\text{O}_2(\text{g})}$, atm	$P_{\text{K}_2\text{CrO}_4(\text{g})}$, atm	% K as molecule ^a
1100	9.46×10^{-9}	5.91×10^{-9}	2.81×10^{-9}	37
1200	1.37×10^{-7}	8.57×10^{-8}	1.33×10^{-7}	66

$$^a \text{ \% K as molecule} = \frac{2P_{\text{K}_2\text{CrO}_4(\text{g})}}{P_{\text{K}(\text{g})} + 2P_{\text{K}_2\text{CrO}_4(\text{g})}} \times 100$$

TABLE II. - EQUILIBRIUM VAPORIZATION RATE, G, AT 1000 K

Vaporizing compound	Vaporization process ⁽¹⁾	G, g cm ⁻² sec ⁻¹	
		M ≡ Na	M ≡ K
MCl	(a)	$5.16 \cdot 10^{-7}$	$1.27 \cdot 10^{-6}$
M ₂ SO ₄	(b)	$5.87 \cdot 10^{-12}$	$1.11 \cdot 10^{-10}$
M ₂ CrO ₄	(c)	$(4.22 \cdot 10^{-12})$	$2.71 \cdot 10^{-12}$

(1) Processes

where $x + y = 1$

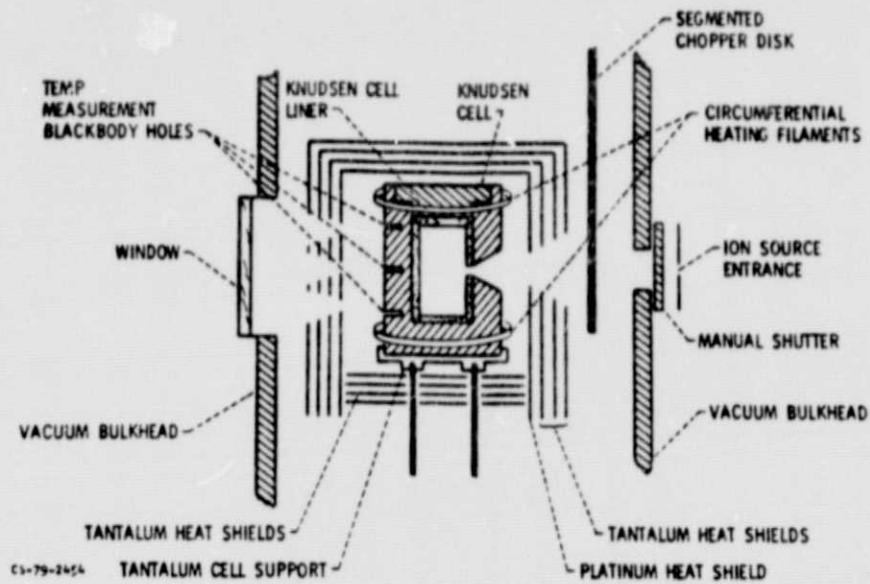


Figure 1. - Schematic representation of Knudsen cell inlet.

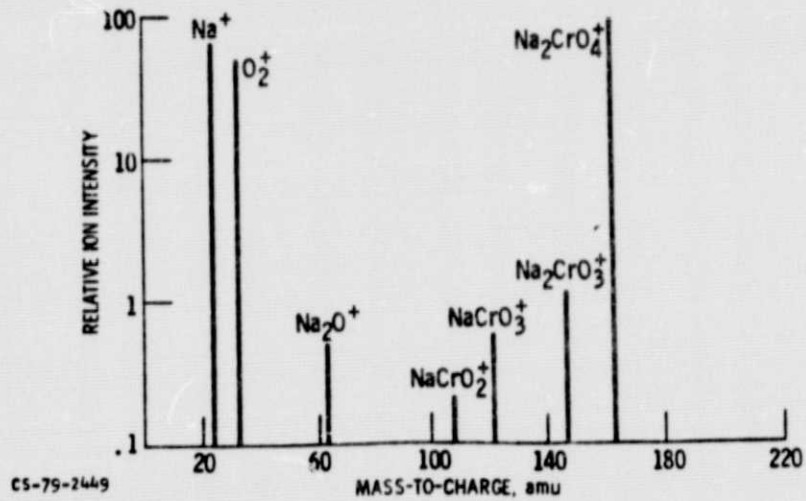


Figure 2. - Mass spectrum of Na₂CrO₄(l) at 1224 K in Pt-10 Rh Knudsen cell.

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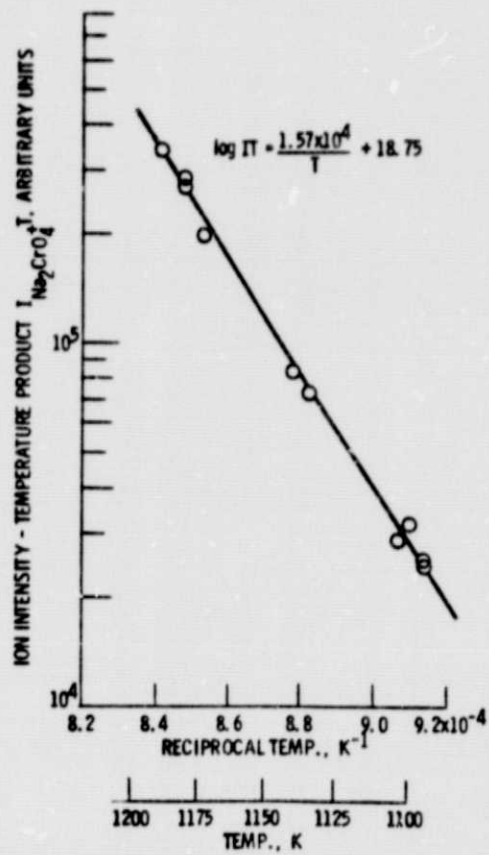


Figure 3. - Temperature dependence of $\text{Na}_2\text{CrO}_4(\text{g})$ species over $\text{Na}_2\text{CrO}_4(\text{l})$.

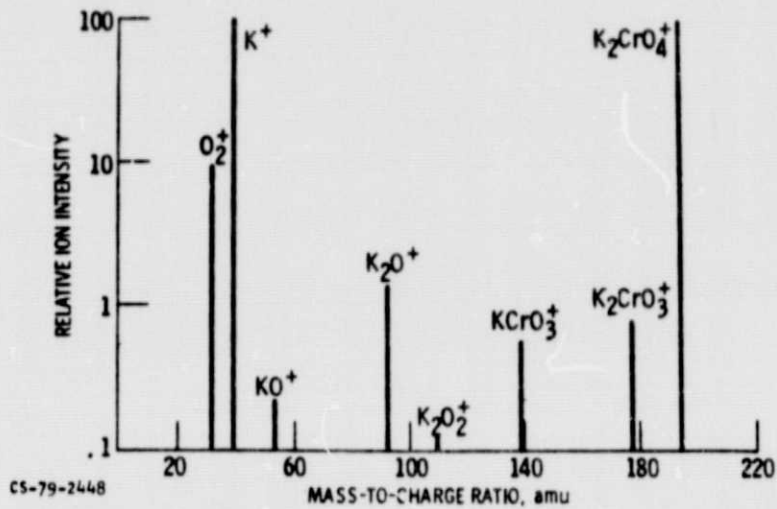


Figure 4. - Mass spectrum of $K_2CrO_4(l)$ at 1293 K in zirconia liner in Pt-10 Rh Knudsen cell.

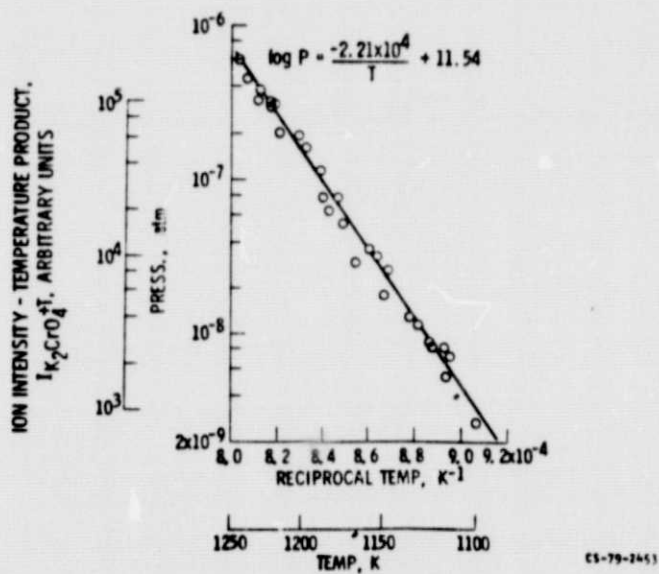


Figure 5. - Temperature dependence of $K_2CrO_4(g)$ species over $K_2CrO_4(l)$.